

THERMORESPONSIVE BEHAVIOUR OF METAL ORGANIC FRAMEWORKS

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CHOMPOONOOT NANTHAMATHEE

SCHOOL OF CHEMISTRY

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Abstract

THERMORESPONSIVE BEHAVIOUR OF METAL ORGANIC FRAMEWORKS

By Chompoonoot Nanthamathee

30 May 2013

School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

In this thesis, we aim to investigate the thermoresponsive behaviour, especially negative thermal expansion (NTE), in metal dicarboxylate metal organic frameworks (MOFs) using X-ray diffraction techniques. Four materials with the UiO-66 topology $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ (bdc = 1,4-benzenedicarboxylate, bpdc = 4,4'-biphenyldicarboxylate and 2,6-ndc = 2,6-naphthalenedicarboxylate) were investigated, all of which contain a zero-dimensional inorganic cluster. All four members show NTE behaviour over the observed temperature ranges as a result of the twisting motion of the carboxylate groups of the organic linkers. This twisting motion introduces a concerted rocking motion within the inorganic cluster which causes an apparent decrease in the size of the cluster and hence overall volume contraction. Alteration of the structure of the organic linker has an effect on the magnitude of the expansivity coefficient which is believed to be related to the existence of specific vibrational modes of that particular organic linker.

Four members of the MIL-53 family $[\text{Al}(\text{OH})(\text{bdc})]$, $[\text{AlF}(\text{bdc})]$, $[\text{Cr}(\text{OH})(\text{bdc})]$ and $[\text{VO}(\text{bdc})]$ were studied. All four materials show elements of NTE behaviour related to a “wine rack” thermo-mechanical mechanism which is determined by the connectivity of the framework. The thermoresponsive behaviour in these materials is dominated by the changes in the plane of the pore opening. These changes result from a combination of three distinct types of motion of the bdc linker including the rotation of the bdc linker about the chain of the inorganic octahedra, the “knee cap” bending mode of the carboxylate groups about the O-O vector and possibly the transverse vibrations within the bdc linker. The latter motion was not evident in this work due to the limitations of the structure refinements. The former two motions appear to be correlated and depend on the rigidity of the metal-centred octahedra which is determined by the constituent metal cation and anion types. The rigidity of the octahedra is also found to play an important role in determining whether the material undergoes a “breathing” phase transition at low temperature.

$[\text{Sc}_2(\text{bdc})_3]$ shows NTE behaviour over the observed temperature range which is partially driven by a “wine rack” thermo-mechanical mechanism, but with an opposite framework compression direction when compared to the MIL-53 types MOFs. This is due to the presence of an additional bdc connecting linker in the plane of the pore opening. This extra connection inverses the compression direction and also impedes the structural changes in the plane of the pore opening. The contraction of the chain of inorganic octahedra is the main contributor to the overall unit cell contraction and is caused by the twisting motion of the carboxylate groups of the bdc linker while the magnitude of this contraction is determined by the flexibility of the chain of inorganic octahedra.

Declaration

The work described in this thesis was conducted between September 2009 and September 2012 under the supervision of Dr. Martin P. Attfield in the School of Chemistry, The University of Manchester. No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning. All the materials, figure and data presented in this work are my own original work, except where specifically stated and acknowledged.

Chompoonoot Nanthamathee

The University of Manchester, Summer 2013

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1. Introduction

1.1 Thermoresponsive behaviour of solids

Thermoresponsive behaviour is one of the basic physical properties of solid materials. It describes the characteristic of a particular solid when heat is applied to it. Several possibilities occur when the solid responds to the application of thermal energy such as a chemical reaction, decomposition, phase transition, positive thermal expansion (PTE), zero thermal expansion (ZTE) and negative thermal expansion (NTE). In this work, we are focusing on the latter four responses which will be discussed individually in detail.

1.2 Phase transitions

The most common example of a phase transition is possibly the phase transition of water when the temperature is increased. This involves a transition from one state to another, such as from a liquid state to a gaseous state through a process called vaporization. The phase transition can occur from a crystalline to a crystalline phase, a crystalline to an amorphous phase or an amorphous to an amorphous phase. Only the first type of transition will be discussed here. The phase transition between two solid crystalline materials that have an identical chemical composition but different crystal structure is called a polymorphic transformation. Changes after the phase transition involve both the physical and chemical properties of the solids.

The occurrence of a phase transition is driven by the change of free energy ΔG that is associated with temperature or pressure changes and is given by:

$$\Delta G = \Delta H - T\Delta S$$

Equation 1.1

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

Equation 1.2

where $\Delta E, \Delta H, \Delta S$ and ΔV are the internal energy, enthalpy, entropy and volume changes of the system during the phase change. As the temperature is increased, the internal energy and entropy is also increased while the change in energy due to solid volume changes is very little when compared to those of internal energy and entropy. A phase transition is normally favoured towards a structure with lower internal energy as the entropy has a small effect on the free energy. The phase transition of a structure with higher internal energy is favoured at high temperature because the term $T\Delta S$ might surpass the internal energy.

Classification of polymorphic phase transitions is ambiguous and is dependent on the criterion used. If described from a thermodynamic point of view, two kinds of phase transition are categorized which include first order and the second order phase transitions. The first order phase transition is accompanied by a discontinuity of the first derivative of the thermodynamic quantities and usually involves bond breaking and a rearrangement of bonds. A second order phase transition is accompanied by a continuity of the first derivative of the thermodynamic quantities and a displacement of atoms without breaking any bonds. Hence, the first order phase transition normally requires higher activation energy because of bond breaking.

Beyond the thermodynamic classification, there are several types of polymorphic phase transition that depend on the defining criterion. If the rate of transformation is used as a criterion, phase transition can be differentiated into two types, a rapid phase transformation and a slow phase transformation. A rapid phase transition occurs in a fast fashion and is reversible because the energy difference between the two polymorphs is small. This type of transition is associated with a bond angle change, a displacement of constituent atoms or changes in the second coordination sphere. If this phase transition occurs under the influence of pressure, it is called a dilational displacive transformation; on the

other hand, if the transition is influenced by temperature, it is called a thermal displacive phase transition.

A classic example of a displacive phase transition is the transformation of β -quartz to α -quartz. β -quartz is a high temperature form of quartz while the α form is referred to as the low temperature phase. The structure of quartz is made of two helical chains of silica tetrahedra running along the c axis which has 6-fold symmetry in the β phase and 3-fold symmetry in the α phase. Upon heating, a displacive phase transition from the α form to the β form occurs at $\sim 573^\circ\text{C}$ due to rotations of the silica tetrahedra as depicted in **Figure 1.1**.

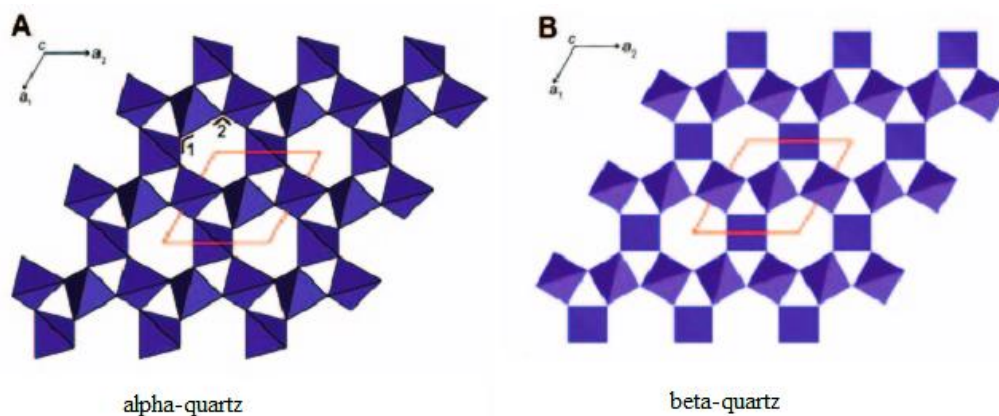


Figure 1.1 Schematic representing a displacive transition of the low-temperature quartz to the high-temperature quartz. The frameworks are viewed along the c axis and the unit cell of each structure is shown in red.^[1]

On the other hand, a slow phase transition, known as a reconstructive transformation involves breaking and reforming of both primary coordination and nearest-neighbour coordination bonds. This type of transition takes place at a much slower rate and requires high activation energy. Also, the transformed structure has no structural or no symmetry relation to the parent structure. An example of a reconstructive phase transition is the transformation of silica polymorphs from quartz to tridymite and to cristobalite where the structural changes between these three structures occurs by the breaking of the Si-O primary bond followed by the rearrangement of SiO_4 tetrahedra.

Another important type of phase transition is an order-disorder phase transition which cannot be added to the aforementioned classification since it can be either fast or slow transformation depending on a particular material. This transition involves changes of an element in the structure from a random to non-random distribution due to changes in pressure or temperature. An example of an order-disorder phase transition is the transformation from indialite to cordierite. Upon cooling, the Si and Al atoms move into a non-random distribution among the tetrahedral sites.

Regardless of its unquenchability, displacive phase transitions are studied more widely than reconstructive phase transitions as its occurrences can be observed by the variation of structural parameters, such as bond lengths or bond angles, in terms of temperature or pressure. Also, the fact that the transformation between the structures is related to their internal symmetry makes it possible to theoretically interpret the observation of displacive phase transitions. This is more difficult for a reconstructive phase transition.^[2-3]

1.3 Thermal expansion

Thermal expansion is an important and very common property in solids. Ideally, if considering the potential well of a diatomic molecule as shown in **Figure 1.2**, when the temperature is increased, the molecule vibrates more due to the energy gained. The interatomic bond lengths are unchanged with the temperature and follow a harmonic potential well. However, in reality, increasing the temperature causes the bond distance to elongate according to the asymmetric feature of an anharmonic potential well and as a result expansion occurs.

How much the interatomic bond length expands depends on the bond strength of the bound atoms in the observed system. This means that a stiff bond will expand less than a weak one. In a crystal at very low temperatures, atoms located next to each other in the lattice vibrate an infinitesimal amount. In this

condition, the crystallographic unit cell axes and unit cell volume have a particular value. As the temperature increases, the atoms vibrate more resulting in greater interatomic distances and this leads to the increasing of unit cell axes and unit cell volume from which thermal expansion coefficients can be determined.

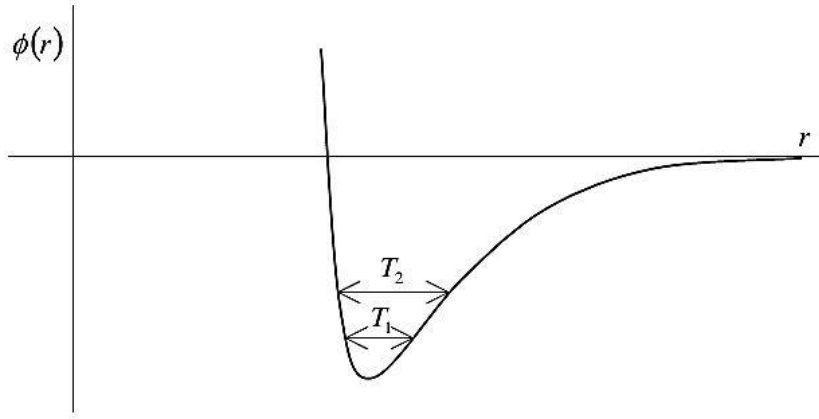


Figure 1.2 Illustration of anharmonic potential well as a function of interatomic distance (r) and potential energy $\phi(r)$.^[4]

The coefficient of volumetric thermal expansion (α_v) can be expressed as shown in Equation 1.3:

$$\alpha_v = \frac{1}{V} \left[\frac{\partial V}{\partial T} \right]_P \quad \text{Equation 1.3}$$

where α_v is the volumetric coefficient of thermal expansion, V is the volume, T is the temperature and P is the pressure.

Solids can expand isotropically where the extent of expansion is equal in every observed direction. This is commonly seen in materials that possess cubic symmetry. The determination of the linear thermal expansion coefficient in one direction only is sufficient for isotropic expansion. However, if anisotropic expansion occurs then the solid expands by different amounts in each direction

and determination of the linear thermal coefficient in every direction is required. The coefficient of linear thermal expansion (α_L) is expressed as shown in Equation 1.4:

$$\alpha_L = \frac{1}{L} \left[\frac{\partial L}{\partial T} \right]_P \quad \text{Equation 1.4}$$

where α_L is the coefficient of linear thermal expansion and L is the length.

Several techniques can be used to measure the extent of thermal expansion. Three of these techniques are based on the same principle where a displacement at the end of the specimen sample is observed while it is heated in a furnace. Only the detection method sets these three techniques apart. The first method which is the most popular technique is called dilatometry. This technique detects the displacement of the end of the specimen sample at a sensor by means of push rod.

The second method is interferometry where the displacement of the end of the specimen sample is measured in terms of the number of wavelengths of monochromatic light. This technique is more accurate than the dilatometry method but it is not as widely used as dilatometry because it is dependent on the optic reflectance of the specimen surface. The third technique is thermomechanical analysis which relies on a thermomechanical analyser. The displacement of the specimen is measured in terms of an electrical signal.

However, only the coefficient of thermal expansion is obtained when performing these three techniques and a rationalisation of the mechanisms responsible for the observed thermal behaviour is not possible. This is where diffraction and spectroscopic techniques become essential in the study of thermal expansion behaviour as diffraction gives the crystallographic details of a crystalline solid including observations of the temperature-dependence of crystallographic parameters such as unit cell edge, unit cell volume and the crystal structure that allows some insight into the origin of thermal expansion behaviour

to be deduced in the studied materials. The energy of vibrational modes accounting for the thermal expansion can also be investigated by spectroscopy and neutron scattering techniques.

1.4 Zero/Negative thermal expansion

Not all materials expand upon heating. However, the idea that materials contract or stay unchanged when the temperature is raised seems to oppose intuition due to the fact that a larger space is required for larger amplitude of atomic vibration. Preferably, contraction upon heating is called negative thermal expansion in order to indicate its anomaly and to indicate the negative value of the expansivity coefficient, α . This unusual phenomenon is rare and has been found only in certain solid materials. Possible contributions to NTE behaviour can either be vibrational modes or non-vibrational contributors (e.g. electronic effects). The latter is found to be pronounced at low temperature when the contributions of the vibration are small.

From a thermodynamic point of view, thermal contraction can be explained by considering the relation of the volume dependence of entropy that is given by:

$$\alpha_v = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \chi_T \left(\frac{\partial S}{\partial V} \right)_T \quad \text{Equation 1.5}$$

where χ_T is the isothermal compressibility and S is the entropy. In general cases, the increase of entropy would be expected to be accompanied by an increase of volume since the compressibility is always positive value so α_v is positive. A negative value of α_v indicates that the entropy of the system increases when such system is compressed and this is why NTE behaviour is anomalous.^[4]

Only the vibrational contributions of a solid will be focused upon here. When mentioning the vibrational modes in solids, it is usually related to anharmonicity and the subject of lattice dynamics where the latter deals with the propagation of waves generated in the lattices. The contribution of vibrational modes to thermal expansion of a solid can be described by the quantification of the anharmonicity which can be indicated according to the Mie-Grüneisen theory of the thermal expansion of solids. This theory generally states that the expansivity coefficient α should be proportional to the specific heat, C_V as given by:^[5]

$$\alpha = \frac{\gamma C_V}{V} \quad \text{Equation 1.6}$$

where γ is known as the Grüneisen constant which is dimensionless and can be determined from experiments. This constant is used to describe the anharmonicity of solids and can be defined by the volume dependence of frequencies of lattice vibration $\omega_j(V)$ which is given by:

$$\gamma_j = \frac{-d \ln \omega_j}{d \ln V} \quad \text{Equation 1.7}$$

where γ_j is the Grüneisen value of lattice mode j . In a harmonic solid, which is an ideal system, the ω_j is independent of volume which means all Grüneisen constants of all lattice modes are equal to zero. The deviation of these constants from zero, therefore, indicates the degree of anharmonicity. The larger the value of the Grüneisen constant means the greater degree of anharmonicity. The bulk Grüneisen parameter, γ , is given by:

$$\gamma = \frac{\sum_i C_{V,i} \gamma_i}{\sum_i C_{V,i}} \quad \text{Equation 1.8}$$

where $C_{V,i}$ are the vibrational mode i contributions to the heat capacity. Equation 1.6 and Equation 1.8 indicates that the NTE material will have a negative bulk Grüneisen parameter which results from a domination of the vibrational modes whose frequency ω_j decreases as the volume of the material decreases. An example of these vibrational modes are the transverse vibrational modes which generally have lower frequency than the longitudinal modes and are found to contribute their negative microscopic Grüneisen value to the bulk Grüneisen parameter at low temperature leading to NTE behaviour.^[6]

1.5 General mechanisms responsible for NTE

This thesis is focused mainly on the NTE behaviour of materials therefore the mechanism behind NTE behaviour will be discussed. The studies of negative thermal expansion behaviour began about fifty years ago with the discoveries of low thermal expansion materials such as cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), lithium aluminium silicates (LiAlSiO₄-LAS), silica glass (SiO₂) and sodium zirconate phosphate ($\text{NaZr}_2\text{P}_3\text{O}_{12}$ -NZP).^[7-9] These materials have become well-known low thermal expansion ceramics that have been studied thoroughly.

The study of thermal expansion behaviour in solid materials became more attractive when the negative thermal expansion of zirconium tungstate (ZrW_2O_8) was reported.^[10] This was the first time that NTE behaviour had been intimately related to the crystal structure of the solid. As the curiosity of how this phenomenon occurs grew, numerous attempts at explaining the origin of this anomalous behaviour were successfully made. Many techniques have been used

to study and to elucidate the possible mechanisms. For example, neutron and X-ray diffraction^[10] can be used to monitor the temperature dependence of the lattice parameters, atomic positions and thermal parameters, Raman and inelastic neutron scattering^[11] can be used as tools to probe the energy and frequency of lattice vibrations, and X-ray or neutron total scattering and atomic pair distribution function analysis^[12-14] can be applied to investigate how the actual bond lengths and the average transverse displacement of atoms in a solid vary as it is heated.

The advances of computer-based techniques^[15] allow the researcher to predict the NTE behaviour in materials and to compare the prediction with the experimental results. For instance, molecular-dynamics simulation can be used to determine the thermodynamic parameters, such as, to calculate lattice vibrational modes or phonons occurring in the observed solid. This technique models the minimum energy in a lattice and can include the effect of temperature on the atomic vibrations in the potential energy model which will provide some insights into the dynamic properties of the observed system.

There are several mechanisms responsible for the NTE behaviour reported to date. Classification of these mechanisms is difficult as some of them are unique and based on the inherent nature of those particular materials. Herein, the mechanisms are classified into two major groups including vibrational effects and non-vibrational effects. Each of these mechanisms will be reviewed here together with examples of NTE materials exhibiting each NTE mechanism.

1.5.1 Vibrational effects

Vibration in a crystal is based on the same concept as molecular vibration. However, some considerations need to be added as the vibrations occurring in a crystal have less degree of freedom than that in a molecule and the periodic and rigid nature of a crystal make the basis of vibrations in the crystal more complex. In crystals, an atom vibrates that not only leads to its displacement from its mean position but also has an effect on other vibrating atoms. Thus, the propagation of

waves through the crystal is generated. The vibrations in a crystal are called lattice modes and can be classified into two modes, transverse vibrations and longitudinal vibrations. Both of these vibrational modes possess acoustic and optical modes and the numbers of each mode depend on the number of atoms in the unit cell.

Displacement of an atom in a parallel direction to the atomic bond axis is called a longitudinal vibration which is the main factor contributing to thermal expansion in a solid. An increase of longitudinal vibrations gives rise to an increase of the average M-X bond which consequently makes the M...M distance elongate as shown in **Figure 1.3**. On the other hand, transverse vibrations in which the atomic displacement is perpendicular to the atomic bond axis generates the opposite effect. An increase of the amplitude of the vibration at X atom reduces the M-X-M bond angle which draws the two M atoms closer giving a consequentially shorter M...M distance.

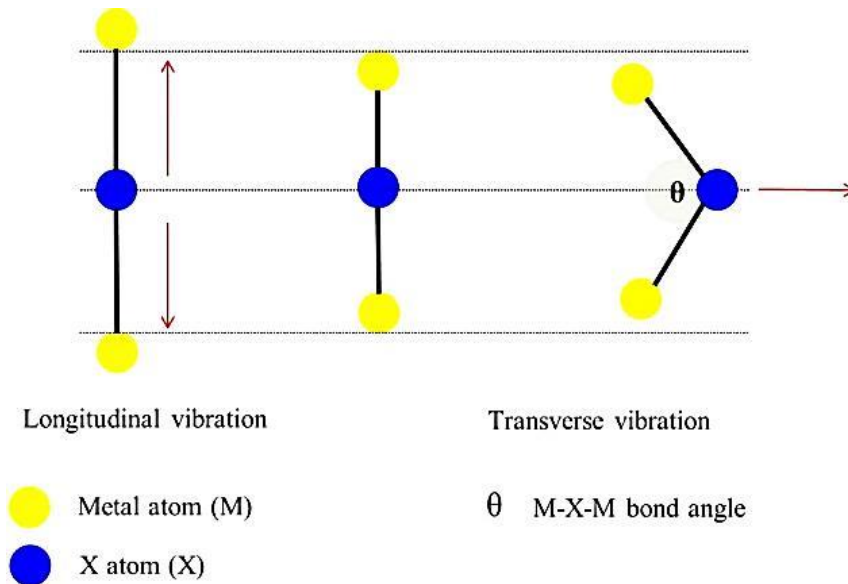


Figure 1.3 Illustrating lattice vibration modes which are a longitudinal vibration (left) and a transverse vibration (right). The longitudinal vibration increases the M...M' distance whereas the transverse vibration decreases the M...M' distance.

Hence, materials containing the M-X-M linkages can exhibit NTE due to the transverse vibrations occurring at the X atoms. However, most solid materials, although consisting of M-X-M linkage do not exhibit NTE. This is because the occurrence of NTE depends greatly on the nature of M-X-M linkage and the geometry and the rigidity of the structure of the material.

Dove and co-workers found that the presence of some low energy vibrational modes is responsible for the NTE behaviour in some materials. These particular phonon modes are called Rigid Unit Modes (RUMs) and describe the vibrational modes when the constituent polyhedra within a solid are considered as rigid bodies.^[16] For instance, in a system consisting of corner-sharing MO_4 tetrahedra, the atoms at the M-O-M linkages will involve the vibrations of rigid tetrahedra without any distortion of internal bonding of the tetrahedra. Thus, RUMs will require only low energy as motion at the relatively loose M-X-M linkages would cost less energy than dealing with the internal bonding of the MO_4 tetrahedra.

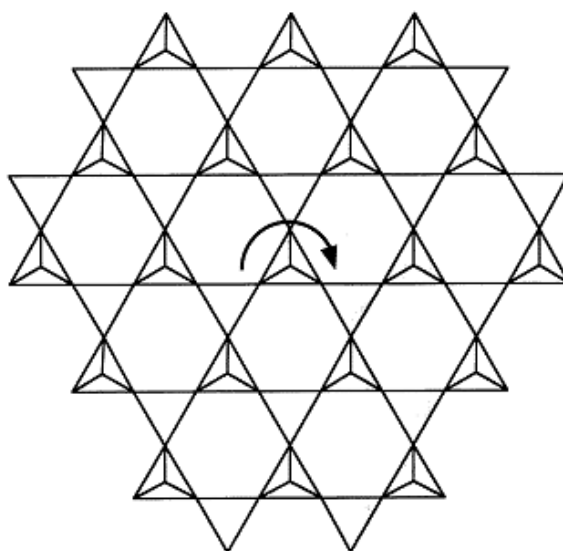


Figure 1.4 The two-dimensional structure of tridymite. The black arrow indicates the rotation of one triangular unit which causes an inward motion of the other triangular units.^[17]

Figure 1.4 shows that the rotation of the triangle introduces the rotation of its neighbouring triangles. This contributes to the overall reduction in the total area (or volume) of the framework. The triangle will continuously rotate as a result of the propagation of the RUMs phonon until reaching an equilibrium value. The phonon modes that are not regarded as RUMs normally have a higher frequency. This is because they involve the distortion of the constituent polyhedra which, of course, requires much more energy. However, the low frequency vibrational modes that cause a minimum and finite distortion of the structural polyhedra are also crucial in some particular instances if their energy is lower than that of the transverse vibration of the M-X-M bonds. These vibrational modes are referred to as quasi-RUMs (QRUMs) and are more energetically favourable in some systems and can play the same role in the consideration of NTE behaviour.

The basis of RUMs has theoretically and geometrically proven to cause a reduction of the volume of a framework material. By considering the simple perovskite system in two dimensions as shown in **Figure 1.5**, the area $A(\theta)$ of the unit cell can be written as a function of tilting angle (θ) as shown in Equation 1.9.

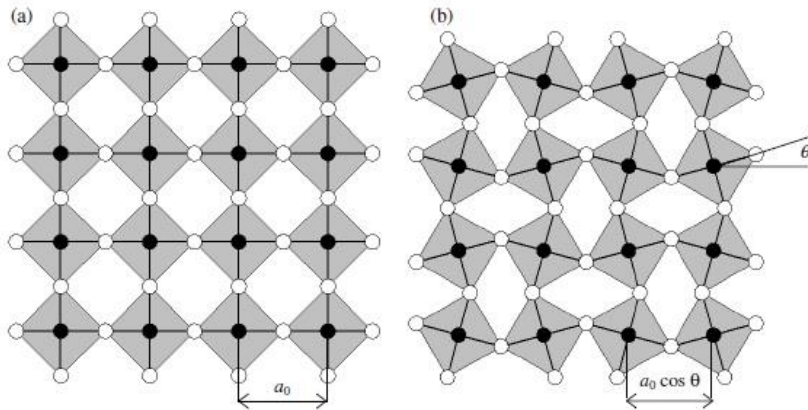


Figure 1.5 Illustrating the possible RUMs occurring in a two-dimensional square lattice of rigid octahedra MO_6 . a_0 is the unit cell length and θ is the tilting angle of the tetrahedra from its reference axis.^[4]

$$A(\theta) = A_0 \cos^2 \theta \approx A_0 (1 - \eta_A \theta^2)$$

Equation 1.9

The geometric parameter, η_A , is connected to the vibration mode. As the temperature increases, the thermal average of the tilting angle $\langle \theta^2 \rangle_T$ increases leading to the reduction of the unit cell area as given in Equation 1.10. If rule of equipartition of energy is applied to Equation 1.10, then $\langle \theta^2 \rangle_T$ can be written in term of temperature (T), moment of inertia of the rigid bodies (I) and the vibrational frequency (ν) as shown in Equation 1.11.^[18-19]

$$A(T) = A_0 \left(1 - \eta_A \langle \theta^2 \rangle_T \right) \quad \text{Equation 1.10}$$

$$A(T) = A_0 \left(1 - n_A \frac{k_B T}{I \nu^2} \right) \quad \text{Equation 1.11}$$

where k_B is Boltzmann constant.

Therefore, the lowest frequency vibrational mode will give the largest negative contribution to the framework area, and the NTE effect.

1.5.1.1 Zirconium tungstate (ZrW_2O_8) and its metal-substituted related phases

Zirconium tungstate (ZrW_2O_8) is used as an archetypal material in the studies of NTE behaviour. It exhibits isotropic NTE over a large temperature range, from 0.3 K to 1050 K with phase transition from cubic ($P2_13$) to cubic ($Pa\bar{3}$) being observed at 428 K. The coefficient of thermal expansion over the temperature range of 0.3 K – 350 K is $-9.1 \times 10^{-6} \text{ K}^{-1}$ and decreases to $-5 \times 10^{-6} \text{ K}^{-1}$ above the phase transition temperature.^[10]

One of the preferable characteristics of NTE materials is the absence of a phase transition within the temperature range that NTE is expressed as the phase transition may lower the symmetry of a crystal structure which might cause

anisotropic NTE and thus is impractical for many applications. However, zirconium tungstate is an exception as its structure after phase transition is still cubic which means it shows isotropic NTE behaviour over all the temperature range observed, although the coefficient of thermal expansion is slightly reduced. ZrW_2O_8 is a framework structure consisting of ZrO_6 octahedra and WO_4 tetrahedra. Each corner of ZrO_6 octahedra links with WO_4 tetrahedra but only 3 corners of WO_4 tetrahedra link with the ZrO_6 octahedra leaving one free corner on every WO_4 tetrahedra which gives the ZrW_2O_8 framework unusual flexibility.^[20] The framework of ZrW_2O_8 is shown in **Figure 1.6**.

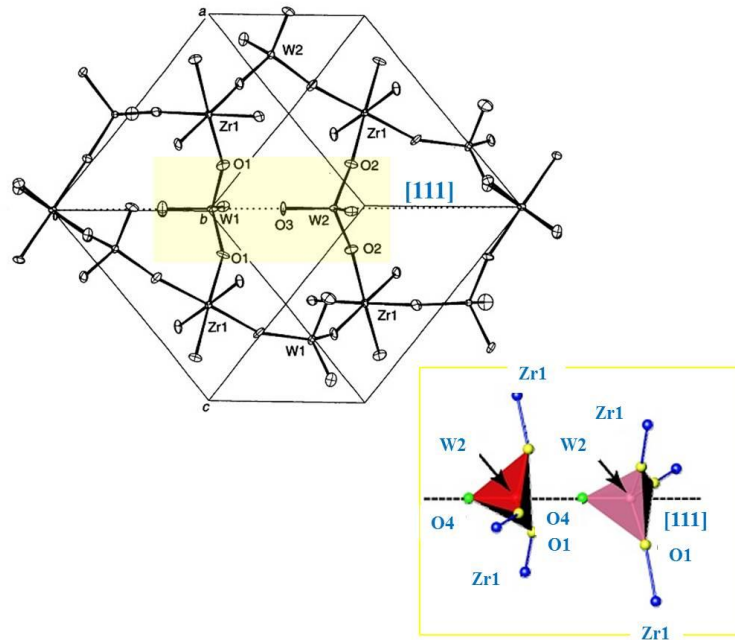


Figure 1.6 The structure of ZrW_2O_8 which consists of ZrO_6 octahedra and WO_4 tetrahedra. Only three corners of WO_4 tetrahedra link with ZrO_6 , while every corner of ZrO_6 octahedra is linked with the tetrahedra. Two WO_4 units align along the $[111]$ direction as can be seen from the inset, The rearrangement of these two units is found to be responsible for the phase transition occurring in ZrW_2O_8 .^[10]

The terminal oxygen atoms of the WO_4 tetrahedra are highly mobile as they do not link to the octahedra unit.^[21] Therefore, they are found to assist in the phase transition process. The order-disorder phase transition from the low to high symmetry cubic structure in ZrW_2O_8 is caused by the reorientation of two WO_4

tetrahedral units that lie along the body diagonal of the unit cell. **Figure 1.7** shows the long-range O^{2-} migration between the two adjacent WO_4 units which is the origin of the phase transition found in this material.

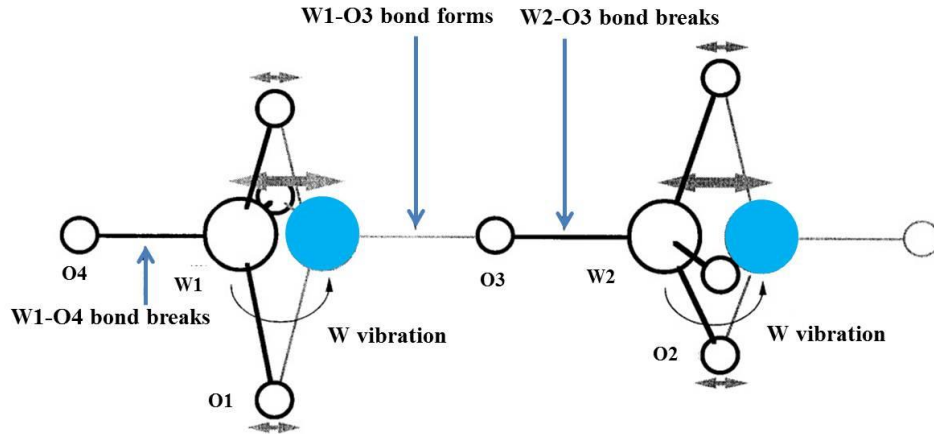


Figure 1.7 Illustrating the reorientation of the two WO_4 tetrahedra unit aligned along the diagonal body of the ZrW_2O_8 .^[22]

The NTE behaviour in ZrW_2O_8 originates from the transverse vibrations of Zr-O-W linkages coupled with concerted tilting of rigid ZrO_6 octahedra which gives rise to the overall volume contraction. Low-frequency phonon modes within an energy range of 3-8 meV were observed and were confirmed to be the significant contributions to NTE found in ZrW_2O_8 .^[17]

Effects of the metal on typical NTE behaviour of ZrW_2O_8 were investigated by substituting the two metal sites, Zr and W by Hf and Mo, respectively. The thermoresponsive behaviour of HfW_2O_8 was found to be very similar to that of ZrW_2O_8 except that the phase transition in HfW_2O_8 occurred at a slightly higher temperature ($T_{trans} = 448$ K).^[22] Whilst in $HfMo_2O_8$ and $ZrMo_2O_8$, there were no phase transitions observed. A further study of a series of $Zr_{1-x}Hf_xW_{2-y}Mo_yO_8$ showed that increasing the amount of Hf substitution has a less significant effect on the thermal behaviour of the observed phases whereas the Mo amount has more effect on the phase transition behaviour of such phases.^[23-24]

1.5.1.2 Zirconium vanadate (ZrV_2O_7)

Zirconium vanadate (ZrV_2O_7) is another material that exhibits isotropic NTE. Slightly positive thermal expansion (PTE) is observed up to 375 K, at which point a phase transition occurs. Contraction emerges above 375 K with a coefficient of thermal expansion between $-7 \times 10^{-6} \text{ K}^{-1}$ to $-10 \times 10^{-6} \text{ K}^{-1}$. ZrV_2O_7 has a similar framework structure to ZrW_2O_8 but is more rigid. It is comprised of corner sharing ZrO_6 octahedra linked with oxygen atoms of V_2O_7 groups. The V-O-V linkages that join two VO_4 units together are slightly distorted from being linear upon cooling which causes the phase transition.^[17] The difference between the structural framework of ZrW_2O_8 and ZrV_2O_7 is shown in **Figure 1.8**.

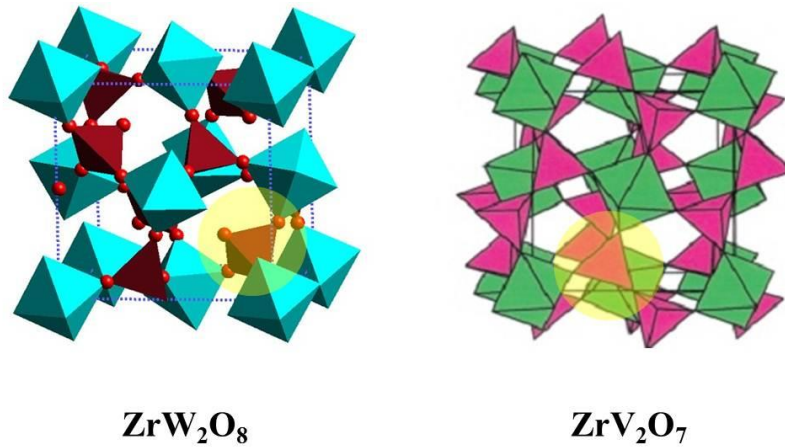


Figure 1.8 The ZrW_2O_8 structure (left) in comparison with the ZrV_2O_7 structure (right) in which the two MO_4 tetrahedra in ZrW_2O_8 are separated while in the ZrV_2O_7 structure the two nearby VO_4 tetrahedra are linked.^[4, 6]

The NTE behaviour found in ZrV_2O_7 is attributed to the transverse vibrations of the V-O-V linkages. No RUMs but rather QRUMs were observed in this material since the transverse vibrational modes of the V-O-V linkage are involved in distortion of the polyhedra which requires higher frequency vibrational modes.

1.5.1.3 Scandium tungstate ($\text{Sc}_2\text{W}_3\text{O}_{12}$) and its metal-substituted related phases

An additional trend for enhancing the NTE behaviour of solid materials is to vary the cation size as has been done in the studies of the NTE behaviour in ZrW_2O_8 and ZrV_2O_7 . A corollary of altering the cation types is the possibility of eliminating phase transitions which is an undesirable event in the NTE behaviour of materials. In general, some solids undergo displacive phase transitions from low to high symmetry as the temperature is increased. Before a phase transition occurs, the unit cell volume usually increases with increasing temperature. Then a reduction of the unit cell volume is observed after achieving a higher structure. The ultimate aim is to get rid of the phase transition if possible or to lower the phase transition temperature and hence NTE will be exhibited over a wider temperature range.

The studies of the NTE behaviour in the $\text{A}_2\text{M}_3\text{O}_{12}$ family were observed to investigate these effects. Their framework structure comprises of octahedrally coordinated trivalent metal A (Sc, In, Al, Y, Hf, Zr, Lu, Cr, Fe) and tetrahedrally coordinated hexavalent cation M (Mo or W).^[25] Each corner of the AO_6 octahedra is linked with the MO_4 tetrahedra. Their NTE behaviour is attributed to the transverse vibrations of A-O-M linkages concerted with tilting and rocking modes of polyhedra. The average A-O-M angle decreases as the temperature is increased which draws the average A...M distances nearer causing the overall contraction. The coefficient of thermal expansion in each material was measured by X-ray diffraction and by dilatometry measurements and it was found that increasing the A^{n+} cation size moves the phase transition to the lower temperature. In general, framework collapse depends on the balance between oxygen-oxygen repulsion and oxygen-oxygen attractive interactions. If the A^{n+} cation has a strong electronegativity, the effective negative charge on the oxygen atom will be less thus the oxygen-oxygen repulsion is reduced. Once the oxygen-oxygen attractive force overcomes the repulsive force, the framework collapses.

Incorporating a large cation into the framework might cause an effect on the magnitude of the coefficient of thermal expansion. As larger cation sizes

increase the oxygen-oxygen distances, the oxygen-oxygen repulsive force is reduced which enhances the NTE effect. The trend of the ionic radii of some constituent metal is shown in **Figure 1.9** and coefficients of thermal expansion in some selected materials containing corresponding metals are summarised in **Table 1.1** which follow the aforementioned trend.

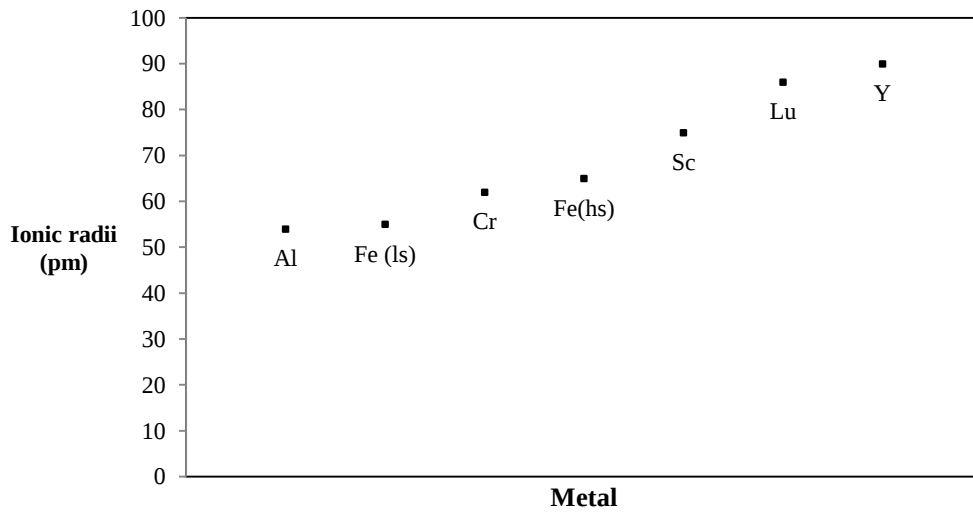


Figure 1.9 The trend of the ionic radii of some metals.^[26] ls and hs is referred to low spin and high spin configuration.

Table 1.1 Coefficients of thermal expansion of some members of $A_2M_3O_{12}$ family

Materials	$\alpha_V (10^{-6} K^{-1})$	Temperature observed (K)	Phase transition
$Al_2Mo_3O_{12}$ ^[27]	-2.83	298 - 1073	473 - 523
$Cr_2Mo_3O_{12}$ ^[27]	-9.39	298 - 1073	623 - 673
$Fe_2Mo_3O_{12}$ ^[27]	-14.82	298 - 1073	773 - 823
$Sc_2W_3O_{12}$ ^[28]	-2.2	10 - 450	-
$Lu_2W_3O_{12}$ ^[29]	-6.8	400 - 900	-
$Y_2W_3O_{12}$ ^[30-31]	-7.0	15 - 1373	-

1.5.1.4 Zeolites and zeotypes

Zeolites are crystalline microporous aluminosilicates whose pores lie in the range of 1 – 20 Å. They are known for many potential applications such as catalysis, molecular sieving and ion exchange. More than 150 different naturally occurring or synthetically produced zeolites exist with open framework structures that are comprised of alternating, corner sharing SiO_4 tetrahedra and AlO_4 tetrahedra. The variety of microporous materials has been expanded by incorporating other elements such as Ti, P and Ga into the framework and these are called zeotypes. An example of a zeolite is shown in **Figure 1.10**.

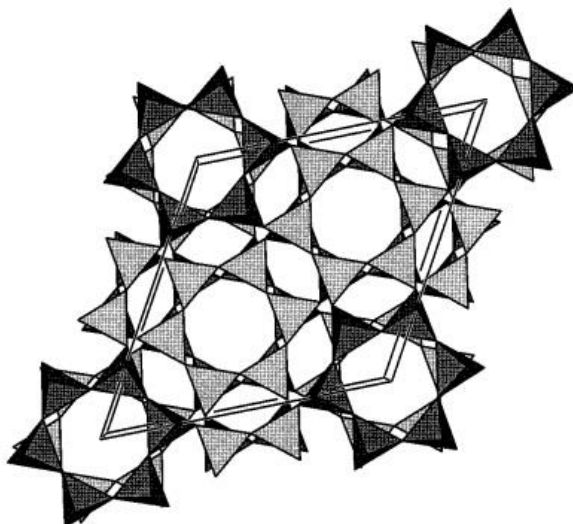


Figure 1.10 The framework of chabazite (CHA) viewing along the c -axis which is made by stacking of double six rings in a fashion of AABBC. It exhibits NTE over the temperature range of 293 – 873 K with $-0.5 \times 10^{-6} \text{ K}^{-1} \leq \alpha_v \leq -16.7 \times 10^{-6} \text{ K}^{-1}$.^[32]

The NTE behaviour of zeolites and zeotypes has been explored extensively by means of computer simulation techniques such as lattice dynamic calculations^[33] and free energy minimization,^[34] and experimental techniques such as X-ray diffraction and inelastic neutron scattering. The computer simulation techniques were used to predict the coefficient of thermal expansion in some selected materials whereas experimental techniques were used to verify the

NTE behaviour of the zeolites. The first zeolite reported to exhibit NTE was SiO₂ faujasite that has a coefficient of thermal expansion of $-4.2 \times 10^{-6} \text{ K}^{-1}$ over the temperature range of 25 – 573 K,^[35] and the first NTE behaviour of a zeotype was reported from AlPO-17 which has a coefficient of thermal expansion of $-11.7 \times 10^{-6} \text{ K}^{-1}$ over the temperature range of 18 – 300 K.^[36] The latter value is larger than that observed in ZrW₂O₈. More zeolites and zeotypes that exhibit NTE behaviour are summarized in **Table 1.2**.

Table 1.2 Coefficients of thermal expansion exhibited over stated temperature ranges for some zeolite/zeotype microporous materials

Framework type code	Observed temperature range (K)	Coefficient of thermal expansion ($\times 10^{-6} \text{ K}^{-1}$)
MFI ^[37]	393 - 975	-15.1
AFI ^[37]	424 - 774	-14.5
DOH ^[37]	573 - 996	-3.1
MTN ^[37]	463 - 1002	-5.0
DDR ^[37]	492 - 1185	-8.7
ITQ-1 ^[38]	50 - 500	-12.1
ITQ-3 ^[38]	50 - 500	-11.4
SSZ-23 ^[38]	50 - 500	-10.3
ITQ-7 ^[39]	473 - 873	-5.6
ITQ-9 ^[39]	293 - 873	-10.0
MAPO-17 ^[39]	323 - 773	-4.6
CIT-5 ^[39]	373 - 973	+14.9
AlPO ₄ -31 ^[39]	323 - 823	+32.8
FER ^[40]	420 - 560	-24.2
LTA ^[41]	100 - 300	-22.1
CHA (AlPO-34) ^[42]	110 - 460	-24.03
CHA (GaPO-34) ^[42]	260 - 460	-16.03
AEI ^[42]	105 - 455	-26.01

As zeolites and zeotypes are porous materials, their pores are occupied by guest molecules, such as water or any unreacted starting solvent whose size is commensurate with the framework pore size. Guest molecules must be excluded from the pores before examining the NTE behaviour of the framework only such materials. Otherwise, the NTE behaviour found might not be purely intrinsic but rather include the effect of guest molecule departure or motion. An example of

this phenomenon was found in the revelation of NTE behaviour in zeolite rho which was attributed to the effect of dehydration.^[43]

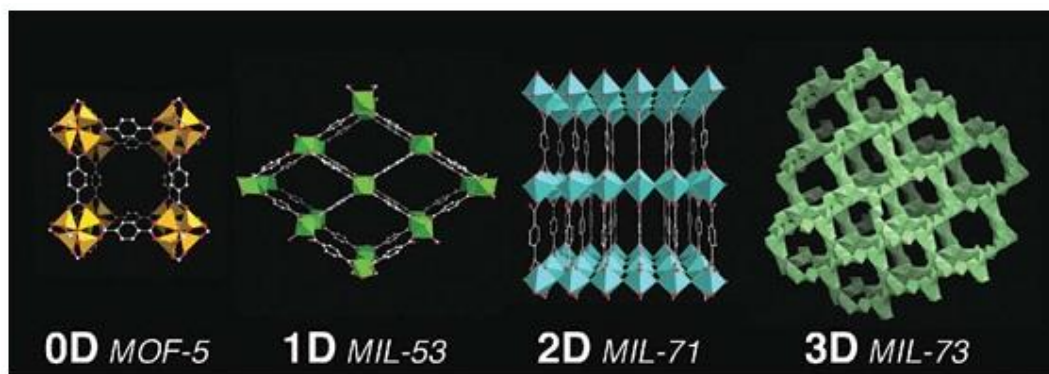
The widespread occurrence of the NTE behaviour founded in zeolites and zeotypes is attributed to the transverse vibrations of oxygen bridging atoms, M-O-M' coupled with dynamic rocking of rigid tetrahedra, as commonly found in other metal oxide systems. These motions decrease the angles of M-O-M' linkage which subsequently shortens the M...M' non-bonding distances. However, the magnitude of the coefficient of thermal expansion depends on the compositional element, framework density and framework architecture.

All the materials mentioned up to this point are metal oxides with NTE behaviour often being related to transverse vibrations to M-O-M bonds. However, more recently NTE behaviour has been observed in materials with more complex linkages between the M cations. One family of such NTE materials are Metal-Organic Framework (MOF) materials. In the past, this type of material has been referred to as coordination polymers before it was redefined by Omar Yaghi in 1995.^[44] Since then, the term MOFs has been used widely for all microporous materials that are made from the interaction between metal centres and organic linkers forming extended three-dimensional structures. The interaction between the metal centres and the organic linkers can either be ionic, covalent, coordinate covalent or Van der Waals interactions.

1.5.1.5 *Metal Organic Frameworks (MOFs)*

MOFs have become very attractive over the fifteen years since their discovery as they possess a great diversity in their framework structure. The vast diversity of the structures of MOFs arise from the numerous possibilities available for the synthesis of MOFs as nearly all the cations from the periodic table and any desired organic linkers can be combined. The coordination of the metals with the organic linkers yields metal-ligand polyhedra, so-called secondary building unit (SBUs) which in most cases are metal-oxide inorganic units. The construction of

the SBUs is greatly dependent on the nature of the constituent metals, the organic linkers and the conditions of the synthesis. According to Kitagawa *et al.*, the inorganic components of MOFs are classified into four categories based on their dimensionality. Examples of four materials with corresponding inorganic components are shown in **Figure 1.11** (a). The dimensionality of the inorganic components includes zero-dimensional for the inorganic clusters or single ions, one-dimensional for the inorganic chains, two-dimensional for the inorganic sheets and three-dimensional for the inorganic framework. Each of the resulting materials will have a different pore system and may be used in different applications.



(a)

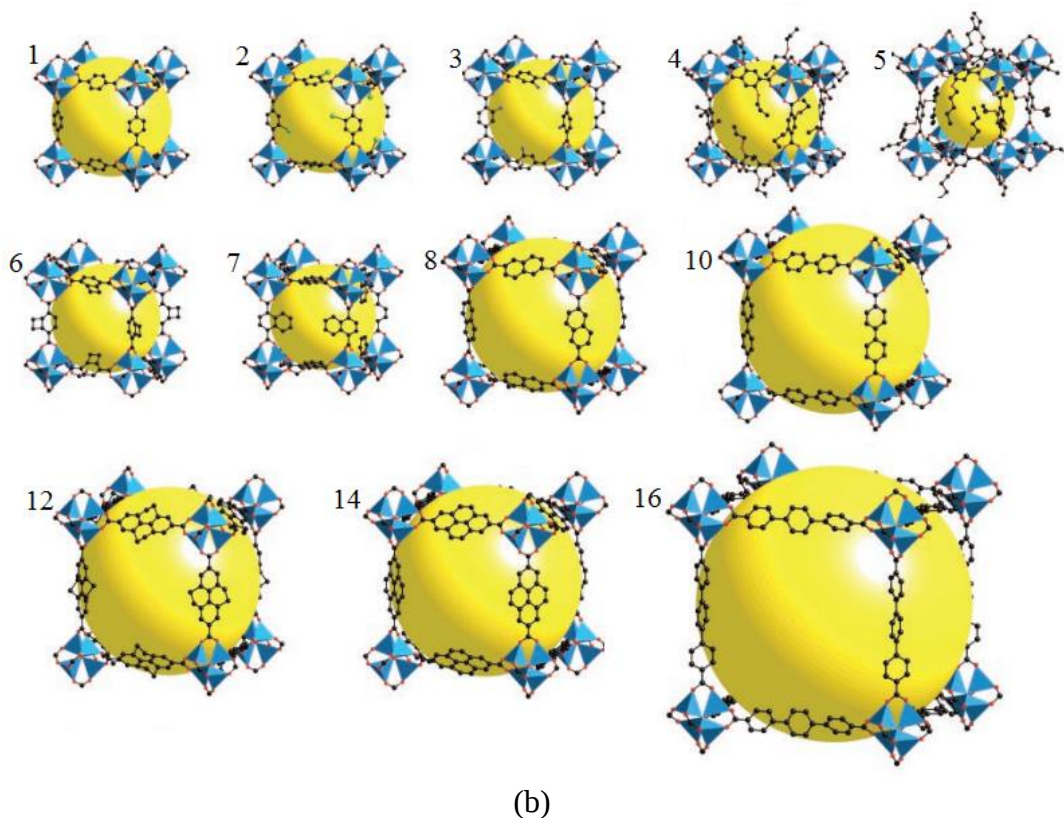


Figure 1.11 (a) The dimensionality of the inorganic components in MOFs^[45] (b) The structure of IRMOF 1 – 16 resulting from the reticular synthesis method.^[46]

A wide variety of the organic linkers can be chosen ranging from alkyl chains to aromatic systems as the carbon backbone. The latter is preferred over the former as it adds rigidity to the MOF framework. The functional groups also vary greatly ranging from the most common group-carboxylates to phosphonates, sulfonates, pyridines and imidazoles. The modular concept of the synthesis of MOFs gives rise to the concept of the reticular synthesis. This synthesis was designed with the purpose to increase the internal surface area of MOFs. A successful example of this synthesis concept is the series of isorecticular MOF structures (IRMOFs) by Yaghi *et al.* in 2002 as shown in **Figure 1.11** (b). Sixteen members in the series have the cubic topology of MOF-5 structure which consist of identical $\text{Zn}_4\text{O}(\text{CO}_2)_{12}$ inorganic clusters but sixteen different organic linkers. All members of the series have a different pore size and functionality.^[46] Furthermore, the use of longer ligands is occasionally found to create catenated frameworks which give rise to a smaller diameter than expected for the internal

pores of the MOF. Alteration of the organic linkers does not only offer a variation in pore size systems to be achieved but is also found to be a way to alter the functionalities of MOFs and so designs new materials with a specific property for a certain application.^[47] For instance, the chiral organic linkers can be incorporated into the structure in order to create specific local environment that are appropriate for asymmetric synthesis.^[48]

MOFs have become exciting materials due to their interesting properties which mostly surpass the properties of inorganic porous materials like zeolites in the same areas except the property of thermal stability for which are lower than that of zeolites owing to the presence of the organic moieties. MOFs are potentially applicable in many areas. And the most promising applications appearing to be in gas storage,^[49-50] gas adsorption and gas/liquid separation.^[51] These applications emerge from the total accessibility of the overall internal void volume of MOFs that can also be tuned to any desirable size to fit a specific application. MOF-177 (surface area = $4500 \text{ m}^2\text{g}^{-1}$),^[52] MIL-101 (surface area = $5900 \text{ m}^2\text{g}^{-1}$)^[53] and MOF-210 (surface area = $10400 \text{ m}^2\text{g}^{-1}$)^[54] are three MOFs that have been reported to have extremely highest surface areas. MOFs have particularly been tested for use in hydrogen storage and CO_2 sequestration. Challenges associated with the application of MOFs for gas storage are to find the most effective and low cost MOFs that have a high capacity of storage at a low pressure and high temperature. Other potential applications of MOFs have been reviewed thoroughly including the uses of MOFs in catalysis,^[55] polymer industry,^[56] magnetic materials,^[57] thin film industries,^[58] as electro-optical devices,^[59] and in biological applications.^[60]

1.5.1.6 *Porous metal cyanides*

Porous metal cyanides is the first family of MOF that was reported to exhibit NTE behaviour. A breakthrough was made by Kepert *et al.*, when they suggested that a material that contains diatomic linker (CN^- group) may exhibit

NTE with an even greater magnitude of thermal expansion coefficient than that seen in metal oxides.

Figure 1.12 shows the comparison of the possible modes of the transverse vibration between a system containing single atomic linkers and a system containing diatomic linkers. It is apparent that the presence of the diatomic linker adds more possibilities for the transverse vibrational modes and lower energy phonon modes. It is also noteworthy that in a material bearing a single atomic linker once a transverse vibration occurs, the neighbouring polyhedra must move in a concerted manner. In contrast, the transverse vibration in a material containing diatomic linkers does not necessarily require movement of other neighbouring polyhedra. This leads to a significantly larger number of RUMs in the materials bearing diatomic linker. The presence of the diatomic linker not only increases the number of RUMs but also implies significant structure flexibility with respect to the geometric connectivity of the rigid coordination polyhedra.

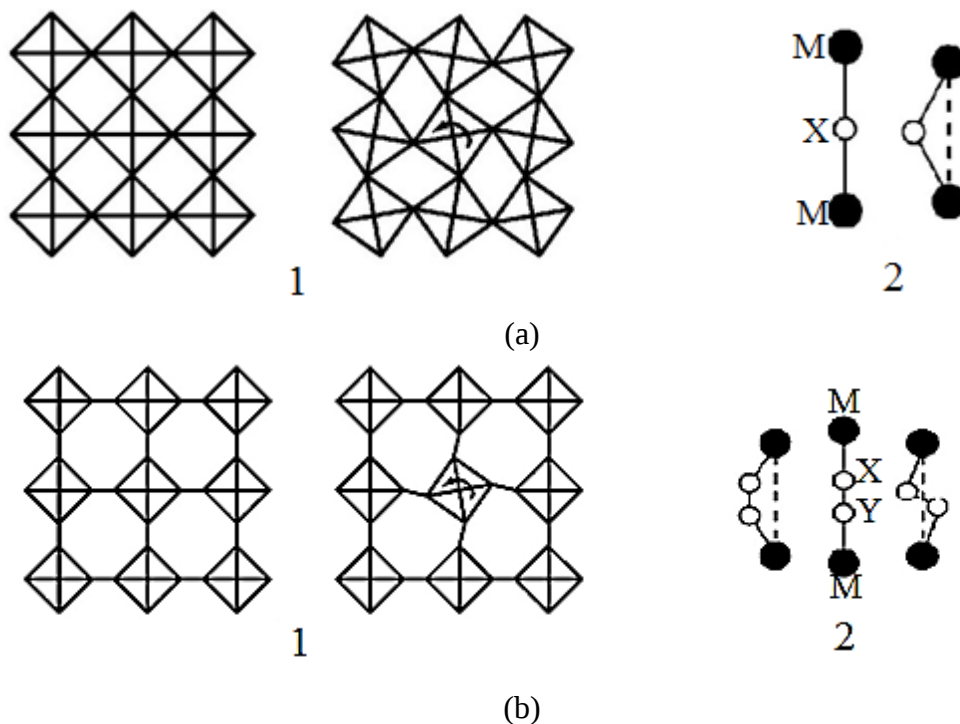


Figure 1.12 The framework flexibility and the representative local vibrational modes that contribute to the NTE behaviour in two dimensional perovskite topology containing (a) single-atomic linker M-X-M (b) diatomic linker M-X-Y-M.^[61]

Zinc cyanate ($\text{Zn}(\text{CN})_2$) was the first member of the metal cyanide family that was found to exhibit NTE over the temperature range 14 - 305 K.^[62] Its thermal expansivity is $-18 \times 10^{-6} \text{ K}^{-1}$, which is greater, but exhibited over a smaller range of temperature than that observed in ZrW_2O_8 . Soon after, the NTE behaviour of a number of metal cyanides were reported including $\text{Fe}[(\text{Co}(\text{CN})_6)]$,^[63] $\text{Cd}(\text{CN})_2$,^[64] $\text{Zn}_x\text{Cd}_{1-x}(\text{CN})_2$,^[65] $\text{M}^{\text{II}}\text{Pt}^{\text{IV}}(\text{CN})_6 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Zn}$ and Cd)^[66] and $\text{Er}^{\text{(III)}}[\text{Co}^{\text{(III)}}(\text{CN})_6]$.^[67] A summary of the NTE behaviour of several metal cyanides are tabulated in **Table 1.3**.

Table 1.3 Summary of the coefficient of thermal expansions (α) of porous metal cyanides

Materials	Observed temperature range (K)	Coefficient of linear thermal expansion (10^{-6} K^{-1})
$\text{Fe}[(\text{Co}(\text{CN})_6)]$ ^[63]	14 - 305	$\alpha = -1.47$
$\text{Zn}(\text{CN})_2$ ^[68]	100 - 400	$\alpha = -16$
$\text{Cd}(\text{CN})_2$ ^[64]	170 - 375	$\alpha = -33.5$
$\text{Zn}^{\text{(II)}}\text{Pt}^{\text{(IV)}}(\text{CN})_6$ ^[66]	25 - 375	$\alpha = -3.38$
$\text{Cd}^{\text{(II)}}\text{Pt}^{\text{(IV)}}(\text{CN})_6$ ^[66]	25 - 375	$\alpha = -6.69$
$\text{Er}^{\text{(III)}}[\text{Co}^{\text{(III)}}(\text{CN})_6]$ ^[67]	100 - 375	$\alpha_a = -8$
		$\alpha_c = -9$
$\text{Ag}_3[\text{Co}(\text{CN})_6]$ ^[69]	16 - 500	$+130 \leq \alpha_a \leq +120$
		$-130 \leq \alpha_c \leq -120$
$\text{Cu}^{\text{(I)}}\text{Zn}^{\text{(II)}}(\text{CN})_4$ ^[65]	218 - 368	$\alpha = +0.63$

The mechanism behind the NTE behaviour of metal cyanide frameworks was studied using several approaches and is attributed to the increase of the populated transverse vibrations of the diatomic linker (M-CN-M') upon heating. This has been confirmed by using the total scattering technique that includes an

atomic pair distribution function (PDF) analysis. This method has advantages over the traditional Bragg diffraction experiment and is found to be very useful in case where one needs to inspect the instantaneous structure of the material. The PDF analysis allows researchers to measure the “real” bond distance which complements the results from X-ray diffraction techniques. Moreover, the PDF analysis relies on the radial distribution function between two atoms which means this technique has no model bias. Kepert *et al.* found that as the temperature is increased the transverse vibrations of bridging atoms also increase which is reflected by an increase of the displacement of the CN linkers from the Zn...Zn axis direction as illustrated in **Figure 1.13**.^[68]

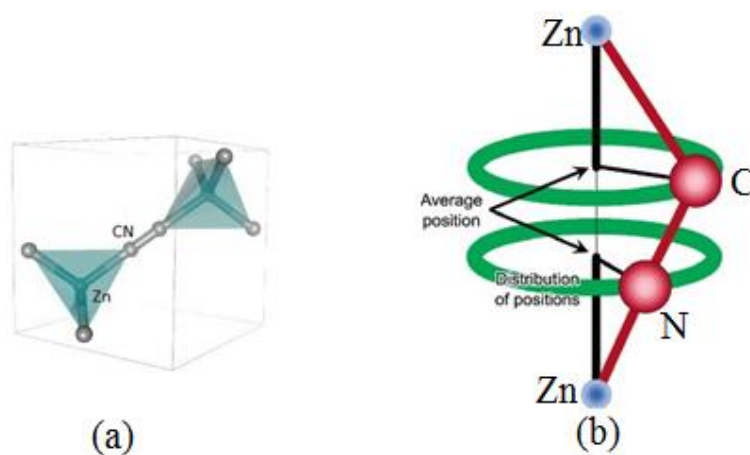


Figure 1.13 a) The unit cell of Zn(CN)₂ b) The apparent bond lengths are derived from Bragg analysis (black line) which results from a structural analysis of the Bragg intensity collecting from variable temperature powder X-ray diffraction and the “true” bond lengths obtaining from PDF analysis (red line). The difference between the apparent bond length and the true bond lengths indicates how much atoms are displaced from the Zn...Zn axis.^[68]

Porous materials are capable of guest molecule adsorption as they contain internal voids of molecular size which whose size is dependent on the framework structure. Therefore, the effects of guest molecule inclusion in the framework on the NTE behaviour of metal cyanides have been studied intensively. It was found that the presence of the guest molecules restricts the transverse vibrations occurring within the framework, subsequently changing the coefficient of thermal

expansion from a negative to positive value.^[66] For instance as shown in **Figure 1.14**, the empty $\text{ZnPt}(\text{CN})_2 \cdot \text{H}_2\text{O}$ material shows NTE behaviour with a coefficient of thermal expansion of $-3.38 \times 10^{-6} \text{ K}^{-1}$. Once water molecules were included inside the framework, the observed expansivity became $+1.82 \times 10^{-6} \text{ K}^{-1}$.

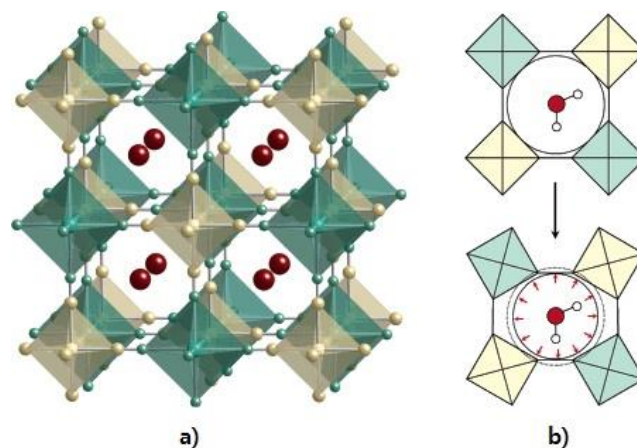


Figure 1.14 (a) The structure of the Prussian Blue $\text{M}^{\text{II}}\text{Pt}^{\text{IV}}(\text{CN})_6$ and (b) the guest molecule inclusion which perturbs the phonon mode of NTE behaviour. PtC_6 (yellow) and MN_6 (green) octahedra and water molecules (red).^[66]

However, the effect of guest molecule inclusion on the NTE behaviour depends deeply on how well the guest molecule fits into the pore volume of the framework. If the size of the guest molecule is commensurate with the pore of the framework the NTE behaviour might be affected greatly. On the other hand, if the guest molecule is small compared to the pore size of the host, the NTE will still be affected but not massively. For example, a water molecule occupies $40 \text{ \AA}^3$ when it is adsorbed into the void volume. The inclusion of a water molecule into the $\text{ZnPt}(\text{CN})_2$ framework which has a void volume of $45 \text{ \AA}^3$ will have a great effect on the NTE behaviour as mentioned above. This is reflected in the coefficients of thermal expansion of empty $[\text{Zn}(\text{Pt})(\text{CN})_2]$ and $\text{ZnPt}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ which are $-3.38(9) \times 10^{-6} \text{ K}^{-1}$ and $+1.82(15) \times 10^{-6} \text{ K}^{-1}$ respectively. In contrast, $\text{CdPt}(\text{CN})_2$ has a void volume of $65 \text{ \AA}^3$ and the presence of water molecules within the pore volume has significantly less effect on the NTE behaviour as reflected in the

coefficient of thermal expansion of the empty $[\text{Cd}(\text{Pt})(\text{CN})_2]$ and $\text{CdPt}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ which are $-6.69 \times 10^{-6} \text{ K}^{-1}$ and $-7.31 \times 10^{-6} \text{ K}^{-1}$ respectively.

The fraction of guest molecules also affect the magnitude of the coefficient of thermal expansion greatly as has been shown for $\text{Cd}(\text{CN})_2$. The magnitude of the coefficient of thermal expansion of $[\text{Cd}(\text{CN})_2 \cdot x\text{CCl}_4]$ increases with increasing x fractional occupancies with the guest-free framework $[\text{Cd}(\text{CN})_2]$ exhibiting $\alpha = -33.5(5) \times 10^{-6} \text{ K}^{-1}$ over the temperature range of 170 – 350 K and the $[\text{Cd}(\text{CN})_2]$ framework with 64% and 100% fractional CCl_4 occupancies exhibiting $\alpha = -16.9(3) \times 10^{-6} \text{ K}^{-1}$ and $\alpha = +10.0(2) \times 10^{-6} \text{ K}^{-1}$ respectively. Undoubtedly, the presence of guest molecules impedes the transverse vibrations of the CN^- group perpendicular to the $\text{Cd}^{2+} \dots \text{Cd}^{2+}$ axis. In the guest-free framework transverse vibrations require low energy and a negative Grüneisen parameter. When guest molecules are incorporated into the void volume, higher energy is required for the occurrence of transverse vibrations hence a less negative or even positive Grüneisen parameter results. The incorporation of a different amount of the guest molecules into the framework has an effect to the NTE behaviour as well as varying the species of guest molecules.^[65, 70] This phenomenon is found to be useful in order to control the coefficient of thermal expansion.

The effect of cation size on the magnitude of the coefficient of thermal expansion was systematically studied. The magnitude of the coefficient of thermal expansion was observed in the Prussian blue analogues $[\text{M}^{\text{II}}\text{Pt}^{\text{IV}}(\text{CN})_6]$ where M^{II} are Mn, Fe, Co, Ni, Cu, Zn and Cd. It was shown that $[\text{NiPt}(\text{CN})_6]$ exhibits the smallest magnitude of NTE with a coefficient of thermal expansion $\alpha = -1.02(11) \times 10^{-6} \text{ K}^{-1}$ whilst $[\text{CdPt}(\text{CN})_6]$ shows the largest with $\alpha = -10.02(11) \times 10^{-6} \text{ K}^{-1}$. The magnitude of the coefficient of thermal expansion was found to vary linearly with cation size $[\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Cd}^{2+}]$ and with the strength of the interaction at M^{2+} -NC linkage. The stronger the M^{2+} -CN interaction, the smaller the magnitude of the atomic displacement occurring perpendicular to M^{2+} -CN bond direction.^[71]

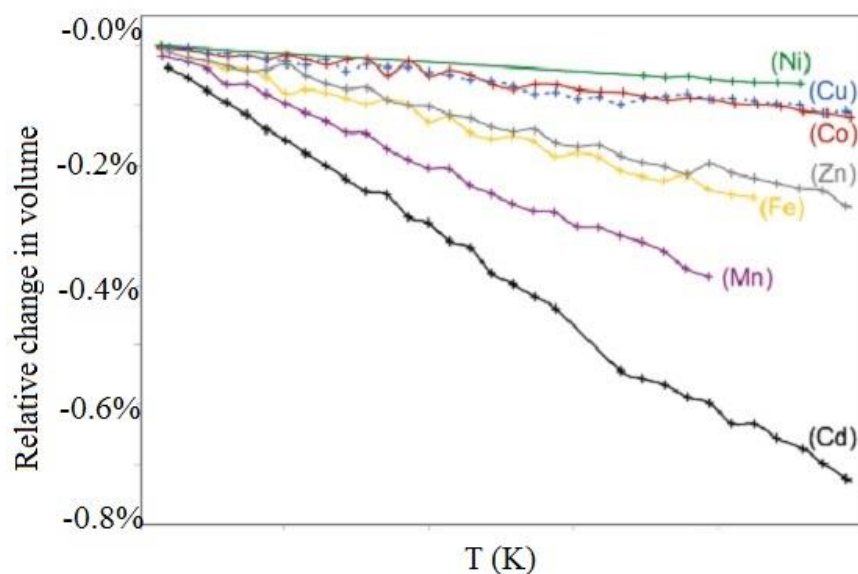


Figure 1.15 The relative change of unit cell volume at 100 K of $M^{II}Pt^{IV}(CN)_6$ as the temperature is increased. M is Ni^{2+} , Cu^{2+} , Co^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} and Cd^{2+} .^[71]

1.5.1.7 Metal carboxylates

The first metal carboxylate to exhibit the NTE behaviour was reported in 2002 and is the anhydrous strontium salt of acetylenedicarboxylic acid, $Sr[C_2(COO)_2]$ which exhibits a small NTE over the temperature range of 30 - 280 K.^[72] Its volumetric coefficient of thermal expansion was found to be $-4.7(1) \times 10^{-6} K^{-1}$. The transverse vibration of the bridging oxygen atom perpendicular to the direction of Sr-O bond was found to play a major role in its NTE behaviour. The structure of $Sr[C_2(COO)_2]$ is shown in **Figure 1.16**.

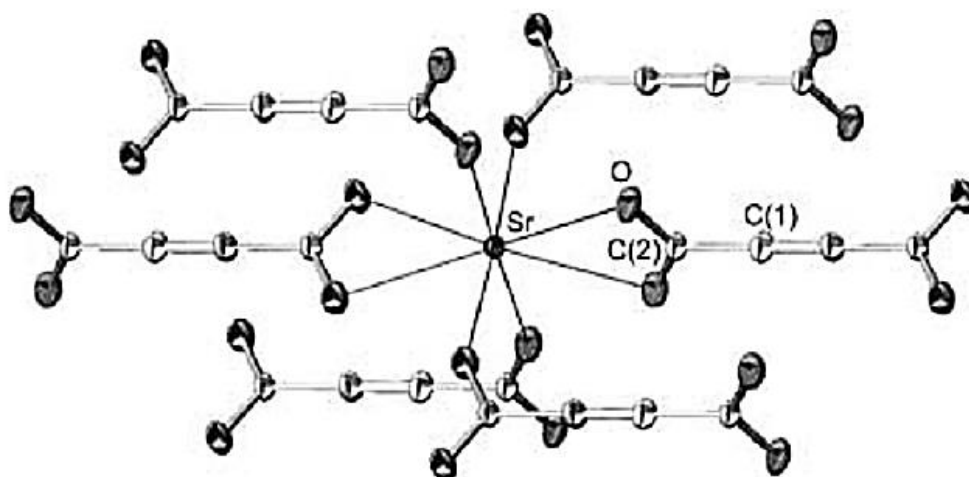


Figure 1.16 The structure of $\text{Sr}[\text{C}_2(\text{COO})_2]$.^[72]

In 2008, the porous metal carboxylate, $[\text{Cu}_3(\text{btc})_2]$, so called (HKUST-1), where $\text{btc} = 1,3,5\text{-benzenetricarboxylate}$, was reported to exhibit NTE behaviour. Its linear coefficient of thermal expansion calculated over the temperature range of $80 - 500 \text{ K}$ is $-4.1 \times 10^{-6} \text{ K}^{-1}$.^[73] The structure of HKUST-1 is made from paddle wheel dicopper tetracarboxylate motifs which are linked together by benzene rings creating three-dimensional cubic framework, as shown in **Figure 1.17**.

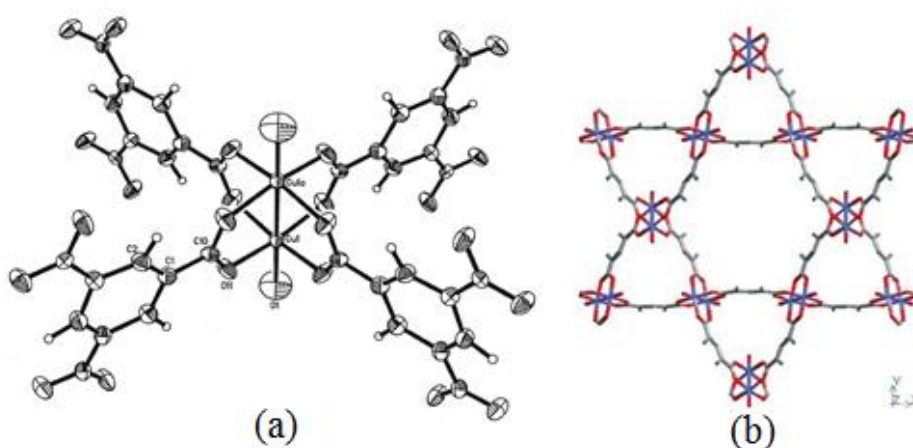


Figure 1.17 (a) The building block of the HKUST-1 structure showing four btc ligands that link two copper atoms together, generating a paddle wheel motif. (b) The three-dimensional structure of HKUST-1 viewed along the $[111]$ direction.^[74]

The structure refinement obtained from both single-crystal X-ray diffraction data and powder synchrotron X-ray diffraction data suggested that there was an apparent decrease of the O...O non-bonding distance which is a result of twisting vibrations at the carboxylate linkage as it is the weakest part of the framework. The thermal population of the vibrational modes of the carboxylate groups of the btc linker is found to cause the deformation of the inorganic cluster as reflected in a rapid decrease of the Cu-O bond distance. Additionally, dynamic motions of the benzene rings such as a tilting vibrational mode and out-of-plane translations are coupled with the vibrational mode at the carboxylate linkage yielding the overall volume contraction. The deformation of the [Cu₂(CO₂)₄] inorganic clusters upon heating was confirmed by combining the techniques of neutron scattering and first principal studies. The distorted [Cu₂(CO₂)₄] inorganic clusters have a higher overall energy per one isolated inorganic unit than the undistorted one. However, the distortion of the [Cu₂(CO₂)₄] inorganic clusters is found to be preferable in HKUST-1 as some energy levels are lower than that of distorted [Cu₂(CO₂)₄] inorganic clusters. And the energy penalty associated with the deformation of the [Cu₂(CO₂)₄] inorganic clusters is outweighed by the energy gain in the changes of the Cu-btc bonds.^[11] The possible vibrations participating in the NTE behaviour of HKUST-1 are illustrated in **Figure 1.18**.

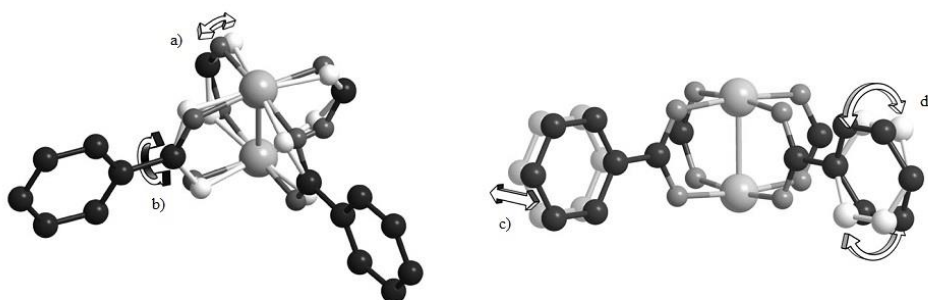


Figure 1.18 The possible vibrational modes that play a major role in NTE in HKUST-1. a) and b) represent twisting vibrations of the carboxylate linkers which is part of a paddle wheel motif, c) represents a translation of the benzene ring in a direction perpendicular to the btc axis and d) represent tilting motions of the benzene ring.^[73]

Another MOF containing carboxylate linkages that exhibits NTE behaviour is MOF-5. The structure of MOF-5 is shown in **Figure 1.19** (a). MOF-5 possesses a simple cubic net where the vertices of the net are replaced by the metal clusters (OZn_4) and the edges of the net are replaced by bdc units. Its unit cell contraction was found during the study of gas adsorption in 2005.^[75] Later on, the prediction of the NTE behaviour and the mechanism responsible for the behaviour was predicted using lattice dynamic simulations.^[15, 76-77] The linear coefficient of thermal expansion obtained over the temperature range studied, 80 – 500 K is $16.0 \times 10^{-6} \text{ K}^{-1}$. A variety of possible vibrational modes that has been suggested to contribute to the NTE behaviour is shown in **Figure 1.19** (b).

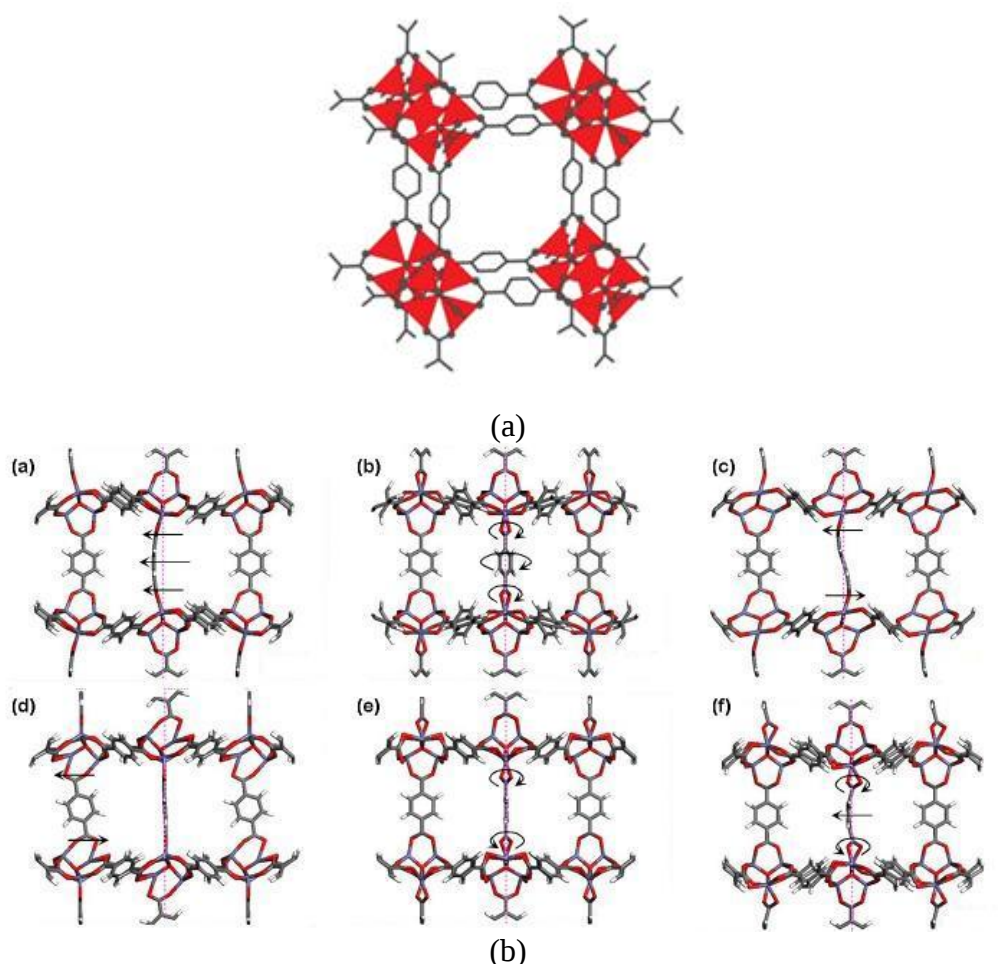


Figure 1.19 (a) The crystal structure of MOF-5, $[\text{Zn}_4\text{O}(\text{bdc})_3]$ where bdc is 1,4-benzenedicarboxylate. (b) Schematic representation of various low frequency vibrational modes influenced by a variety of local motions of the bdc linker.^[77]

These predictions have been verified by means of diffraction experiments. XRD experiments gave results consistent with vibrations of the bdc linkers and the rotations in the inorganic clusters as shown in **Figure 1.20**. These results are consistent with the predicted vibrational modes, as shown in **Figure 1.19** (b) a, b and c, which are lowest energy phonon modes. These transverse vibrational modes were further studied by inelastic neutron scattering and *ab initio* calculation to confirm the type of the transverse vibrations modes that significantly dominate the NTE behaviour of MOF-5. It was found that two possible translations of the benzene ring which are the in-phase and out of phase translations of benzene ring perpendicular to the bdc axis are the main contributors.^[14, 78]

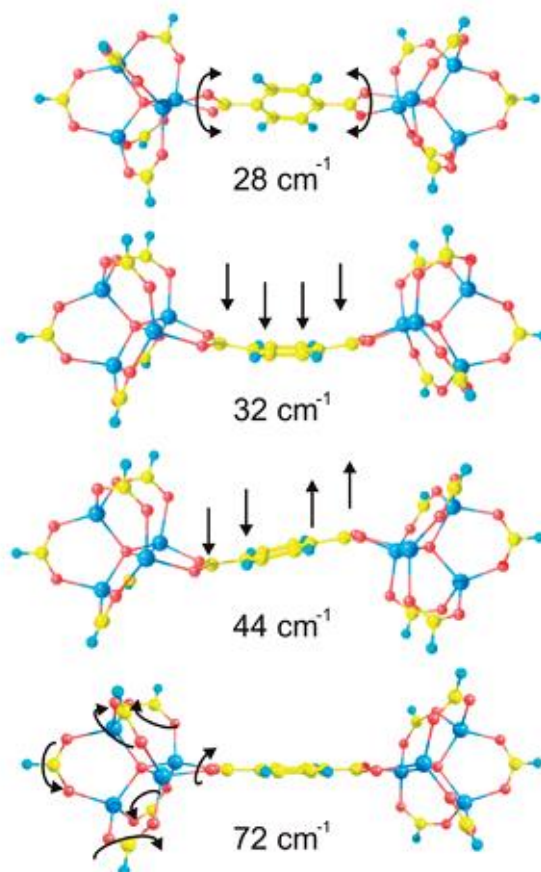


Figure 1.20 Various low frequency vibrational modes for MOF-5. The top to the bottom schemes illustrate libration, in-phase transverse motion, out-of-phase transverse motion, and local rotation of all six carboxylate groups without motion of the aromatic ring respectively. The blue, red, yellow and green balls represent the Zn, O, C and H atoms respectively.^[79]

1.5.2 Non-vibrational effects

The following non-vibrational effects are found to dominate the NTE behaviour only at low temperature so that the vibrational effects cannot overcome this contribution as the vibrational contribution fall off when T^{-3} .

1.5.2.1 Structural static deformation

The NTE behaviour of solid materials can occur due to the structural deformation that occurs when the degree of distortion of the structural framework of such solids increases as the temperature is increased. This particular mechanism is seen in some NTE materials such as $\text{NaZr}_2\text{P}_3\text{O}_{12}$,^[7] siliceous zeolite chabazite,^[32] and $[\text{Ag}_3\text{Co}(\text{CN})_6]$.^[80]

$\text{NaZr}_2\text{P}_3\text{O}_{12}$ is one of the low thermal expansion materials ($\alpha_V = -0.4 \times 10^{-6} \text{ K}^{-1}$), that has been reported since the early stage of the discovery of the NTE behaviour. The NTE behaviour of this material originates from a coupling of the rotation of the constituent ZrO_6 octahedra and the rotation of the PO_4 tetrahedra. This leads to a decrease in the c axis direction accompanied by expansion of other two crystallographic axes as shown in **Figure 1.21**.

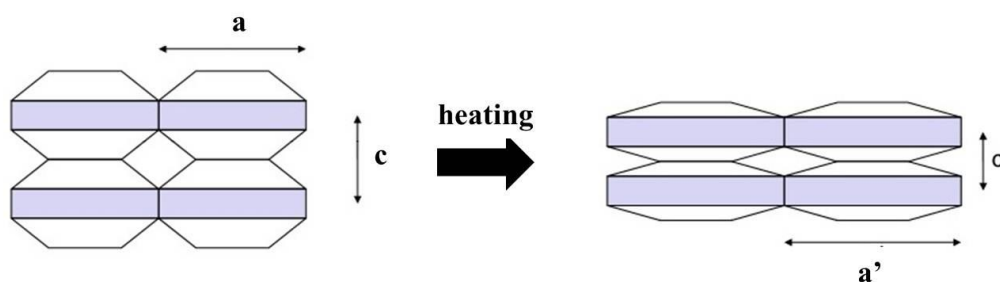
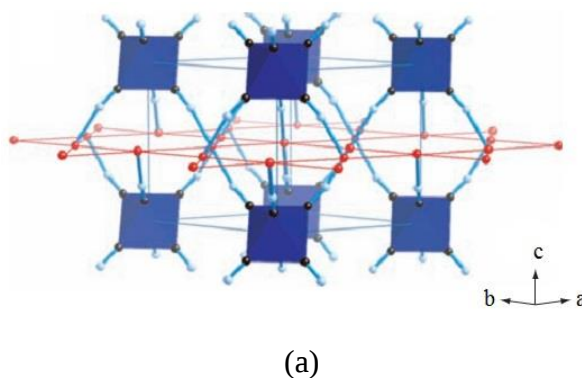


Figure 1.21 The origin of the low thermal expansion behaviour is due to the contraction along the c axis which almost outweighs the expansions along the a and b axes.^[81]

Chabazite is a pure silica which was found to exhibit NTE behaviour with a linear thermal expansion coefficient varying from -0.5×10^{-6} to $-16.7 \times 10^{-6} \text{ K}^{-1}$

over the temperature range of 293 – 873 K. The structure of chabazite is shown in **Figure 1.10**. The NTE behaviour of this material is due to the permanent deformation of the Si-O-Si interpolyhedral bond angles which is influenced by the thermal population of the transverse vibrations of the Si-O-Si bond angles.

$[\text{Ag}_3\text{Co}(\text{CN})_6]$ is a metal cyanide that exhibits colossal NTE behaviour where the term colossal signifies $|\alpha| \geq 100 \times 10^{-6} \text{ K}^{-1}$. Unlike other metal cyanides which the contraction is attributed solely to the transverse vibrations of the CN^- group, the contraction observed in $[\text{Ag}_3\text{Co}(\text{CN})_6]$ is found to be mainly due to the effect of argentophilic ($\text{Ag}^+ \dots \text{Ag}^+$) interaction where the transverse vibration of the CN^- group is still present but not the main contributor to the NTE behaviour. The structure of $[\text{Ag}_3\text{Co}(\text{CN})_6]$ is made of alternating layers of Ag^+ and $[\text{Co}(\text{CN})_6]^{3-}$ ions as shown in **Figure 1.22** (a). Anisotropic thermal expansion was measured in this material. Contraction along the c axis with $-130 \times 10^{-6} \text{ K}^{-1} \leq \alpha_c \leq -120 \times 10^{-6} \text{ K}^{-1}$ was observed together with expansion along the a axis with $+130 \times 10^{-6} \text{ K}^{-1} \leq \alpha_a \leq +120 \times 10^{-6} \text{ K}^{-1}$ as shown graphically in **Figure 1.22** (b). The $\text{Ag}^+ \dots \text{Ag}^+$ contact was found to increase with the increasing temperature and this leads to a strong expansion in the a axis. In order to preserve the framework structure, the alternating layers along the c axis will be pulled closer resulting in a strong contraction along this axis. The structure change with temperature is shown in **Figure 1.22** (b).



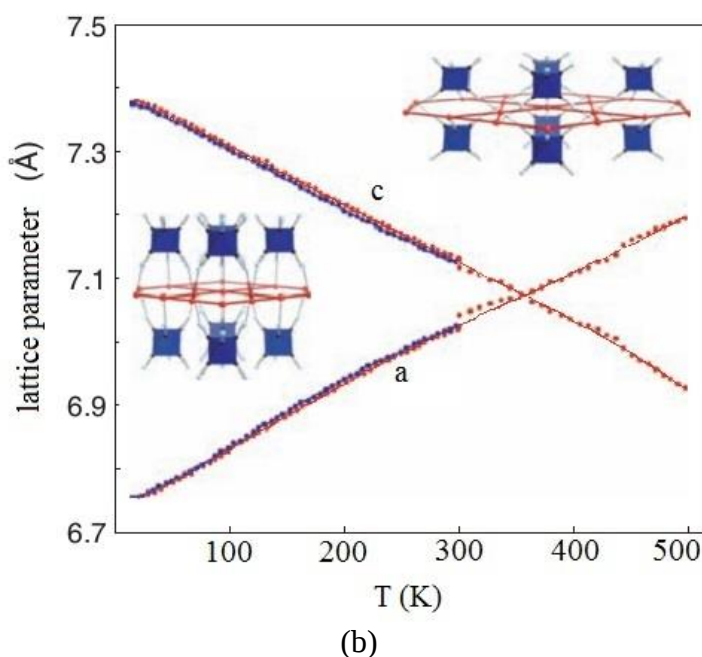


Figure 1.22 (a) The structure of the $\text{Ag}_3[\text{Co}(\text{CN})_6]$ lattice shows the alternating sheets of Ag^+ (red) and $[\text{Co}(\text{CN})_6]^{3-}$ (blue) ions along the c axis. (b) The variation of the unit cell parameters, a and c when the temperature is increased. Insets depict how the structure changes.^[69]

1.5.2.2 *Electronic effects*

In materials containing transition metals, a NTE effect can also occur as a result of atomic radius contraction arising from an electronic effect. This phenomenon is known as charge transfer and occurs within the constituent atoms. Generally, an expansion occurs in an electron-accepting atom while a contraction occurs in an electron-donating atom. The overall expansion or contraction of a particular material will strongly depend on the electron configuration of the constituent elements. The contraction will be observed if the change in the size of electron-accepting atom is relatively small and the change in size of the electron-donor atom is relatively large. There are several materials whose NTE behaviour has been found to be due to such an electronic effect such as samarium fulleride, $\text{Sm}_{2.75}\text{C}_{60}$ and in YbGaGe .

Samarium fulleride is a superconductor that possesses orthorhombic symmetry (space group $Pcab$). Its structure, as shown in **Figure 1.23**, contains

Sm^{2+} ions and C_{60} and a long-range ordered arrangement of tetrahedral Sm^{2+} vacancies accompanied by reorientation of the C_{60} units about three-fold rotation axis. $\text{Sm}_{2.75}\text{C}_{60}$ shows NTE behaviour over the temperature range of 4.2 – 32 K with a coefficient of thermal expansion of $-400 \times 10^{-6} \text{ K}^{-1}$. It was suggested that NTE behaviour in $\text{Sm}_{2.75}\text{C}_{60}$ originates from a valence electron transition from Sm^{2+} to the smaller size Sm^{3+} .^[82]

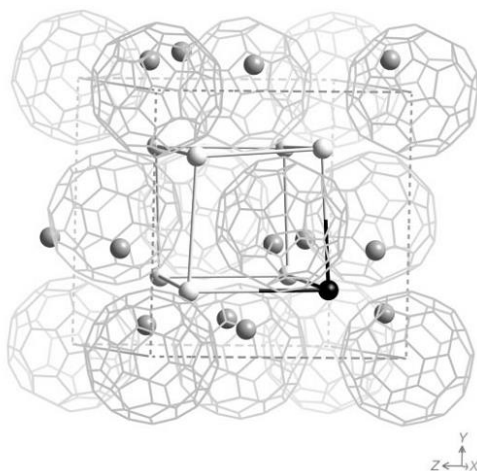


Figure 1.23 The structure of $\text{Sm}_{2.75}\text{C}_{60}$. The tetrahedral samarium defect is shown as a black sphere.^[83]

YbGaGe exhibits zero thermal expansion (ZTE) over the temperature range of 100 – 400 K. NTE behaviour along the two hexagonal axes of the unit cell YbGaGe outweigh an expansion along the third axis yielding coefficient of thermal expansion close to zero. The NTE behaviour in this material is strongly dependent on the overlapping of the 4f band of Yb and the 4p band of Ga. Upon heating, the electrons from the 4f band of the Yb shift to the 4p band of Ga. This causes a reduction in size of the Yb ions whereas the size of Ga atoms is barely changed hence a contraction occurs.^[84] The charge transfer diagram of YbGaGe is shown in **Figure 1.24**.

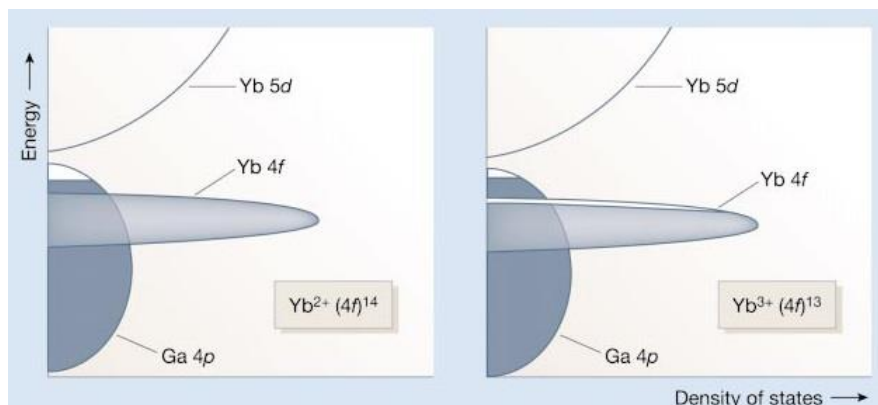


Figure 1.24 As the temperature increases, electrons shift from the 4f band of Yb^{2+} to the 4p band of the Ga atom. This causes the Yb^{2+} ion to become smaller in size while the size of the Ga atom has no change.^[84]

The atomic radius of an atom relates to not only the electronic configuration, but also the spin configuration. A high-spin state occupies a larger volume than the low-spin state according to the Pauli Exclusion Principle. A contraction may be exhibited when the spin configuration of an atom changes from the high-spin state to the low spin state as the temperature is increased. A good example of this occurrence is in the ZTE behaviour of Invar ($\text{Fe}_{65}\text{Ni}_{35}$). This alloy has a coefficient of thermal expansion of about $-0.5 - 1 \times 10^{-6} \text{ K}^{-1}$ calculated over the temperature range of 293 – 373 K. The small contraction is due to the change of the spin configuration of Fe atoms from the high-spin state to the low-spin state.^[85]

1.5.2.3 Magnetovolume effect

The magnetovolume effect is used as a term to define the relationship between the magnitude of the magnetic moment and the atomic volume. Basically, magnetism favours a larger volume. Therefore, any factor that reduces the magnitude of the magnetic moment will decrease the atomic volume. $\text{Dy}_2\text{AlFe}_{13}\text{Mn}_3$ exhibits an anisotropic NTE behaviour over the temperature range of 245 – 344 K. The volumetric coefficient of thermal expansion is $-1.1 \times 10^{-4} \text{ K}^{-1}$. It was suggested that the contraction correlated with the decreasing magnetic

interaction and the magnetic moment of the compound.^[86] However, the volume contraction due to the magnetovolume effect does not exist over a large temperature range because the rate of ordering of magnetic moments is very fast and consequently discontinues the contraction. Therefore, the trend within this area is to dope an element into the system in order to broaden the temperature range for contraction and to increase the magnetic transition temperature. Several successful experiments have been reported, for instance, one Cr atom was used as a dopant in Tb₂Fe₁₇ giving the ferromagnetic material, Tb₂Fe₁₆Cr. Anisotropic contraction of this material over the temperature range of 292 – 551 K was observed with $\alpha_V = -5.28 \times 10^{-6} \text{ K}^{-1}$. The temperature dependence of magnetisation was also found to increase by 120 K.^[87]

1.5.2.4 ‘Schottky’ contributions

The schottky anomaly describes the occurrence of a peak when the specific heat capacity is observed. It is anomalous because the specific heat capacity normally increases with increasing temperature or stays constant. This effect occurs when a system has a finite number of distinct energy levels resulting from the crystal field splitting of electronic or nuclear energy levels or the tunnelling between alternative atomic sites. The contribution of this effect to the NTE behaviour depends on how the energy levels respond to changes of volume. For instance, in a disordered solid, there is more than one possible site for a particular atom to occupy. If these two sites are close in energy, quantum tunnelling can occur. The height of the energy barrier between these two sites is influenced by changes in volume. The effect of tunnelling on the NTE behaviour was observed in KBr when the halide anions were replaced by 0.03% of the CN⁻ anions. Replacement of the Br⁻ anion by a certain amount of CN⁻ causes a reduction of expansivity coefficient from a positive value to a negative value at temperatures below 0.5 K and a large negative value of the Grüneisen parameter (~ 300) was observed at 0.1 K due to tunnelling occurring between the different (111) orientations for the CN⁻ anions.^[4, 88]

1.6 Applications of NTE materials

Discovering new NTE materials is of significant interest due to their potential use in controlling the overall coefficient of thermal expansion of a single component or composite materials applied in many areas of applications. Examples of some materials that use NTE materials as a mixing material for controlling their expansivity coefficient are composites, low thermal expansion or zero thermal expansion alloys such as dental filling alloy,^[89] interface adhesive material^[90], high field superconducting solenoid magnet production^[91] etc.

As can be seen above, NTE materials find uses in many applications but not many in polymer-based materials. The control of the expansivity in polymer materials has not yet been studied widely as there are not many suitable NTE materials to choose from which suitable composite materials can be made.^[76, 92] MOFs may be good candidates to make hybrid MOF/polymer composites of particular expansivity for use in avoiding microcracks during processing other applications as they contain organic linkers which may interact favourably with during the composite formation. To do this requires finding more MOFs with NTE properties and understanding the ways to design and control the NTE behaviour of the MOF. The design of the mechanical properties of MOFs has been reported recently by Goodwin *et al.* who suggest that the expansivity of MOFs can be predicted from the mechanical properties of the underlying mechanical building units, so called XBUs. A combination of different XBUs units is found to yield a different scale of the NTE behaviour.^[93]

1.7 Research aims

The ultimate goal of this research is to discover more MOF materials that possess NTE behaviour for future potential applications, especially for use in formation of hybrid polymer composites. Simultaneously, the research will further

the understanding of the NTE behaviour in MOFs as well as the underlying mechanism of NTE behaviour in MOFs. Knowledge and understanding gained from this work is also important as the occurrence of thermal fluctuation might influence the behaviour of MOFs in gas adsorption, separation and storage processes. A better fundamental understanding of this unusual phenomenon will potentially bring about the design of MOFs with particular mechanical behaviours as suggested by Goodwin *et al.*^[93]

Herein, one of the most common groups of MOF, metal dicarboxylate MOFs, will be investigated with the specific purpose of trying to elucidate factors that influence the NTE properties of these materials. The factors include determining how the organic linker influences NTE behaviour in an isorecticular series of MOFs containing zero-dimensional inorganic clusters. Such behaviour only been theoretically predicted for the IRMOF.

Up to now, the NTE behaviour has only been studied in MOFs containing zero-dimensional inorganic components. Hence, MOFs containing one-dimensional inorganic components of various types will be studied to see how the magnitude and mechanism of NTE is affected. MOFs with one-dimensional inorganic components containing different metal ions, inorganic linking atoms or different number of connecting organic linkers will be studied to determine how the composition, the structure of the inorganic component and the MOF itself influences the expansion behaviour.

X-ray diffraction and crystallography was chosen to investigate the temperature-dependent behaviour of the MOFs materials in this work as they provide a way to simultaneously probe the expansion behaviour and mechanism refined this behaviour and also sample preparation for diffraction studies is ideally suited for MOFs.

1.8 References

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2. Experimental techniques and data analysis

2.1 Synthesis and sample preparation

2.1.1 Solvothermal synthesis and activation of Metal Organic Frameworks (MOFs)

MOFs are generally crystalline solid materials that consist of inorganic parts bonded covalently or coordinatively to the organic parts. The MOFs in this work synthesised under solvothermal conditions. Synthesis of a MOFs need a proper selection of starting materials such as inorganic salts, ligands and solvents. The controlling of the reaction parameters such as pH, concentration, temperature and solvent polarity is also an important step in achieving a desired MOF.

Solvothermal synthesis is classified into two types, isothermal and temperature gradient synthesis, and is based on the fact that the precursor solubility increases with increasing temperature and also takes advantage from the change in the properties of as the solvent e.g. for water, a decrease of viscosity, polarity and ion products as the temperature is increased. Solvothermal synthesis is carried out in a closed-vessel (autoclave) under autogenous pressure which makes the balance of temperature-pressure-volume critical parameter in formation of the MOFs.

The degree of filling of the autoclave needs consideration. **Figure 2.1** shows that at 30 % of filling, water will expand to fill the autoclave at the critical temperature (374.15 °C). If the closed vessel is filled to a higher degree, the expansion of water will occur at below the critical temperature leading to a steep increase of the pressure inside the autoclave which will eventually cause the explosion of the autoclave. If the synthesis involves low boiling point solvents, the pressure may increase at a given temperature so a bigger size of an autoclave or a lower degree of filling are required.

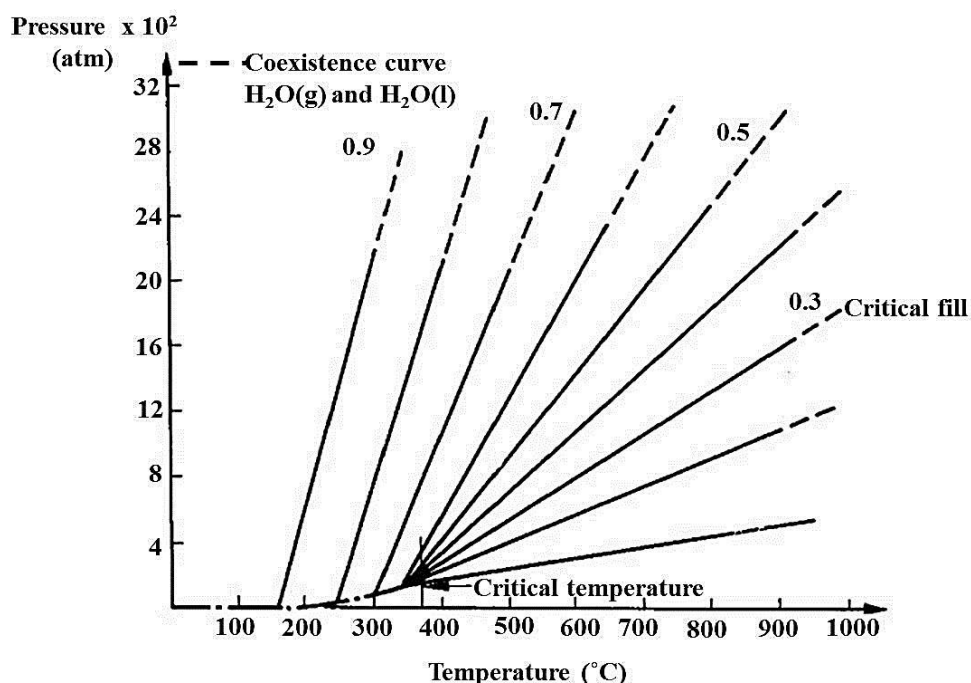


Figure 2.1 The pressure/ temperature dependence of water as a function of degree of filling in the autoclave.^[1]

The synthesis of MOFs normally requires operating reaction temperature in the range of 100 - 250 $^{\circ}\text{C}$ and a pressure that is higher than atmospheric pressure. Solvents typically used in the solvothermal synthesis are water, methanol, ethanol, dimethylformamide (DMF), diethylformamide (DEF), pyridine and acetonitrile. The reaction time is relatively short and varies from a few hours to a few days.

The selection of the MOFs precursors can considerably affect the synthesis as the limitation of the solvothermal synthesis is the solubility of the precursor due to the use of a particular solvent. If water is selected as a solvent, the metal salt can dissolve well while the organic linker is mostly insoluble. Therefore, the addition of a mineralizer is necessary in order to increase the solubility of the precursors in the hydrothermal synthesis. Different inorganic or organic compounds such as alkali metal hydroxides, salts of weak acid or chlorides can be used as a mineralizer which will later form a complex with the starting materials. This complex is characterised to have high solubility but readily dissociates when some growth parameters such as temperature are varied. The addition of a

mineralizer and increasing of the temperature or pressure assists the solubility of the precursors to ensure that the amount of the precursor in the solution reaches the requirement for the occurrence of supersaturation. Once supersaturation is overcome, the nucleation process may start. If the critical nuclei radius of the forming MOFs particle is achieved, then crystal growth is proceeds. The growth process is controlled by supersaturation and is terminated when the growth units are exhausted.^[1]

Due to the porous characteristic of MOFs, as-synthesised MOFs are generally obtained with an inclusion of guest molecules inside the internal void volume of MOFs. The as-synthesised MOFs are therefore activated before using in order to occlude the guest molecules that pack inside the void volume of MOFs. The activation procedure varies with the nature of such particular MOF.

The syntheses of all the MOFs in this work include the following steps (i) mixing the precursors and placing the mixture in a Teflon-lined stainless steel autoclave or a glass vial, (ii) heating the mixture to the appropriate temperature for a certain period of time, (iii) taking the reaction vessel from the oven and cooling it in air to room temperature, (iv) recovering the solid product by mean of filtration, followed by washing with solvents that can dissolve any of the residual starting materials and drying the sample at 70 °C in a drying oven and (v) solvent exchanges and/ or calcination.

2.1.2 Sample preparation

The inclusion of any guest molecules within the void volume of a MOF can influence the thermoresponsive behaviour of MOFs. All samples in this work were further activated by packing them in capillary tubes, heating them under dynamic vacuum and flame-sealing the capillary tube under vacuum to ensure the absence of any guest molecules from the void volume. Powder samples, were ground before introducing them into a borosilicate or aluminium capillary tube (0.5 mm in diameter). The sample was packed to the desired length in the

capillary tube and was then attached to the activation system consisting of a high vacuum pump PT50 kit Oerlikon Leybold Vacuum system and a carbolite tube furnace. The time spent in the evacuation process was dependent on the nature of the sample and was normally 24 – 48 hours. The capillary tube was then flame-sealed and the sealed end coated with super glue/ epoxy resin.

The sample preparation of a single crystal involved a selection of a suitable single crystal which was later inserted into a 0.2 mm diameter borosilicate capillary tube. The capillary tube was attached to the activation system and activated in a similar manner to that discussed for powder samples. The capillary tube was then flame-sealed, coated with super glue at the sealed end and was ready for data collection.

2.2 Theory of diffraction

A crystal can be represented by the repetition of a small repeating unit of an extended crystal lattice called a unit cell that represents the symmetry and the structure of the overall bulk crystal. The entire crystal structure can be generated from translating this unit along the three major crystallographic axes, x , y and z .

If an incident wave interacts with a point or an array of objects, such as a crystal that is an array of atoms extending in three-dimensions, is scattered new waves will be generated and are called diffracted beams. These diffracted beams interfere with each other generating interference. There are two types of interference, constructive interference and deconstructive interference. If the diffracted waves are in-phase, constructive interference occurs. In contrast, deconstructive interference occurs when the diffracted beams are out of phase.

An X-ray is an electromagnetic wave that can be diffracted by a crystal as its wavelength has a magnitude of 10^{-10} m which is of comparable magnitude to interatomic distances. The result of the diffraction is formation of a regular array of diffraction spots that is called a reciprocal lattice.

The relationship between the real crystal lattice and the reciprocal lattice is presented in **Figure 2.2** (a) and (b). The following expressions are used to relate the real lattice to the reciprocal lattice:

$$a^* = \frac{b \times c}{V}, b^* = \frac{c \times a}{V}, c^* = \frac{a \times b}{V} \quad \text{Equation 2.1}$$

where a , b and c are the vectors defining the real lattice, a^* , b^* and c^* are the vectors defining the reciprocal lattice and V is the unit cell volume.

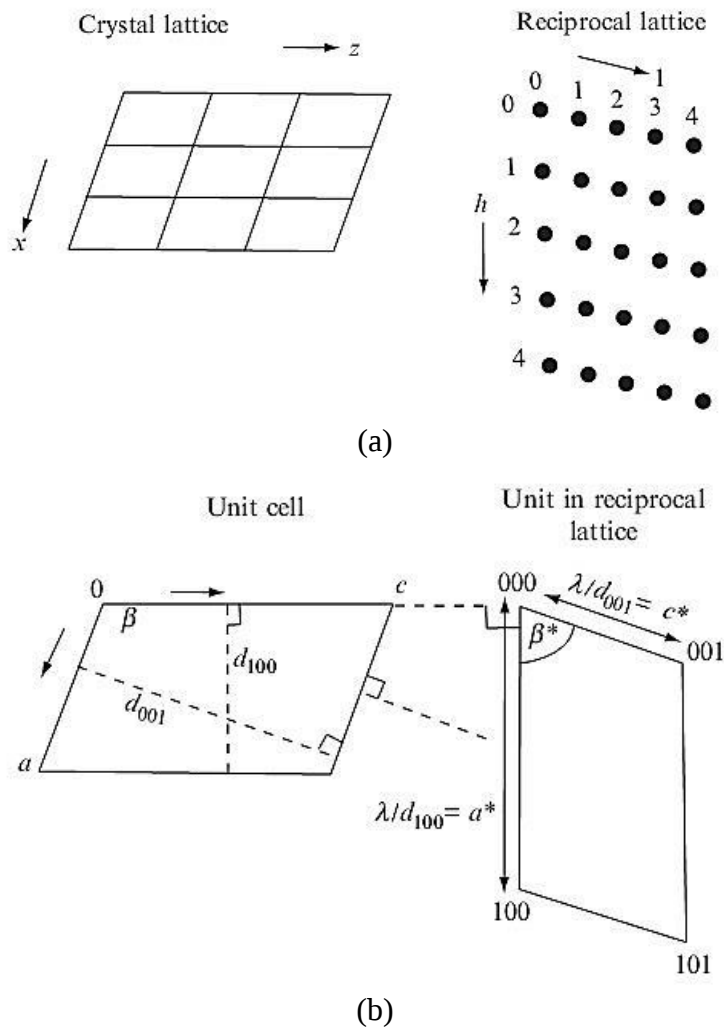


Figure 2.2 (a) The diffraction of a real lattice shown as a projection along the y -axis gives a regular array of the reciprocal lattice, the point representing diffraction from the families of planes. (b) The relationship between the real lattice and the reciprocal lattice.^[2]

A reciprocal lattice differs from a real lattice in several ways. First of all, each point of the reciprocal lattice is not a repetitive point like in the case of the real lattice. Each point of the reciprocal lattice represents a diffracted beam from a set crystal plane (hkl). While the position of the reciprocal lattice point is inversely related to the interplanar distance, d_{hkl} and also represents the direction normal to the plane of diffraction. The reciprocal interplanar spacing d_{hkl}^* is related to the real interplanar spacing by the expression:

$$\left| d_{hkl}^* \right| = \frac{K}{d_{hkl}} \quad \text{Equation 2.2}$$

where K is a constant.

The Bragg equation is used to describe the condition of diffraction that is shown geometrically in **Figure 2.3**. In order for diffraction to be observed, the incident beam diffracted from two successive planes (hkl) must interfere constructively. To satisfy this condition, the path difference for beams from successive planes is expressed as shown in Equation 2.3.

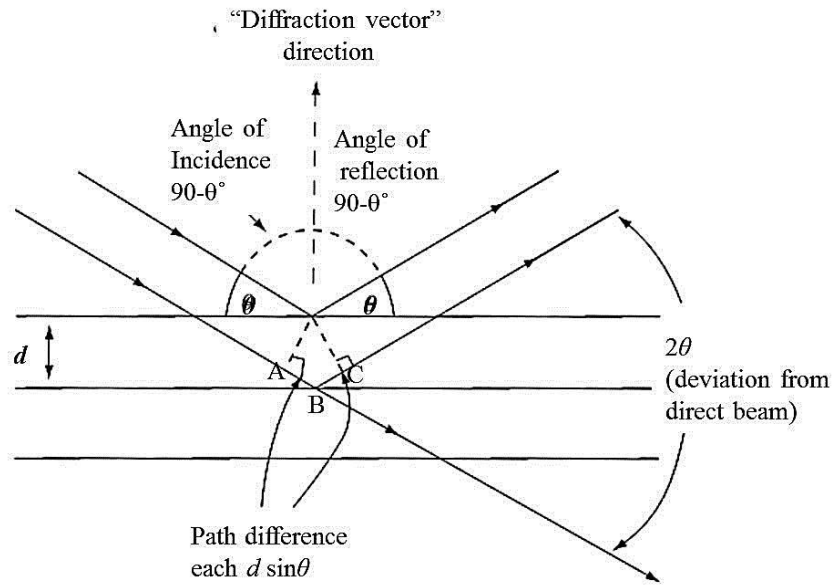


Figure 2.3 A diagram of Bragg's reflection. Two arrays of incident beam hit the two planes that is separated by a spacing d at the angle θ . The resulting waves are said to be constructive if the path difference is equal to an integer number of the incident wavelength.^[2]

$$AB + BC = n\lambda \quad \text{Equation 2.3}$$

Where $AB + BC$ must be an integer number of the wavelength λ of the diffracted beam and $AB = BC = d \sin \theta$. Such that the Bragg equation is given by:

$$2d \sin \theta = n\lambda \quad \text{Equation 2.4}$$

where θ is the incident angle and n is the order of diffraction.

While the Bragg equation gives a geometric condition for diffraction, the reciprocal lattice gives all the possible solutions to the diffraction equation. A tool that is used to connect the Bragg equation to the reciprocal lattice point is called the Ewald method. The Ewald method utilizes the sphere of a radius $1/\lambda$ as shown in **Figure 2.4**. If any point hkl of the reciprocal lattice intersects with the surface of the Ewald sphere, that point satisfies the Bragg equation.

Table 2.1 Summary of the seven crystal systems

System	Unit cell dimension	Essential symmetry	Bravais lattice
Triclinic	$a, b, c, \alpha, \beta, \gamma$ any value	None, $\bar{1}$	P
Monoclinic	a, b, c, β any value $\alpha, \gamma = 90^\circ$	One unique two-fold rotational axis, $2/m$	P, C
Orthorhombic	a, b, c any value $\alpha, \beta, \gamma = 90^\circ$	Three perpendicular two-fold rotational axes, mmm	P, C, I, F
Tetragonal	$a = b, c$ $\alpha = \beta = \gamma = 90^\circ$	One four-fold rotational axis, $4/m$ or $4/mmm$	P, I
Trigonal	$a = b, c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	One three-fold rotational axis, $\bar{3}$ or $\bar{3}m$	P or R
Hexagonal	$a = b = c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	One six-fold rotational axis, $6/m$ or $6/mmm$	P
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Four three-fold rotational axes, $m\bar{3}$ or $m3m$	P, I, F

It is arbitrary to choose a unit cell but the smallest cell that possesses the highest symmetry is the most preferable. By considering the number of lattice points in a unit cell, unit cells are classified into two lattice types that are primitive cell and non-primitive cell. A primitive cell (designated **P**) has only one lattice point in a cell. Non-primitive cells, containing more than one lattice point, are body-centred (designated **I**) having two lattice points, face-centred (designated **F**) having four lattice points and side-centred cell (designated **A**, **B** and **C**) having two lattice points. The combination of the seven crystal systems and the four lattice types leads to 14 cell choices known as Bravais lattices and they are shown in **Figure 2.5**.

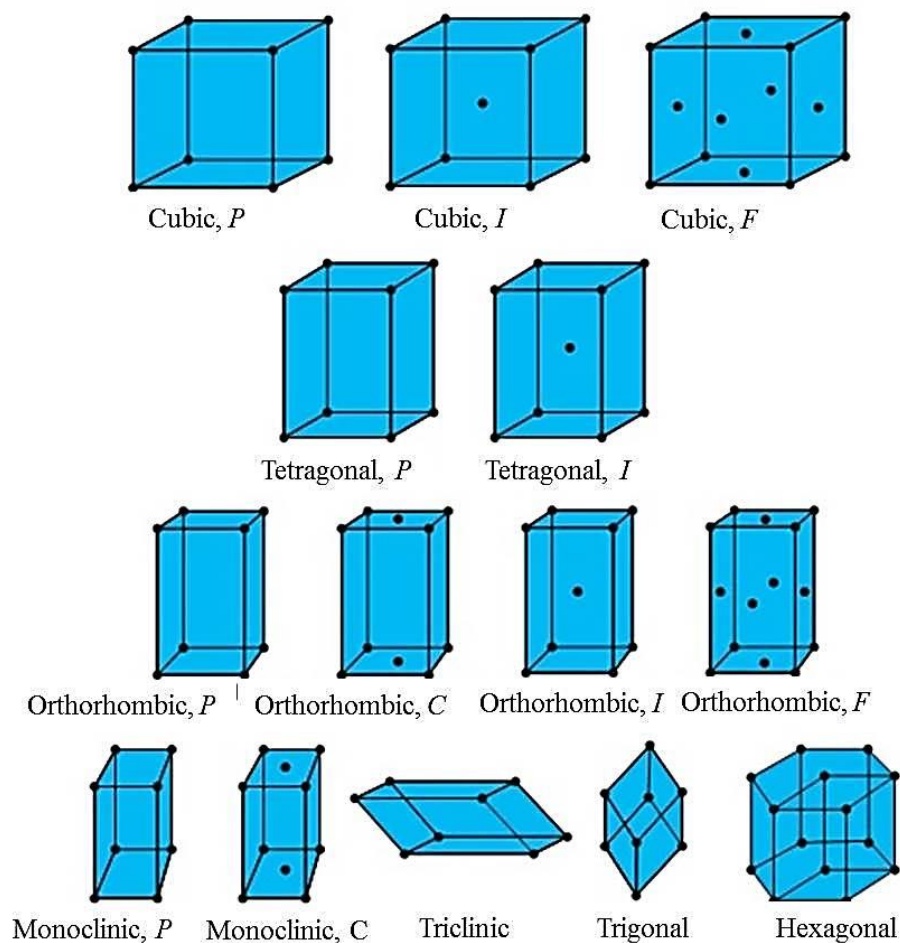


Figure 2.5 The fourteen Bravais lattices.^[3]

Symmetry operations, including rotation and reflection through a fixed point, is called a point symmetry operation and this leads to 32 point groups. Translational symmetry is applied to these 32 point groups through screw axes and glide planes in order to create a three-dimensional arrangement in a crystal. This gives rise to 230 different combinations called space groups.

The space group symbol gives all the details about the symmetry operation present in a particular cell. For example, the orthorhombic space group *Imma* belongs to the parent point group *mmm* and has a body centred lattice type. It has 2_1 axis in the direction *x*, *y* and *z* and mirror plane normal to the *x* and *y* axes and an *a*-glide plane perpendicular the *z* axis with glide direction along the *x* axis.

2.2.2 Structure factor

If a unit cell consists of n atoms, one reflection is the sum of the contributions of all atoms in the unit cell. The structure factor, $F(hkl)$ therefore the sum of $f(hkl)$ of the individual atoms and is expressed as shown in Equation 2.5.

$$F(hkl) = \sum_{j=1}^n f_j \exp[i2\pi(hx_j + ky_j + lz_j)] \quad \text{Equation 2.5}$$

f_j is the atomic scattering factor of atom j and describes the X-rays scattered by electrons distributed randomly over the atomic volume. The amplitude of the scattering of an atom, therefore, depends on the nature of such atom and is plotted as a function of $\sin\theta/\lambda$ as shown in **Figure 2.6**. The position of the j th atom is given by the fractional coordinates (x_j, y_j, z_j) . The exponential term is represented a relative phase.

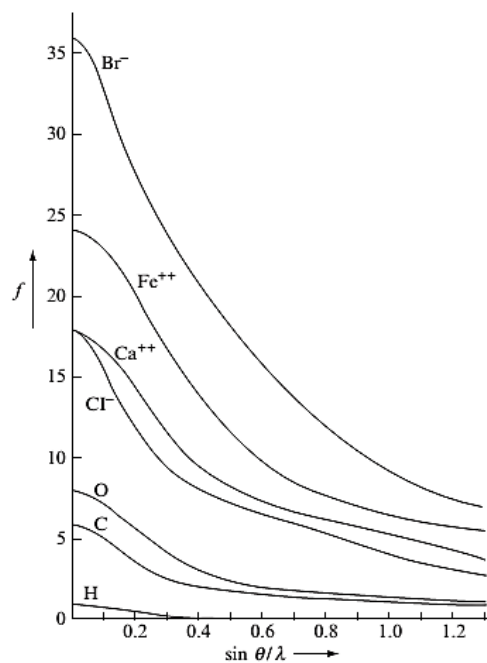


Figure 2.6 Some atomic-scattering-factor curves for atoms, given as a function of $\sin \theta / \lambda$

In a diffraction experiment, the intensity of the scattered X-rays (I_{hkl}) is measured and is related to $F(hkl)$ as given in Equation 2.6:

$$I_{hkl} = SLp|F_{hkl}|^2 \quad \text{Equation 2.6}$$

where S is the scale factor

L is a Lorentz correction factor

p is a polarisation correction.

The $F(hkl)$ is reduced by the effect of thermal vibration and atomic displacement. The thermal vibration can be isotropic, equal in all directions, or anisotropic (not equal in all directions). The experimental value $F(hkl)$ is thus corrected by atomic displacement parameter and is given by Equation 2.7 if isotropic behaviour is assumed.

$$F(hkl) = F_{novib} \exp \left[\frac{-B_j \sin \theta}{\lambda^2} \right] \quad \text{Equation 2.7}$$

where F_{novib} is the value of $F(hkl)$ containing stationary atoms

B_j is the atomic displacement parameter and is given by:

$$B_j = 8\pi \langle u_j^2 \rangle \quad \text{Equation 2.8}$$

where $\langle u_j^2 \rangle$ is the mean square amplitude of displacement of the j^{th} atom from its equilibrium position.

If the thermal vibration of atoms is in an anisotropic manner, the experimental value $F(hkl)$ is given by:

$$F(hkl) = F_{novib} \exp \left[2\pi^2 \left\{ U_r^{11} h^2 (a^*)^2 + U_r^{22} k^2 (b^*)^2 + U_r^{33} l^2 (c^*)^2 + 2U_r^{23} klb^*c^* + 2U_r^{31} hla^*c^* + 2U_r^{23} hka^*b^* \right\} \right] \quad \text{Equation 2.9}$$

Where U_r^{ij} is a component of asymmetric tensor (3 x 3 matrix) U_r that describes the anisotropic harmonic motion of the r^{th} atom

a^*, b^*, c^* are the reciprocal unit cell length

h, k, l are the Miller indices

2.2.3 Structure solution method

A Fourier summation of the structure factor, $F(hkl)$ leads to the electron density at any point x, y, z in the unit cell, represented by $\rho(xyz)$ and is expressed as:

$$\rho(xyz) = \frac{1}{V_c} \sum_{all} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)] \quad \text{Equation 2.10}$$

where V_c is the volume of the unit cell.

$|F(hkl)|$ can be obtained from the intensity of the reflections as aforementioned. In contrast, the phase of the same reflection cannot be derived directly from the experiment. In order to calculate the electron density, however, both the intensity of the each reflection and the phase corresponding to each reflection must be known. The loss of the phase information is known as the phase problem.

To obtain the phases, the computational process is involved by starting from rough estimates of the phases and then undertaking an iterative process to improve the estimates. This is performed based on the idea that if one has a

structural model, the diffraction pattern and the phases of all reflections can be calculated. The general steps to obtain the phases start from forming a starting model by means of a structure solution method or using a known similar structural model. The observed intensities (I_{obs}) will be combined with a set of estimated phases to calculate the electron density using Equation 2.10. The structural model will be improved by inspection of the electron density map and designating molecular feature such as the model-solvent boundaries or specific groups of atoms. The improved model is then used to calculate the structure factor $F(hkl)$ using Equation 2.11. At this step, one will be able to get the calculated intensity (I_{calc}) and the calculated phases.

$$F(hkl) = \iiint_{xyz} \rho(xyz) \exp[2\pi i(hx + ky + lz)] dx dy dz \quad \text{Equation 2.11}$$

The cycle is repeated by computing a new $\rho(xyz)$ from a new set of calculated phases and the I_{obs} until the process reaches a convergence when the $I_{calc} \approx I_{obs}$.

There are several options of the structure solution method such as the Patterson method, direct methods, anomalous dispersion, isomorphous replacement and molecular replacement. All of these will not be further discussed here. All initial structural models used in this work were obtained from previously reported crystal structures. The reader is referred to the reference provided if interested in details.^[4-6]

2.2.4 Structure refinement

2.2.4.1 *Least-squares refinement*

The best set of atomic parameters was obtained by refining the structural model using a full matrix non-linear least square technique. The least-squares refinement is introduced and is used to find a function $y = f(x)$ that fits a series of observations (y_i) and to minimize the sum of the square of the deviations between the experimental data and calculated data D which is given in Equation 2.12.

$$D = \sum_i w_i [y_i - f(x_i)]^2 \quad \text{Equation 2.12}$$

In crystal structure refinement, the function $f(x)$ refers to the amplitude of the calculated structure factor $|F_{calc}|$ and the series of observations y_i refers to the observed structure factor amplitudes $|F_{obs}|$. The term w_i is a weighting factor that reflects the reliability of the data with the most reliable data exerting a greater influence. The weighting factor is defined by $1/\sigma^2$ where σ is the standard deviation. Thus, Equation 2.12 can be re-written as shown in Equation 2.13.

$$D = \sum_{hkl} w_{hkl} [|F_{obs}| - |F_{calc}|]_{hkl}^2 \quad \text{Equation 2.13}$$

The minimization can also be done on $|F^2|$ instead of $|F|$ and is given in Equation 2.14.

$$D = \sum_{hkl} w_{hkl} [|F_{obs}^2| - |F_{calc}^2|]_{hkl} \quad \text{Equation 2.14}$$

There are several sets of parameter that can be refined additionally in order to minimize the function D . These parameters include atomic positions (x_i, y_i, z_i) , temperature factor B_j , occupancy n_i for each atom j and the scale factor, G . The structure factor F_{calc} is then expanded by including the additional parameters and is given as following:

$$F_{calc} = G \cdot \sum_j n_j f_j \exp[2\pi i(hx_i + ky_j + lz_i)] \cdot \exp[-B_j (\sin \theta) / \lambda]^2 \quad \text{Equation 2.15}$$

2.2.4.2 *Reliability factor*

The progress of the refinement is monitored by the reliability R factor, and the weighted R factor which are defined as shown in Equation 2.16 and Equation 2.17. A perfect fit between the calculated model and the observed data give $R = 0$. Both R factors are reported as percentage.

$$R = \frac{\sum ||F_{obs}| - |F_{calc}||}{\sum |F_{obs}|} \quad \text{Equation 2.16}$$

$$R_w = \sqrt{\frac{\sum w_i (|F_{obs}|^2 - |F_{calc}|^2)}{\sum w_i (|F_{obs}|^2)}} \quad \text{Equation 2.17}$$

2.2.4.3 *The derivation of results*

The final cycle of least-squares refinement yields the primary numerical results which are three positional coordinates and a number of displacement parameters together with an estimated standard deviation (or e.s.d.) for each one. The primary numerical results are used to derive the secondary results which are bond lengths, bond angles and other distances provided together with the e.s.d for each one. The e.s.d is needed as it helps to state the reliability of the geometric results.

Distribution is the term used to describe the frequency with which different values are found for some measurable quantity. There are two particular distributions in crystallography including the Poisson distribution and the Normal distribution. The Poisson distribution is related to the intensity output of the X-ray tube (in quanta per second) which is the basis of counting statistics whereas the diffraction intensity follows the Normal distribution. The histogram of the intensity of 114 diffractions superimposed on a curve of an ideal normal distribution is shown in **Figure 2.7**.

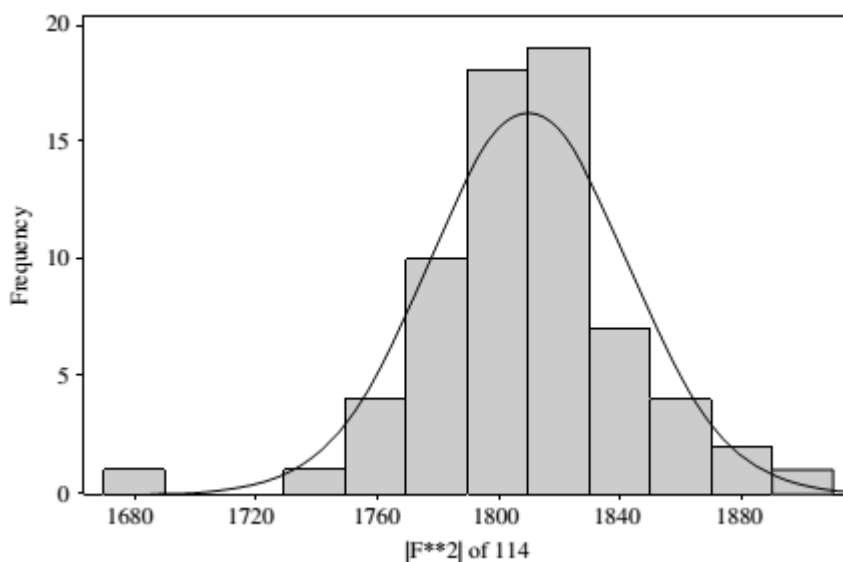


Figure 2.7 Histogram showing intensities of the 114 reflection, superimposed on a curve of the corresponding ideal normal distribution.^[4]

Two important values are used to describe the characteristic of a distribution. These values are the mean and the variance. The latter value relates to the standard deviation. For a discrete distribution, the mean is defined as:

$$\bar{x} = \frac{1}{N} \sum_{i=1}^n f_i x_i \quad \text{Equation 2.18}$$

where the N members of the population of each take one of the n different values of x , and f_i is the number of members of the population having the value x_i . The variance of the distribution is defined as:

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^n f_i (x_i - \bar{x})^2 \quad \text{Equation 2.19}$$

and is a measure of the width or spread of the distribution over the different values of x . The variance is the square of the standard deviation σ .^[4]

2.2.5 Single crystal X-ray diffraction

The single crystal X-ray diffraction data in this work were obtained using on a Rigaku AFC12 diffractometer which has four-circle kappa (κ) geometry as shown in **Figure 2.8**.

frames which are stored in a list by the control programme. The hundred reflections were then accurately centred and the unit cell and orientation matrix were calculated based on metric consideration. The Laue symmetry was determined by comparing the integrated intensities of sets of equivalents reflections. The unit cell was then refined by least-squares methods to obtain more accurate lattice parameters. Improvement of the lattice parameter values was achieved by replacing low 2θ reflection with high 2θ reflections in the unit cell determination and refinement.

The optimum scan width values for data acquisition were determined from the width of an intense low angle reflection. This scan width is automatically scaled during data collection to account for the broadening of the reflections due to the increase in $K_{\alpha 1}$ and $K_{\alpha 2}$ splitting at higher Bragg angles. The aperture width at the detector was determined by finding the minimum value that did not truncate the peaks. The vertical size of the aperture was fixed by a manually inserted slit. Data were collected in a ω - 2θ scan mode. The maximum scan time was between 120 s and 240 s per reflection.

After the data collection was complete. The observed intensities, I_{hkl} are converted into observed structure factor amplitudes, $|F_{obs}|$ which are used further in structure solution and refinement. This process is called data reduction. As discussed previously, the observed intensity is related to the structure factor amplitude by Equation 2.6. The correction parameters include the Lorentz factor L , the polarisation correction p and scale factor S .

The Lorentz factor corrects for the difference in times required for a reciprocal lattice point to pass through the sphere of reflection. The Lorentz factor is dependent on the method of data collection. The polarisation factor results from the difference in reflection angle. When a monochromator crystal is used it will cause partial polarisation of the diffracted beam, before the partial polarisation introduced by the sample crystal. The scale factor is refined after the basic structure has been determined and is dependent on crystal size, beam intensity and incident wavelength. A correction to account for the absorption of X-ray by the crystal is then applied to the intensity data. Other steps involved in data reduction

include the removal of systematically absent reflections, the averaging of equivalent reflections and the scaling of the intensities relative to the standards to allow for any crystal decay during data collection. In this work, data reduction was performed using the programme CrystalClear-SM Expert 2.0 r13.

2.3 Powder X-ray diffraction

2.3.1 The Rietveld refinement

Diffraction that occurs for a powder sample relies on Bragg's law like that of a single crystal. However, the nature of a powder sample that consists of a large number of small crystallites lying randomly in all possible orientations reduces the spatial characteristic of a three-dimensional pattern of reflection spots to one dimension only so instead of spots diffraction rings are observed. This means that the intensity of a single reflection cannot be extracted, as the intensity of a single powder diffraction peak is an integrated intensity of several reflections. This characteristic is known as the overlap problem which brought about the development of the Rietveld refinement.

The Rietveld method was first introduced by H. M. Rietveld in 1967 and is also known as full profile analysis. This method was developed for use in a neutron diffraction data. The refinement program has been developed over these five decades and has been widely used for various types of analysis. The principle of the Rietveld method relies on the minimization of the residual function, D , using a non-linear least squares method:

$$D = \sum_{i=1}^n w_i \left(y_i(obs) - \frac{1}{c} y_i(calc) \right)^2 \quad \text{Equation 2.20}$$

where: a weighing factor $w_i = \frac{1}{y_i(obs)}$

$y_i(obs)$ is the observed intensity at the 2θ point i^{th}

c is a scale factor

$y_i(calc)$ is the calculated intensity at the 2θ point i^{th} . It is calculated based on the assumption that the background contributions have been subtracted from $y_i(obs)$ and the scale factor is not included within $y_i(calc)$.

The summation is over all data points. The diffraction intensity at 2θ point i^{th} is dependent on several parameters as shown in Equation 2.21. They include the background value, diffraction intensity and relating correction parameters, peak position and peak-shape profile.

$$y_i = S_F \sum_{j=1}^m \frac{f_j}{V_j^2} \sum_{k=1}^n L_k |F_{k,j}|^2 \eta_j(2\theta - 2\theta_{k,j}) P_{k,j} A_j + BKG_i \quad \text{Equation 2.21}$$

Where: $S_F \sum_{j=1}^m \frac{f_j}{V_j^2}$ is the scale factor of each phase

L_k is the Lorentz-polarization correction which is dependent on the instrument

F_k is a generalized structure factor which includes the reflection multiplicity, the atomic scattering factor and the temperature factor.

$\eta_j(2\theta_i - 2\theta_{k,j})$ is the peak-shaped profile function

P_k is the preferred orientation

A_j is the absorption factor of phase j

BKG is the background value described by a polynomial function of 2θ

The least squares minimization process is performed until the best fit between the entire observed powder diffraction pattern and the entire calculated pattern based on the simultaneously refined models of crystal structures is achieved. The peak shape function $\Phi(\theta)$ is affected by the instrumental broadening arising from several parameters such as sampling effect, detector resolution and sample features such as sample aberration, transparency, sample displacement and sample-caused broadening. The peak shape presented is given by a convolution of these parameters with an addition of wavelength dispersion and background function:

$$\Phi(\theta) = \Omega(\theta) \otimes \Lambda(\theta) \otimes \Psi(\theta) + b(\theta) \quad \text{Equation 2.22}$$

where Ω is instrument broadening

Λ is wavelength dispersion

Ψ is specimen function

b is background function.

Several choices of peak shape function can be chosen to fit the peak profile such as a Gaussian peak shape function (η_G), Lorentzian peak shape function (η_L) and pseudo-Voigt peak shape function (η_{PV}). A Gaussian function is a centrosymmetric function as represented in the dash-dotted line in **Figure 2.9**.

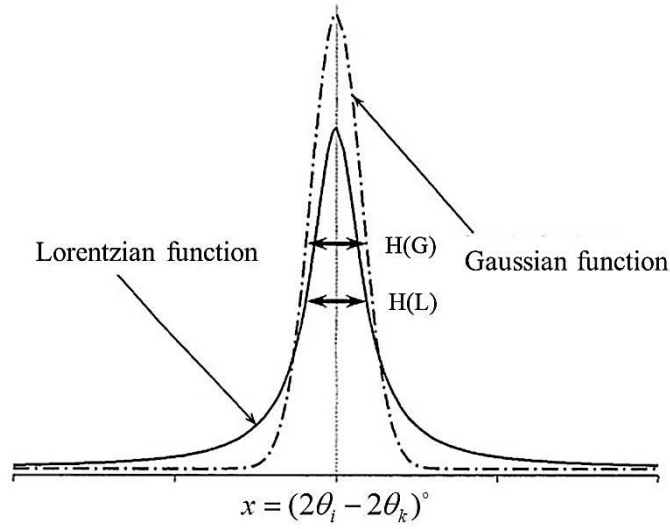


Figure 2.9 The illustration of the peak shape function, the dash-dotted line depicts a Gaussian function and Lorentzian function is represented by the solid line and full width at half maximum (FWHM) of Gaussian and Lorentzian peaks are designated as H(G) and H(L) respectively.^[7]

It has been used since the early period of developing Rietveld refinement for neutron diffraction data and is given by:

$$\eta_G(2\theta - 2\theta_k) = \frac{2}{H} \sqrt{\left(\frac{\ln 2}{\pi}\right)} \exp\left(\frac{-4 \ln 2 (2\theta - 2\theta_k)^2}{H^2}\right) \quad \text{Equation 2.23}$$

where: 2θ is the measured angle and $2\theta_k$ is the Bragg angle

H is the full width at half maximum (FWHM) which varies with θ and is given by:

$$H^2 = U \tan^2 \theta + V \tan \theta + W \quad \text{Equation 2.24}$$

where U , V and W are free variables and can be refined during the full profile fitting.^[8]

When the Gaussian peak shape function was applied to the powder patterns collected from laboratory X-ray diffractometers, a good fit was not achieved. The peak shape function, therefore, was further modified. A Lorentzian

function seemed to apply well for the powder patterns obtained from laboratory X-ray diffractometers as it corrects for the asymmetric behaviour in the tail of the reflection. The Lorentzian function is shown graphically as a solid line in **Figure 2.9** and is given by:

$$\eta(2\theta - 2\theta_k) = \frac{2}{\pi H} \left(\frac{1}{1 + \frac{2(2\theta - 2\theta_k)^2}{H^2}} \right) \quad \text{Equation 2.25}$$

where the variation of the FWHM is given by:

$$H = \frac{U}{\cos \theta} + V \tan \theta \quad \text{Equation 2.26}$$

U and V are free variables which can be refined during the profile fitting process.

The shapes of real Bragg peaks, however, are rarely described by a pure Gaussian or a pure Lorentzian function as they mostly result from a mixture of both functions. The two functions can be combined by using a mathematical method called a convolution which results in a Voigt function. As the convolution is a complex procedure, a much simpler procedure of combining the two functions is used instead and it is known as a pseudo-Voigt function which is a linear combination of a Gaussian function and Lorentzian function, where $0 \leq v \leq 1$ is a fractional parameter relating to the peak intensities of η_G and η_L , and is given by Equation 2.27.^[9]

$$\eta_{pV} = v\eta_L + (1-v)\eta_G \quad \text{Equation 2.27}$$

The peak shape function used in this work is referred to the fourth peak profile function in the GSAS software,^[10-11] and is a modified pseudo-Voigt that additionally accounts for the specimen-caused broadening. This peak profile

function includes crystallite size broadening and microstrain broadening. The crystallite size broadening commonly causes Lorentzian-shaped intrinsic tail in the peak profile and sometime contributes to Gaussian peak shape or both. While, the microstrain broadening contributes to the Gaussian-shaped function. Furthermore, these specimen-caused broadening parameters significantly affect the FWHM value.

The effect of crystallite size on the line broadening occurs as a sample observed has a deviation in crystallinity from the ideal one such as having a finite crystallize size. The effect of a finite crystallite size is normally negligible if the crystallite size is larger than 0.1 – 1 micrometre. The fourth peak shape function in GSAS accounts the this effect with the two profile term, LX (Lorentzian) and GP (Gaussian) The relation of the average crystallite size (p) and the GSAS peak shape profile terms is given by:

$$p = \frac{18000K\lambda}{\pi LX} \quad \text{Equation 2.28}$$

and

$$p = \frac{18000K\lambda}{\pi\sqrt{GP}} \quad \text{Equation 2.29}$$

where K is Scherrer constant which is related to the crystal shape and is approximately equal to 1.

Another parameter contributing to the line broadening is the lattice strain or microstrain which is classified into two types, uniform strain and non-uniform strain. The uniform strain does not contribute to the line broadening as it arises from the isotropic deformation of the unit cell which causes the shift of the peaks. Typically in the GSAS programme, the effect of uniform microstrain is already included in every peak shape profile options both Gaussian and Lorentzian peak shape function which are the GU term for Gaussian function and LY term for Lorentzian function.

However, if one needs to include the non-uniform strain that causes anisotropic peak broadening, the fourth peak shape profile in the GSAS programme is the most suitable choice. The anisotropic strain parameters S_{HKL} are added into this peak shape profile function. These anisotropic strain parameters are derived by restricting the strain component in terms of the first and the second order terms allowed by lattice symmetry as given by Equation 2.30. Therefore, different crystal systems have different numbers of these terms. For instance, there are six anisotropic broadening terms for orthorhombic symmetry which are S_{400} , S_{040} , S_{004} , S_{220} , S_{202} and S_{022} and there are only two anisotropic broadening terms for cubic symmetry which are S_{400} and S_{220} .^[7, 8]

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L \quad \text{Equation 2.30}$$

where $\sigma^2(M_{hkl})$ is variance of Miller indices hkl

The term S_{HKL} is the anisotropic broadening term defined for $H + K + L = 4$.

The purpose of the refinement is to seek the best fit between the observed data and the calculated model so to know when to terminate the refinement; parameters indicating the best fit are needed. There are several R-indices used in the Rietveld refinement including:

The profile R-factor (R_p):

$$R_p = 100 \times \frac{\sum_{i=1}^n \left| y_i(obs) - \frac{1}{c} y_i(calc) \right|}{\sum_{i=1}^n y_i(obs)} \quad \text{Equation 2.31}$$

The weighted profile R-factor (R_{wp}):

$$R_{wp} = 100 \times \sqrt{\frac{\sum_{i=1}^n w_i \left(y_i(obs) - \frac{1}{c} y_i(calc) \right)^2}{\sum_{i=1}^n w_i (y_i(obs))^2}} \quad \text{Equation 2.32}$$

The structure R-factor (R_F):

$$R_F = 100 \times \frac{\sum_{i=1}^n \left| \left(I_K('obs') \right)^{1/2} - \frac{1}{c} \left(I_K('calc') \right)^{1/2} \right|}{\sum_{i=1}^n \left(I_K('obs') \right)^{1/2}} \quad \text{Equation 2.33}$$

I_K is the intensity assigned to the K th Bragg reflection at the end of the refinement. The 'obs' is put in the quotation marks because the Bragg intensity, I_K is rarely observed directly; instead the I_K values are obtained from programmatic allocation of the total observed intensity in a 'scramble' of overlapped reflection to the individual reflections according to the ratios of those reflection intensities in the calculated pattern.

The goodness of fit (χ^2):

$$\chi^2 = 100 \times \frac{\sum_{i=1}^n w_i \left(y_i(obs) - \frac{1}{c} y_i(calc) \right)^2}{N - P - C} \quad \text{Equation 2.34}$$

where N is the number of data points

P is the number of parameter

C is the number of constraints applied.

The R-expected:

$$R_e = \frac{R_{wp}}{\sqrt{\chi^2}} \quad \text{Equation 2.35}$$

The background value is found to considerably influence these R-indices. Originally and ideally, Rietveld did the refinement by subtracting the background from the crystalline contributions and defining it with a polynomial function prior to the actual refinement. This procedure has been further modified in modern day in some Rietveld programs where the background is included without prior subtraction directly in the least squares calculations by manually setting footing marks defining areas of background between the diffraction peaks and describing it by a polynomial. These background sections are excluded in the Rietveld refinement. These modifications have often influenced the results i.e. lowering the R-indices.^[13]

Amongst all the R-indices, R_{wp} is the most straightforward and meaningful indicator as it is calculated from the square root of the quantity minimized, scaled by the weighted intensity. Another useful indicator is the goodness of fit (χ^2) which is equal to one if the model is ideal. This index has no statistical basis but is very important in indicating the quality of the refinement. The best way to judge the quality of the refinement is by the inspection of the final difference plot together with a consideration of the R-indices.^[14]

The precision of the Rietveld refinement is indicated by the estimated standard deviation (e.s.d.). This e.s.d. does not arise from the experimental error but rather the minimum probable error from random errors. For instance, an incomplete structural model which is a systematic error may appear as a random error in the calculation of e.s.d. The best way to assess the accuracy of the refinement and the e.s.d is by comparing the results from an identical material to single crystal diffraction results. In general, the e.s.d from the Rietveld refinement is found to be underestimated by three times when compared to that in single crystal study.^[15]

2.3.2 The Le Bail Method

The Le Bail method is a whole powder pattern decomposition method when individual Bragg components are extracted without reference to a structural model, but are constrained by adjustable unit cell parameters. It is found to be powerful in providing the structure factor used in *ab initio* structure determination and thus complements the Rietveld method as it assists the structure determination and the structure refinement.

The Le Bail profile fitting is performed in a similar way to the Rietveld refinement except that the refining of the structural parameters is excluded. The least squares refinement is performed on a residual function of the intensity at any point in the pattern as given by:

$$y_i = BKG + \sum_k I_k \eta(2\theta - 2\theta_k) \quad \text{Equation 2.36}$$

2.3.3 Synchrotron powder X-ray diffraction

A synchrotron is a particle accelerator that produces synchrotron radiation. It is based on the phenomenon that when the charge particles, usually electrons are accelerated to a high speed and are forced to alter their trajectory, X-rays are generated. The electrons are generated from the electron gun and accelerated using a linear accelerator to the desired energy before injection into the storage ring that is circular in shape and comprises of magnets. The higher speed of the charge particles, the larger the storage ring required.

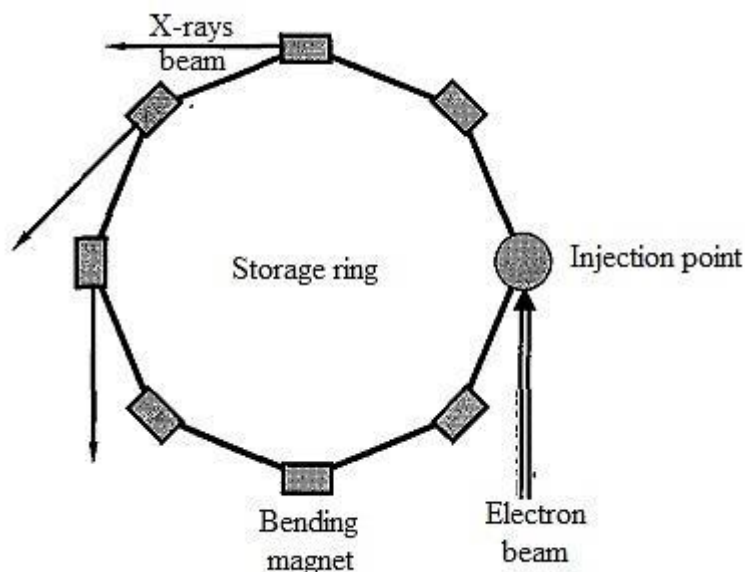


Figure 2.10 A schematic illustration of the storage ring.^[7]

The storage ring is kept under vacuum in order to increase the lifetime of the electron beam by minimizing loss of the electrons from the electron beam through collision with air molecules. The pressure in the vacuum chamber is very low, about 10^{12} times lower than the atmosphere. The bending electromagnets are fitted to the storage ring in order to control the electron beam in the orbit and the bending path of the electron beam.

The resulting radiation emitted is a continuous spectrum which means a full-range of X-rays is emitted. The desired wavelength of the X-ray is selected for a specific application using crystals or gratings. This makes the synchrotron the most useful facility as it allows a great variety of experiments and applications to be accessed, such as X-ray diffraction and X-ray spectroscopy.

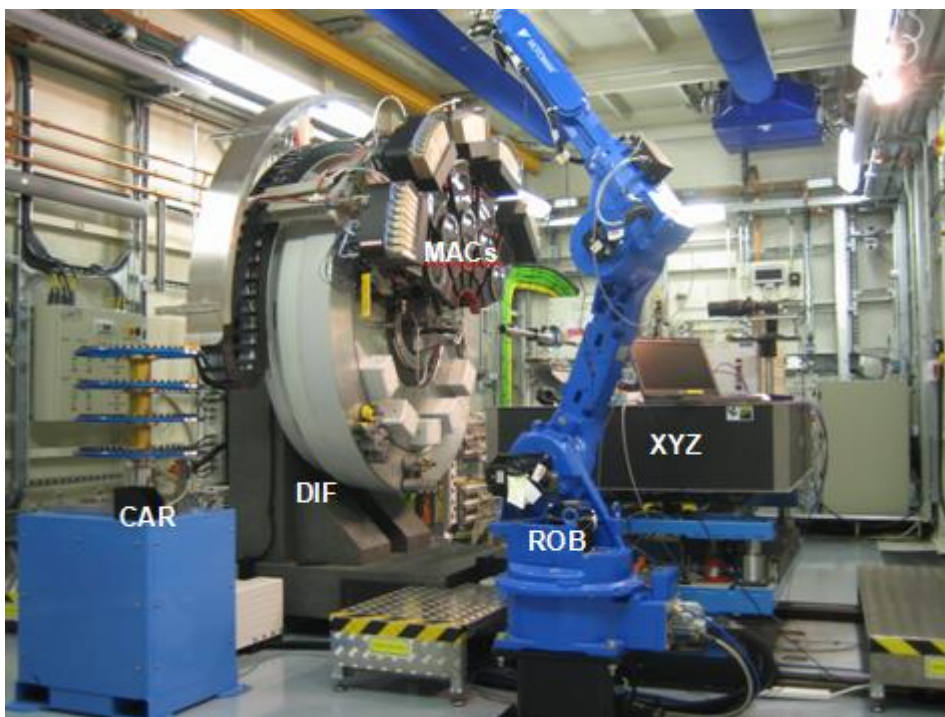
In terms of X-ray diffraction, the synchrotron becomes very useful as it offers highly collimated intense photon beam with high wavelength resolution. The photo beam generated covers a wider range of wavelength which means it can be tuned to a desired wavelength to fit the experimental condition. In addition, the data collection can be performed using a very short data acquisition time with much better data quality e.g. very high signal-to-noise and signal-to-background and very high counting statistics (millions of counts) in few seconds.

2.3.4 Beamline I11 at the Diamond Light Source (DLS), Oxford, United Kingdom

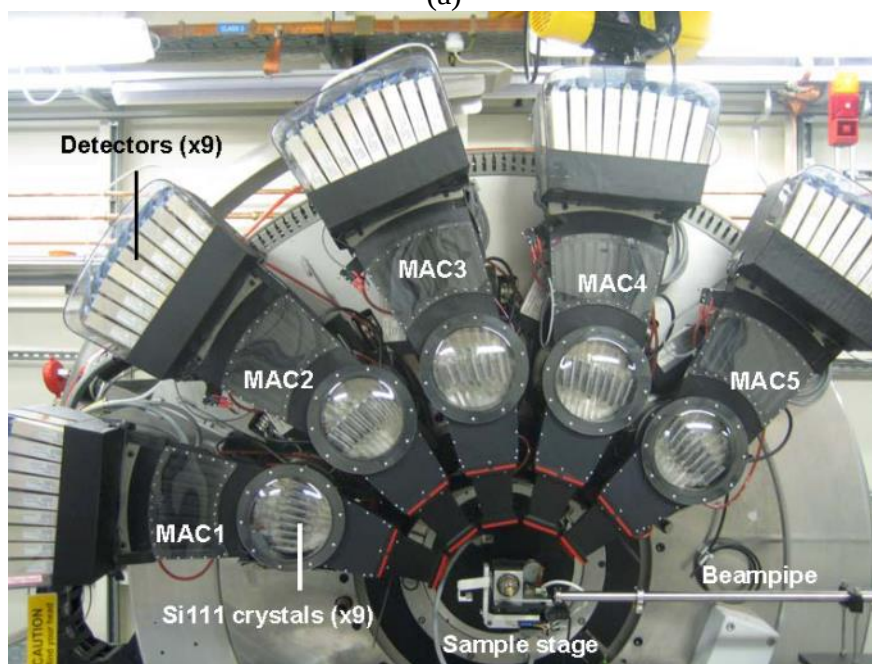
All the synchrotron powder diffraction patterns were collected at beamline I11 High Resolution Powder Diffraction, Diamond Light Source (DLS), UK. The diffractometer at I11 has 3 coaxial, high precision rotary stages (θ -, 2θ - and δ -circle). The three circles are mounted on a large granite base with motorized xyz movement for accurate positioning of the instrument's centre of rotation in the X-ray beam. A capillary or flat-plate sample spinner is mounted at the centre of a θ -circle face plate which is used to accept pre-aligned specimens attached to the magnetic holder. The precise wavelength will be determined by the scientist prior to the experiment using a standard silicon sample.^[16] The experimental hutch that the diffractometer is positioned is shown in **Figure 2.11** (a).

The five identical nine-multianalysing crystal (MAC) arms, each of which consists of 9 Si(111) crystals, are mounted on the 2θ -circle at 30° interval as shown in **Figure 2.11** (b). This means 45 powder patterns are obtained simultaneously by each crystal-detector combination as 2θ is scanned. The whole powder pattern over 2θ range of 3° - 145° needs only to scan the 30° angular range between arms plus a few degrees extra to provide sufficient overlap. The recorded patterns are then merged into a single pattern.^[16]

There are several options of experiment that can be chosen such as a variable temperature diffraction which can operate under a large temperature range, 11 K to ~ 1273 K using a various types of heating and cooling sources.



(a)



(b)

Figure 2.11 (a) Diffractometer at beamline I11 with a robotic arm used for sample loading (ROB) (b) The orientation of the sample stage, the beam pipe and the 5 multianalysing crystal (MAC) detectors.^[17]

In this work, the thermodiffraction studies over the temperature range of 12 – 500 K were performed. To reach a relatively low temperature, 12 K, a

cooling source called a PheniX cryostat was used. The PheniX cryostat offers the range of temperature from 11 K – 295 K and the set-up is as shown in **Figure 2.12** (a), (b) and (c).

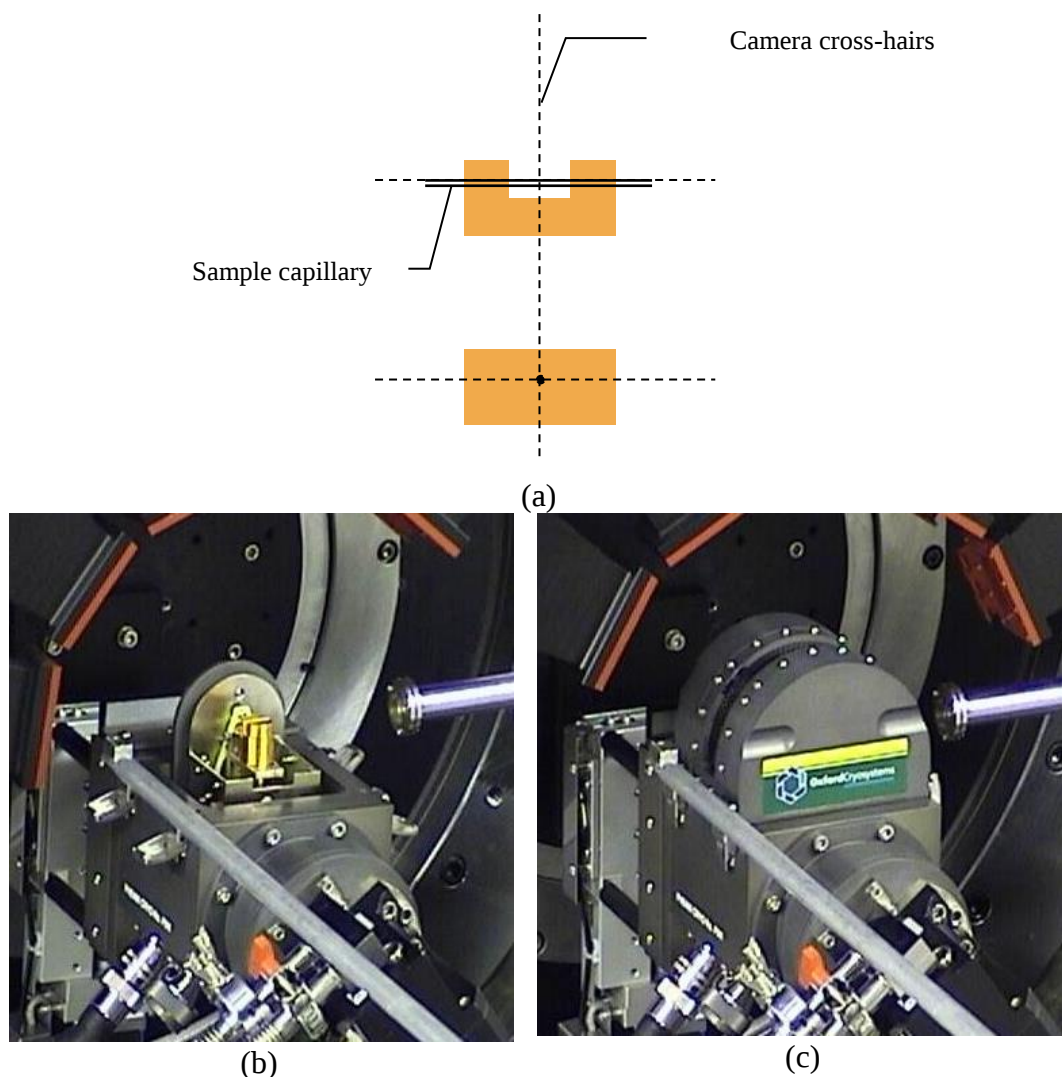


Figure 2.12 (a) The illustration of the side view of the PheniX copper holder when the sample is loaded. (b) The sample stage that the sample has already been mounted. (c) The metal cover that uses to keep the sample at a constant temperature.^[17]

The PheniX cryostat is available with a capillary tube stage as shown in **Figure 2.12**. The sample stage is allowed to tilt gently in order to reduce preferred orientation effects. To get a better heat conduction, the sample is required to pack in an aluminium capillary tube that was attached to the PheniX copper holder

which was later placed on the sample stage. After the sample alignment was done, the sample stage was covered by the outer cover to obtain a vacuum atmosphere.

A cryostream was used for temperature control for the studies over the temperature range of 100 K – 500 K. This set-up is also available with a capillary tube spinner. The sample was packed in a glass capillary tube to a length not longer than 4 centimetres. The capillary tube was then loaded into a brass holder as shown in **Figure 2.13 (a)**. The bottom part of the brass holder contains a soft iron base that allows the brass holder to be attached tightly to the magnetic head of the sample spinner as shown in **Figure 2.13 (b)**. The sample is aligned with the assistance of a camera positioned inside the experimental hutch. The sample was spun during the data collection in order to minimize preferred orientation and sample effects.

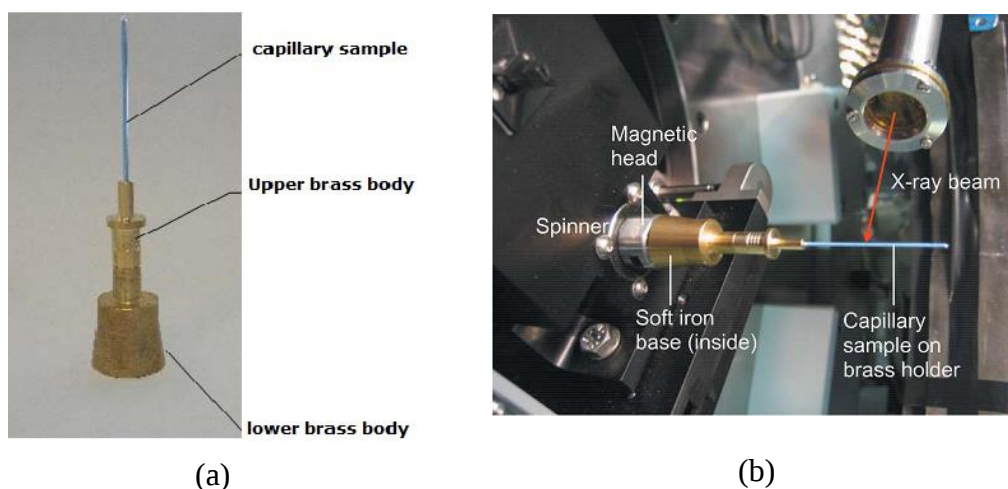


Figure 2.13 (a) Sample loaded in capillary tube is attached to the brass holder (b) The capillary holder is attached to the sample spinner in the position where the X-ray beam is targeted in the middle of the capillary tube.^[17]

2.3.5 Laboratory based-powder X-ray diffractometer, University of Manchester

Powder X-ray diffraction was used intensively in this work. For instance, it was used as an analytical technique to identify the products synthesised and to perform preliminary thermodiffraction studies on the candidate materials. The diffractometer used was a Philips X'Pert powder X-ray diffractometer set up in Bragg-Brentano geometry with Cu K α radiation ($K_{\alpha 1} = 1.54056 \text{ \AA}$ and $K_{\alpha 2} = 1.54439 \text{ \AA}$). The X'Pert diffractometer and the Bragg-Brentano geometry are shown in **Figure 2.14** (a) and (b).



(a)

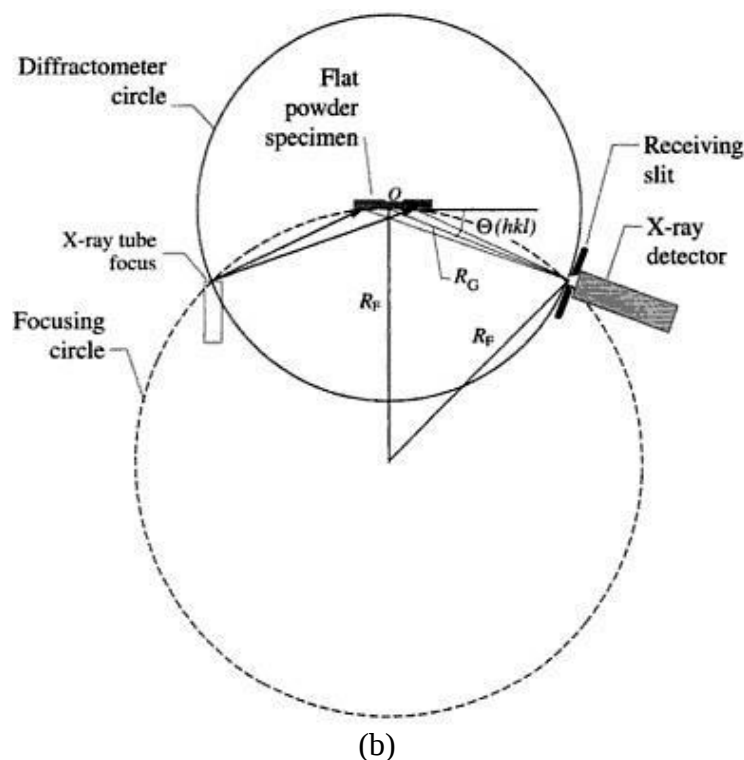


Figure 2.14 (a) A Philips X'Pert diffractometer (b) A schematic illustration of the Bragg-Brentano geometry.^[18]

In collecting the diffraction data for phase identification, a normal flat plate sample holder was used. The fixed divergence slit and the anti-scatter slits were $1/8^\circ$ and $1/4^\circ$. Samples were ground properly to ensure a random orientation of crystallites was achieved before loading onto a Si plate. Typically, the step size used is 0.016° and the diffraction patterns were allowed to collect for 30 minutes over the 2θ range of 3° to 60° .

The preliminary thermodiffraction studies were performed on all the candidate materials using a slightly adjusted diffractometer set-up. The rotating sample stage of the diffractometer was replaced by the furnace stage (XRK-900), as shown in **Figure 2.15**. The furnace stage comprises of a furnace that can operate up to 900°C and a flat plat sample holder. To collect data, the powder sample was loaded into the sample holder which was later inserted into the furnace and screwed tightly to ensure a closed system was achieved. The furnace was connected to a high vacuum Oerlikon Leybold Vacuum pump PT50 kit which allows one to heat the sample under vacuum.



(a)



(b)

Figure 2.15 (a) The Philips X'Pert diffractometer equipped with a reactor chamberXRK-900 set. (b) The sample holder of the reactor chamber XRK-900.

The sample stage was aligned prior to the data collection. The slits used were $1/8^\circ$ and $1/4^\circ$. The step size and the data collection time were varied to fit the diffraction characteristics of the sample. The samples were pre-heated and evacuated in the furnace to ensure the absence of any possible guest molecule before cooling the sample back to room temperature before data collection. The data collection is then started following the program that has been set.

2.4 Other techniques

2.4.1 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is one of the most powerful techniques for structure determination especially for organic molecules. The basic principal of this technique concerns the difference between the energy levels of the spin state of the atomic nuclei which correspond to energy of radio frequency.

If I represents the spin quantum number of the nuclei, the nuclei with odd mass numbers such as ^1H , ^{29}Si will have the spin state, $I = n/2$, where n is an integer. Nuclei with an even mass number but an odd atomic number such as ^{14}N , have the spin state, $I = 1$ and nuclei with an even mass number and an even atomic number, like ^{16}O have the spin state, $I = 0$. The nuclei that have a spin state that is not equal to zero are considered to have a magnetic moment and will be able to probe by the NMR technique.

The spin state is said to be degenerate if no external magnetic field, H_0 is applied. The energy level is then separated if the external magnetic field is applied and the number of the energy level is given by $2I + 1$. This means the nuclei with spin number $I = 1/2$ will have two allowed spin states that are I and $-I$. The higher the external magnetic field is applied, the more separated of the energy levels the spin state of the nuclei. If the radio frequency $\nu = \frac{\Delta E}{h}$ is applied to the system, the magnetic resonance occurs. The resonance frequency for each atom is different and depends on the local electronic environment or shielding.

The resonance frequencies are expressed in term of the chemical shift, δ that defines the difference between the resonance frequency of the nuclei of the sample (ν_{sample}) and the resonance frequencies of the nuclei of the standard (ν_{standard}) in the scale of part per million (ppm).

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{standard}}}{\nu_{\text{standard}}} \times 10^6 \quad \text{Equation 2.37}$$

The negative δ means the nuclei experiences greater shielding of the external magnetic field while the positive δ means the nuclei experiences a large external magnetic field and resonates at a higher frequency.

The NMR spectroscopy in liquid is not complicated as the molecules have no interaction and move freely which is not the case for a solid sample. The

interaction between atoms in solid sample makes the NMR spectra complicated. For instance, nuclei with $I = 1/2$ such as ^{29}Si have dipole-dipole interactions to the neighbouring nuclei that effect the magnetic strength of individual nuclei and leads to a variation of the chemical shift and a broadening of the peak. This interaction can be diminished by spinning the sample about the axis that lies at 54.7° to the direction of the magnetic field at a frequency of 2 – 10 kHz. This angle is known as the magic angle spinning (MAS).

The magic angle spinning has a side-effect which is appearance of spinning sidebands in the NMR spectrum. These spinning sidebands, however, can be separated from the main peak of the sample by increasing the spinning frequency. Probing nuclei that have $I \geq 1$ is tricky as they have quadrupole moments and have more allowed energy levels which lead to a peak broadening. This effect cannot be removed by magic angle spinning.

Magic angle spinning solid state nuclear magnetic resonance (MAS SSNMR) is useful when one needs to know the local environment of such nuclei. This can be done by assigning the NMR peak and comparing the chemical shift of the peak to those of reported compounds or to the known structures. For example, the ^{27}Al chemical shift of AlO_4 tetrahedra lies between +50 ppm to +80 ppm while the ^{27}Al chemical shift of AlO_6 octahedra lies in the range from -10 ppm to +20 ppm.^[19]

2.4.2 MAS SSNMR experiment

In this work, ^{27}Al and ^{19}F MAS SSNMR data were recorded on a 4 mm probe Bruker solid-state AVANCE III 400 MHz NMR spectrometer integrated with the software called TopSpin2. A sample was ground and packed in a zirconia rotor and inserted into the spectrometer. The calibration was done using adamantane as a standard prior to the data collection. The data were processed and analysed using a program called ACS/NMR processor.

2.4.3 Thermal analysis

Thermogravimetric analysis (TGA) was used in this work to monitor mass loss and mass gain during the heating process. TGA involves heating a small amount of sample at a controlled heating rate under an inert atmosphere such as N₂. The change of sample mass is recorded while the temperature is increased. The analysis is normally performed up to the decomposition temperature of the sample.

TGA plot is presented in terms of percentage of mass loss/ mass gain as a function of temperature. The observed mass loss can be related to the loss of any guest species such as water or solvent molecules. The thermal stability of the sample can also be determined from the TGA measurement. For example, the decomposition temperature of the material can be assigned from the TGA plot.

In this work, all TGA data were recorded under N₂ atmosphere using TGA/ DSC 1 Thermogravimetric Analyzer (METTLER TOLEDO). The heating rate was varied depending on the nature of the samples. The temperature range used was from 25 °C – 600 °C.

2.4.4 N₂ gas adsorption

Adsorption is a process that can be used for the characterization of a porous solid to determine the surface area, the pore size and the pore size distribution. Either gas or liquid can be used in the adsorption measurement. Liquid adsorption is relatively easy to perform but is complicated when interpreting the data. Gas adsorption is therefore preferable. Any gas can be used in the adsorption measurement although N₂ gas is used most frequently as it is abundant and relatively cheap.

Porous solids are categorized into three groups if the pore width is used as a criterion: microporous 2 nm, mesoporous 2 – 50 nm and macroporous > 50 nm. Determination of the surface area is based on the Brunauer-Emmett-Teller (BET)

theory which is a multilayer adsorption theory extended from the Langmuir theory of adsorption that describes the physisorption of the adsorbate as a monolayer. Despite the over-simplified model of the BET theory, it has been used widely and become a standard procedure of surface area determination. The BET equation is expressed as following:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \left(\frac{p}{p_0} \right) \quad \text{Equation 2.38}$$

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right) \quad \text{Equation 2.39}$$

p and p_0 are the equilibrium and saturation pressure of adsorbates at the temperature of adsorption respectively.

v is the volume of adsorbed gas.

v_m is the volume of monolayer adsorbed gas.

c is the BET constant

E_1 and E_L is the heat of adsorption for the first layer and for the second and higher layer respectively.

R is the gas constant = $8.3144621(75) \text{ J K}^{-1} \text{ mol}^{-1}$

T is temperature.^[20]

Adsorption measurement gives an adsorption isotherm which represents the volume of adsorbed gas as a function of relative pressure, p/p_0 . The adsorption isotherms are classified into five types as shown in **Figure 2.16**.

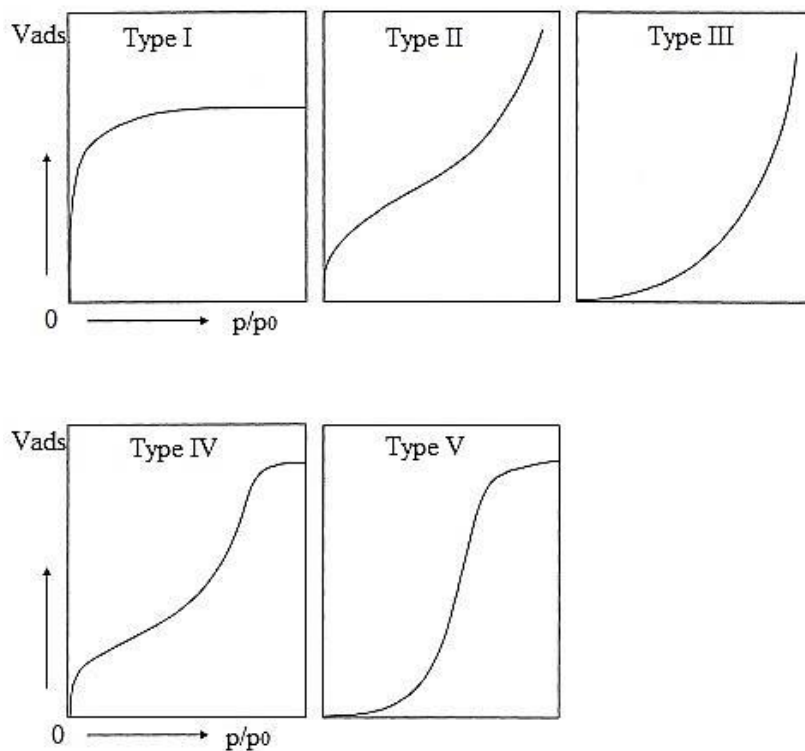


Figure 2.16 Five types of adsorption isotherm defined by Brunauer.^[21]

The type I isotherm is normally referred to as the Langmuir isotherm as it represents the monolayer coverage of the Langmuir mechanism. This type of isotherm is characteristic of a microporous solid as completion of the monolayer coverage occurs at a relatively low p/p_0 value. The plateau indicates a success of monolayer coverage and the surface area of a material can be calculated using the BET method at this point. A rapid increase of the volume of the absorbed gas at a high p/p_0 value indicates an adsorption that occurs in the space between the particles of such material.

A type II isotherm is in sigmoidal in shape and is attributed to monolayer-multilayer isotherm. This type of isotherm is observed in non-porous or macroporous solids. Another commonly observed isotherm is the type IV isotherm which represents the adsorption characteristic of mesoporous solids. Two steps of adsorption are present. The first gradual increase at a low relative pressure (p/p_0) indicates a monolayer coverage. When a plateau is reached, it

means the monolayer coverage is completed. The point of inflection indicates the beginning of multilayer adsorption where a micropore will be filled first. The second plateau is reached when all the mesopores are filled.

A hysteresis loop can often be observed in type IV isotherm and occurs when desorption does not coincide with adsorption and is due to capillary condensation. This phenomenon depends on the pore shape and connectivity of a solid. It is thought to occur because the larger pores are blocked by the filled small pores and cannot be emptied until the smaller pores are emptied which leads to hysteresis.^[21]

2.4.5 N₂ gas adsorption experiment

In this work, the nitrogen adsorption isotherm was collected at ~77 K using ASAP 2010 volumetric adsorption analyser manufactured by Micromeritics. The specific internal surface area was calculated using the BET method over the relative pressure range of 0.001 – 0.9.

2.5 References

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3. Thermoresponsive behaviour of UiO-66 and its isorecticular series

3.1 Introduction

The thermoresponsive behaviour of MOFs that consist of zero-dimensional inorganic clusters and organic linkers has been reported for two of the most well-known MOFs, HKUST-1 and MOF-5. The frameworks of HKUST-1 and MOF-5 are shown in **Figure 3.1** (a) and (b) respectively. They both have cubic symmetry but contain different inorganic clusters as well as the organic linkers. HKUST-1 contains dicopper tetracarboxylate clusters linked by the btc linkers (btc = 1,3,5-benzenetricarboxylate) and was found to exhibit NTE over the temperature range of 80 – 500 K, with the average coefficient of thermal expansion $\alpha_l = -4.1(1) \times 10^{-6} \text{ K}^{-1}$. MOF-5 contains tetranuclear $\text{Zn}_4\text{O}(\text{CO}_2)_6$ clusters linked by the bdc linkers and exhibits NTE over the temperature range of 80 – 500 K, with the coefficient of thermal expansion at 300 K, $\alpha_l = -13.1(1) \times 10^{-6} \text{ K}^{-1}$.^[1-2]

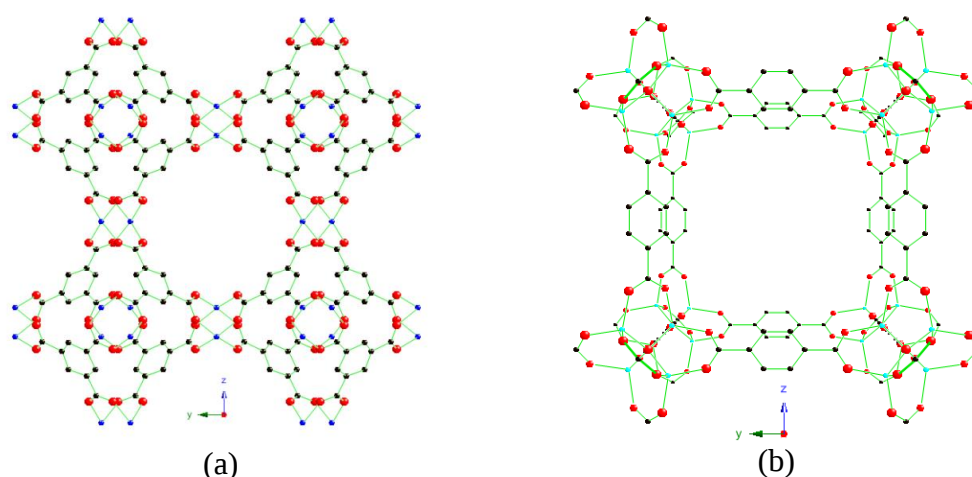
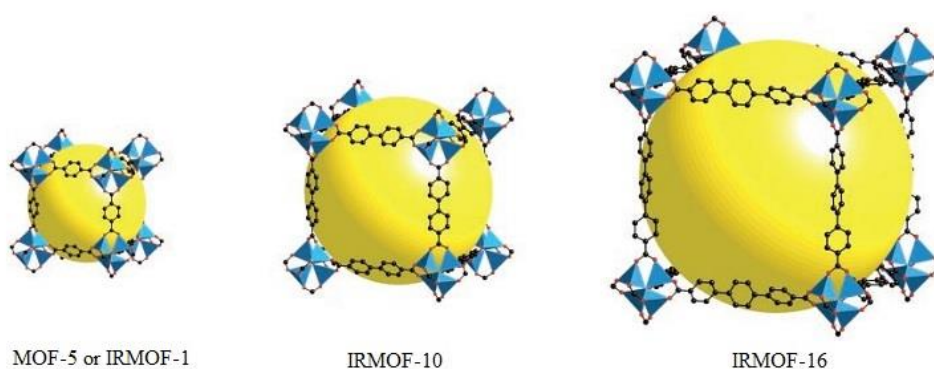


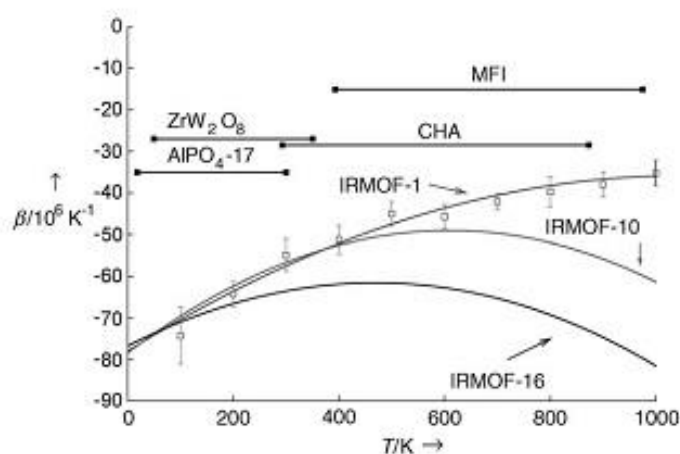
Figure 3.1 (a) The structures of HKUST-1 viewed along the [100] direction where the blue, red and black balls represent the copper, oxygen and carbon atoms respectively. (b) The structure of MOF-5 viewed along the [100] direction where the blue, red and black balls represent the zinc, oxygen and carbon atoms respectively.

The contraction in both materials is found to be dominated by the vibrational modes of the organic linker which itself undergoes an apparent contraction. In addition, the vibrations of the organic linker seem to introduce certain vibrational modes to the inorganic cluster. For instance, contraction in HKUST-1 originates from a combination of the twisting vibrational mode of the carboxylate groups of the btc linker that causes a distortion of the dicopper tetracarboxylate unit and the translation of the benzene ring in the direction normal to the linker core. Similarly to HKUST-1, thermal contraction in MOF-5 is driven by a coupling of the transverse vibrations of the bdc linker itself in the direction perpendicular to the C-C₆H₄-C core and a twisting mode of the carboxylate group of the organic linker that introduces a concerted rocking mode at the ZnO₄ tetrahedra unit.

In the case of MOF-5, several isorecticular members have been reported which allow the prediction of the effect of the organic linker on the thermoresponsive behaviour of these materials to be made. The molecular dynamics simulation study on this isorecticular series predicted that the magnitude of the coefficient of thermal expansion is directly related to the length of the organic linker. **Figure 3.2** shows the isorecticular structures of MOF-5 that are IRMOF-10 and IRMOF-16 and the prediction of the magnitude of the coefficient of thermal expansion of such materials at each temperature in comparison with other well-known NTE materials. It is interesting to note that the coefficient of volumetric thermal expansion for MOF-5 is predicted not to constant unlike what is reported from the experimental study.^[2]



(a)



(b)

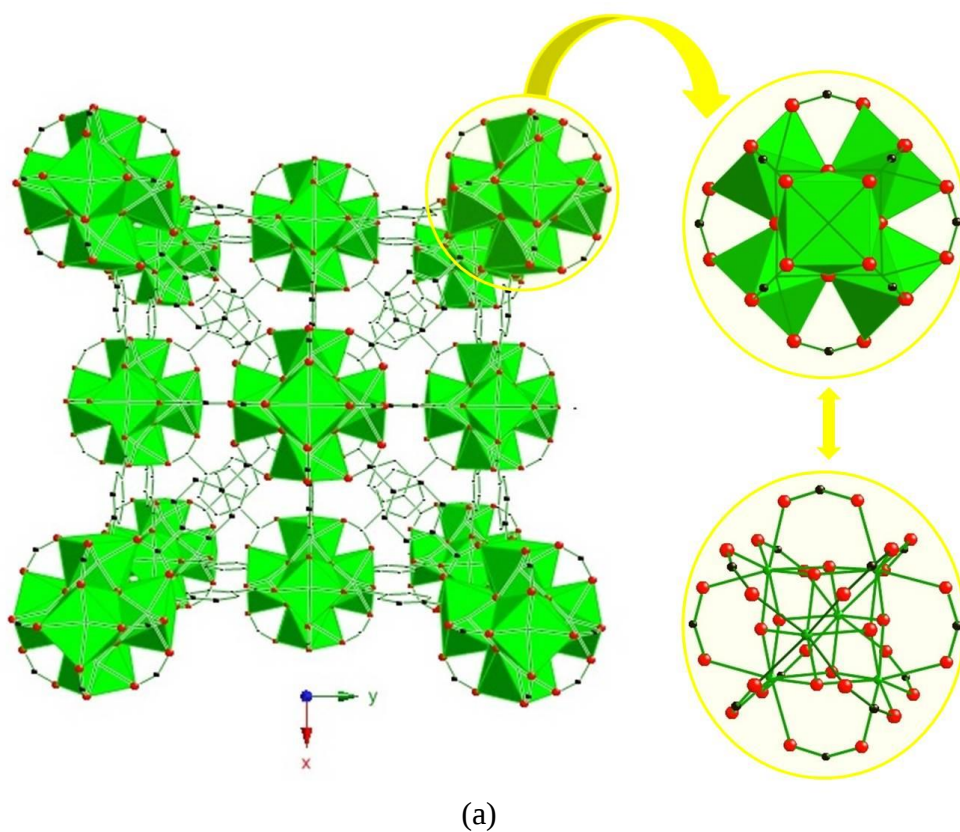
Figure 3.2 (a) The structure of IRMOF-1 (containing bdc linker), IRMOF-10 (containing bpdc linker, bpdc = biphenyl-4,4'-dicarboxylic acid) and IRMOF-16 (containing tpdc linker, tpdc = terphenyl-4,4''-dicarboxylic acid).^[3] (b) The prediction of the temperature dependence of the volumetric thermal expansion coefficients of IRMOF-1, IRMOF-10 and IRMOF-16.^[4]

Another distinctive cubic material consisting of zero-dimensional inorganic clusters that was reported in 2008 is $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, so-called UiO-66. This material has been attracting much attention from researchers due to its high thermal stability (decomposition temperature = 540 °C), its ability to tolerate a variety of solvent including bases or acids, and the pressure. Many potential applications of UiO-66 reported so far concern the functionalization of this robust MOF for uses in adsorptions, gas storage (i.e. H_2 ,^[5] xylene,^[6] CO_2 and CH_4 ^[7-10]) and in catalysis.^[11]

$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ can be synthesised by a solvothermal route at 120 °C. It has a face-centred cubic lattice (cubic: $Fm\bar{3}m$, $a = 20.7004(2)$ Å and $V = 8870.3(2)$ Å³). The structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, as shown in **Figure 3.3** (a), is made of the connection between the hexanuclear octahedral zirconium oxocluster $\text{Zr}_6\text{O}_4(\text{OH})_4$ and the bdc linker. The cluster as shown in the insets of **Figure 3.3** (a) consists of an square antiprism of ZrO_8 or it can be regarded as being made from a Zr_6 octahedron whose triangular faces have capping $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ groups. Twelve edges of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster are linked by the carboxylate groups of the bdc linkers giving a three-dimensional framework

structure whose internal void volume can be accessed through the 0.6 nm triangular windows.

The isorecticular synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ has been successfully made using a variety of the dicarboxylate linkers such as 1,4-naphthalenedicarboxylic acid (ndc), biphenyl-4,4'-dicarboxylic acid (bpdc), *p*-terphenyl-4,4''-dicarboxylic acid (tpdc) and bdc-*X* (*X* = NO₂, NH₂, Br etc.).^[10] This generates UiO-66-framework type materials with a variation of the pore size and the internal surface area. Examples of the homologue are shown in **Figure 3.3** (b).



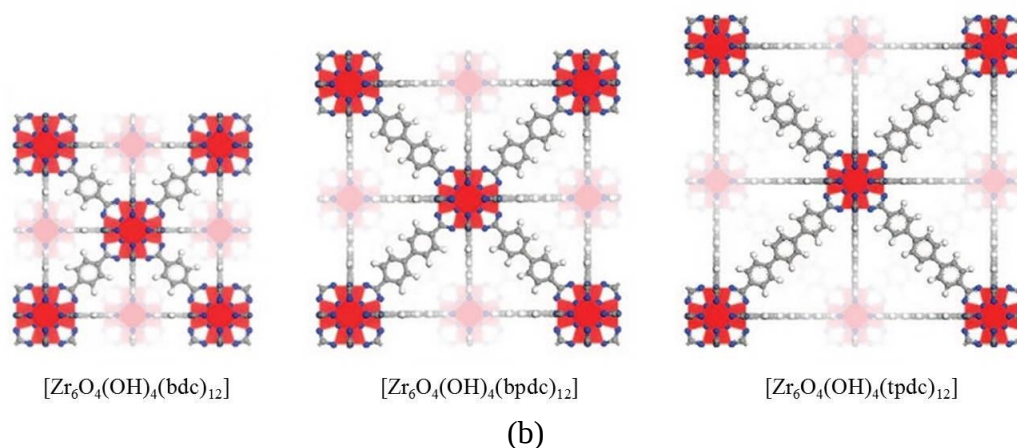


Figure 3.3 (a) The cubic- $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ structure viewing along the $[001]$ direction that is made of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters linked with the bdc linkers. The inset shows the connectivity of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster. The green, red and black balls represent zirconium, oxygen and carbon atoms respectively (b) The framework of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{tpdc})_{12}]$ synthesised via isorecticular synthesis.^[12]

Interestingly, the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ and its isorecticular members were found to dehydroxylate upon heating up to $\sim 300^\circ\text{C}$ as two equivalents of water molecules depart from the cluster which lowers the coordination number of the zirconium atom from eight to seven. The two water molecules result from the elimination of two capping $\mu_3\text{-OH}$ groups with the hydrogen atoms from the two remaining $\mu_3\text{-OH}$ groups which transforms the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster to the Zr_6O_6 cluster as shown in **Figure 3.4**. These water molecules can be reversibly adsorbed under ambient condition in atmospheric air. Researchers have tried to solve the structure of the dehydroxylated form $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ for which there is still some discrepancy. One group suggested that the $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ possesses rhombohedral symmetry (space group $R\bar{3}m$) while another group suggested the same space group (cubic, $Fm\bar{3}m$) as that originally reported.^[9, 13] This discrepancy is believed to arise from a random orientation of the cluster after the dehydroxylation. The crystal structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ is preserved in the dehydroxylated phase, although a slight decrease of the unit cell lattice is observed when compared to the hydroxylated phase.

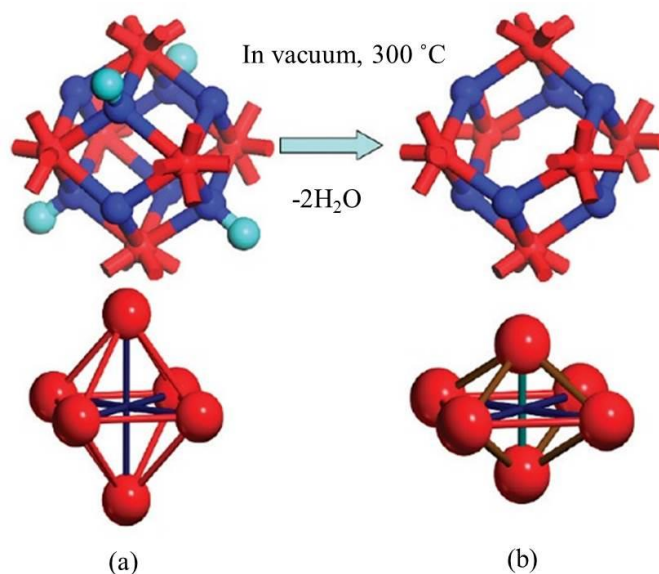


Figure 3.4 The transformation of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster upon the dehydroxylation process that involves the elimination of two equivalents water molecules resulting in the Zr_6O_6 inorganic cluster. (a) Schematic represents the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster before dehydroxylation and (b) Schematic represents the Zr_6O_6 inorganic cluster after dehydroxylation. The red, blue and light blue balls represent zirconium, oxygen and hydrogen atoms.^[13]

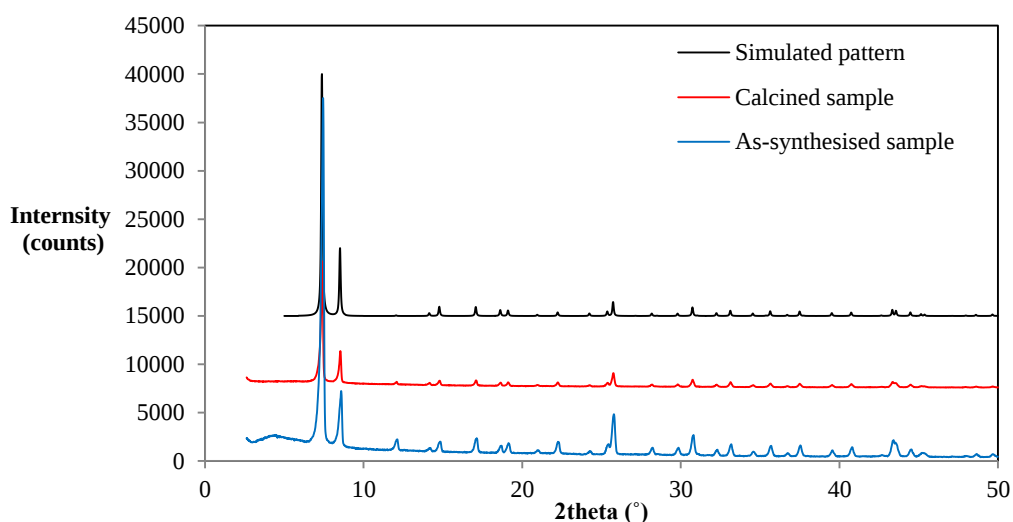
This chapter is aimed to find new NTE MOFs containing zero-dimensional inorganic clusters to see how extensive NTE is in MOFs of this type. The material chosen includes $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ as its thermal behaviour has never been reported before. This study will allow us to determine the mechanism behind the observed thermal behaviour and to study the effect of the inorganic cluster on the thermal behaviour in comparison to that in other systems, such as MOF-5. The effect of the organic linker on the thermal behaviour will also be investigated here as it has never been experimentally examined before. The study will be done by performing powder X-ray thermodiffraction studies on $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ and three isorecticular members including $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ for which the thermal behaviours have not been reported.

3.2 Thermoresponsive behaviour of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$

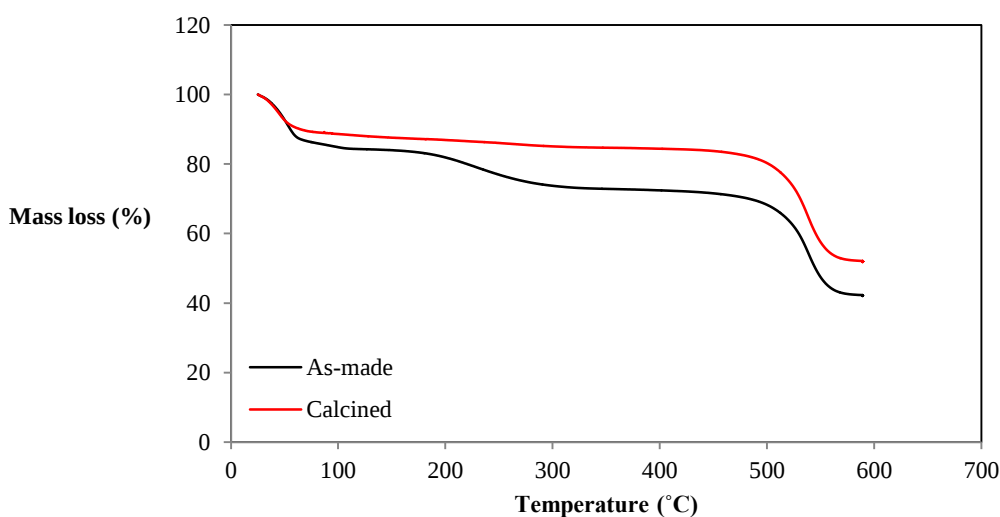
3.2.1 Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$

All chemicals involved in this synthesis were used without any further purification. $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}] \cdot (\text{guest})$ was synthesised by a slightly adjusted solvothermal reaction procedure from that reported previously.^[12] ZrCl_4 (Lancaster Synthesis, 99 %, 0.1942 g) was dissolved in *N,N*-dimethylformamide (DMF) (Sigma-Aldrich, 99.8 %, 5 ml) followed by adding H_2bdc (Sigma-Aldrich, 98%, 0.2769 g) into the mixture. 1.5 ml of acetic acid (Fisher scientific, 37% wt.) was added into the mixture. The mixture was stirred for 30 minutes prior to transferring into a 20 ml Teflon-lined stainless steel autoclave.

The mixture was heated to 120 °C for 24 hours and cooled down naturally to room temperature. The white fine solid powder product was recovered by filtration and washed with 20 ml of DMF, followed by 20 ml of acetone. 100 mg of the dried product was calcined in a tube furnace under air at 250 °C for 6 hours in order to remove the solvent molecules that might be in the pores of as-made $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}] \cdot (\text{guest})$. **Figure 3.5** shows the powder X-ray diffraction patterns of the as-synthesised and calcined samples which are in good agreement with the simulated pattern of the calcined material. This confirms that the samples prepared are mono-phase.



(a)



(b)

Figure 3.5 (a) The powder patterns of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ (b) The TGA curves of the as-synthesised and calcined $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ collected under N_2 with a heating rate of 5°C min^{-1} .

The TGA of the calcined sample shows three mass losses. The first loss at $25^\circ\text{C} - 56^\circ\text{C}$ is the departure of surface-bound guest molecules (4.5 %). The second mass loss shows an infinitesimal gradual change over the temperature range of $56 - \sim 300^\circ\text{C}$. This is due to the dehydroxylation process. It should be noted that the dehydroxylation process was not clearly evident in the TGA data due to the resolution of the equipment. The dehydroxylation process can be investigated by using high resolution TGA and is found to complete when reaching the temperature of $\sim 300^\circ\text{C}$.^[9] The third loss of $\sim 32\%$ at $\sim 460^\circ\text{C}$

corresponds to the departure of the bdc linker from the framework, calculated to be 45% if the ZrO_2 is assumed to be the final breakdown product. The discrepancy between the experimental and the theoretical value arises from the incomplete decomposition of the bdc linker vacancy in the structure.^[13]

3.2.2 Synchrotron powder thermodiffraction study of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$

3.2.2.1 Data collection

$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}] \cdot (\text{H}_2\text{O})$ was packed in an aluminium capillary tube (0.5 mm in diameter) to a length of ~ 4 centimetres and was heated to 250 °C under vacuum at 3.2×10^{-1} mbar overnight prior to data collection. The thermodiffraction study of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ was performed at I11, Diamond Light Source (DLS), UK.

The aluminium tube was loaded into the copper holder before attaching to the cold sample stage. The sample was aligned to the beam axis and covered by a metal cover to allow a vacuum atmosphere to surround the sample during cooling. The sample stage was rocked during the data collection to minimize the sampling and preferred orientation effects. Seven synchrotron powder patterns were collected over the temperature range of 12 – 290 K (data collected at 12 K, 50 K, 100 K, 150 K, 200 K, 250 K and 290 K respectively). The mean wavelength used was 0.827154(1) Å. Each diffraction pattern was collected from 3° to 140° of 2 θ with a 2 θ step size of 0.001° for 30 minutes. The powder patterns were rebinned to 0.003° before the data analysis.

3.2.2.2 Data analysis

The difference between the hydroxylated and the dehydroxylated phases can be preliminarily identified by inspection of the intensity of the (220) reflection. The intensity of this reflection is found to virtually disappear upon the

dehydroxylation process in case of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$. The synchrotron powder X-ray diffraction pattern as shown in **Figure 3.6** therefore belongs to the hydroxylated phase. Additionally, the peak shape of the synchrotron X-ray diffraction patterns had asymmetric character appearing on the right handed side of each peak. Thus, it was assumed that there was present a minor phase of a partially collapsed framework phase, of a partially dehydroxylated phase or of a random linker vacancy phase.^[13] The latter was discounted in this case as the vacancy of the bdc linker will be fully-occupied by DMF molecules which means there is no effect of the framework disorder. Hence, the synchrotron powder X-ray diffraction patterns were initially fitted using a two phase Le Bail fitting.

The starting model used for the Le Bail fitting was taken from the literature (cubic, $Fm\bar{3}m$, $a = 20.7551 \text{ \AA}$).^[12] The first two reflections and the reflections from the aluminium tube were excluded from the powder X-ray diffraction patterns. The background was manually fitted over the 2θ range of $6^\circ - 45^\circ$ where the diffraction pattern was refined. The peak shape function used was a pseudo-Voigt function which includes the effect of crystallite size and microstrain broadening. In the case of cubic $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, the refineable parameters are S400 and S202 to correct for microstrain broadening.

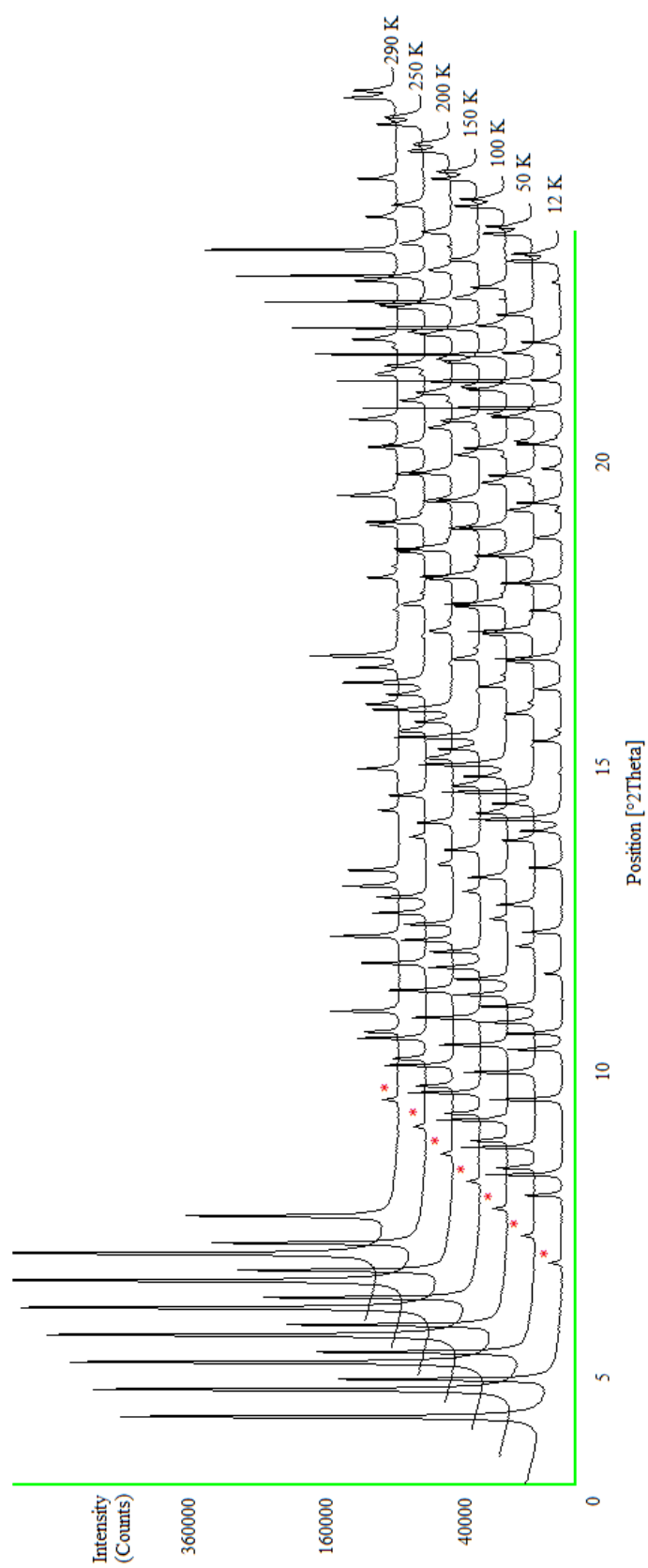


Figure 3.6 The synchrotron powder X-ray thermodiffraction pattern of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$. The (220) reflection is marked by red asterisks.

The Le Bail fitting was performed on 9234 observations. Once the refinement had converged, lattice parameters and peak profile coefficients were subsequently used in the two phase Rietveld refinement. In both phases, the Rietveld refinement was performed using the starting crystal structure taken from the literature.^[12] For the major phase, only the atomic coordinates and the isotropic atomic displacement parameters (U_{iso}) were refined while for the minor phase the occupancies of the three C atoms were additionally refined and were constrained to have the same value during the refinement.

The final cycle of the least-squares refinement involved 34 variables including the phase fraction, detector zero point, unit cell parameters, peak shape profile coefficients, the occupancy of the C atoms (for the minor phase), atomic coordinates of both phases and isotropic atomic displacement parameters (U_{iso}) of all seven atoms in the asymmetric unit of both phases. The U_{iso} of the O atoms were constrained to have the same value during the refinement, as were those of four C atoms.

The final observed, calculated and difference plot for Rietveld refinement is shown in **Figure 3.7**. The crystallographic data for the refinement at 12 K of the major and the minor phases are summarized in **Table 3.1**. The final atomic coordinates, occupancies and isotropic atomic displacement parameters of the major and the minor phases are given in **Table 3.3** and **Table 3.4**. Selected bond lengths and bond angles of the major phase are given in **Table 3.5**. The asymmetric unit and the full crystal structure of the major phase $[Zr_6O_4(OH)_4(bdc)_{12}]$ are shown in **Figure 3.8**. This is a representative final result and all the refinements of all data sets are given in the attached appendix of the CD.

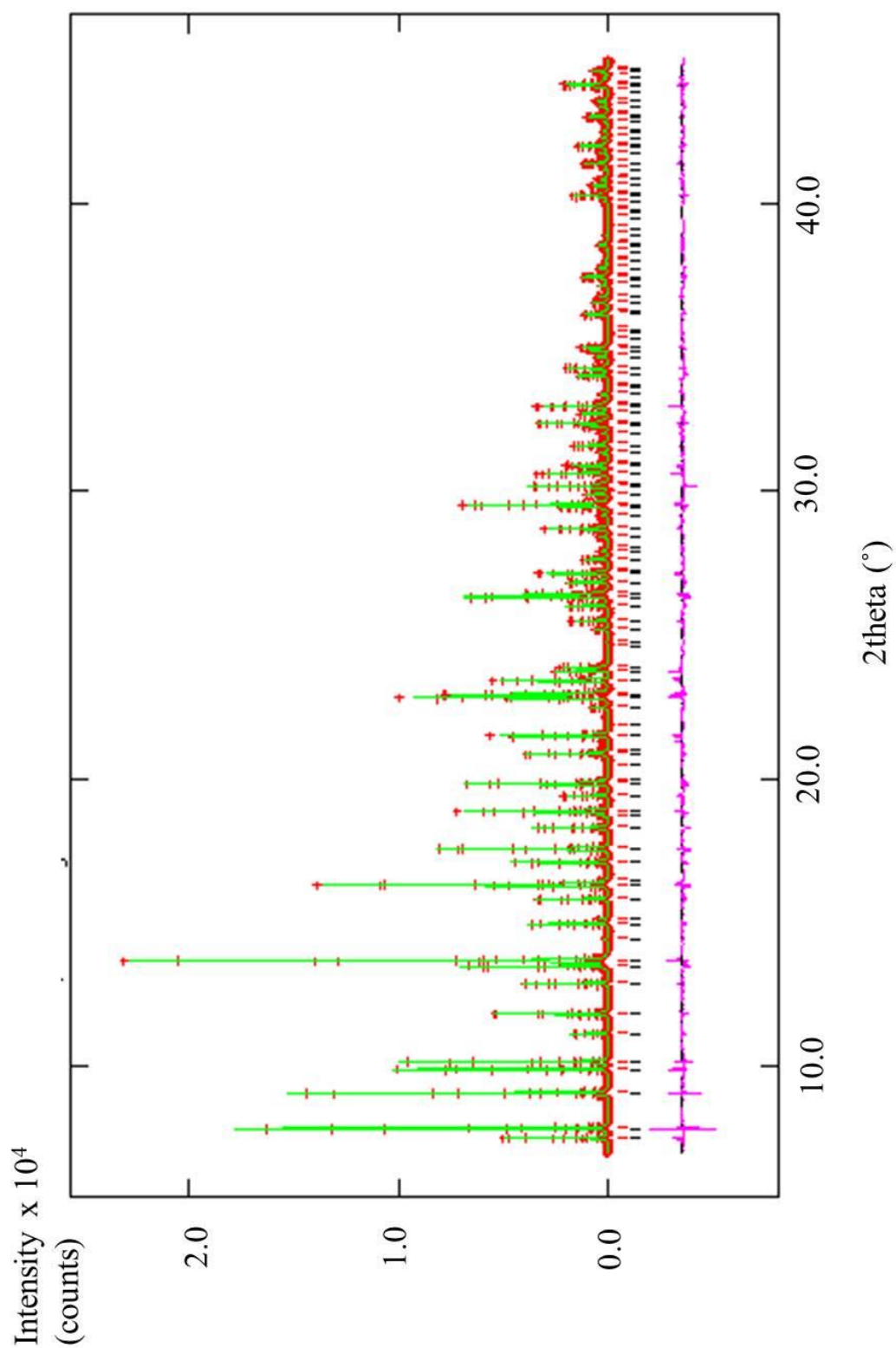


Figure 3.7 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Rietveld refinement of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ at 12 K. The black and red tick marks are the calculated 2θ angles for the Bragg peaks of the major phase and the minor phase respectively.

Table 3.1 Crystal data and structure refinement parameters for the major phase [Zr₆O₄(OH)₄(bdc)₁₂] at 12 K

Formula	Zr ₂₄ O ₁₂₀ C ₁₉₂ H ₉₆
Formula weight	6512.10
Density (gcm ⁻³)	1.215
Temperature (K)	12
Wavelength (Å)	0.827154(1)
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>
a (Å)	20.75633(7)
V (Å ³)	8942.36(9)
Z	1
R _p	0.0538
R _{wp}	0.0690
R _F	0.0389
χ ²	3.822
Number of refined parameters	34
Phase fraction (%)	72
Zero point (°)	-0.05235(6)
Gaussian profile coefficients	GU= 0.000, GV= 0.000, GW= 0.000
Lorentzian profile coefficients	LX = 1.50(1)
Eta	0
Microstrain broadening coefficients	S400 = 0.000146(3), S202 = 0.000059(3)

Table 3.2 Crystal data and structure refinement parameters for the minor phase [Zr₆O₄(OH)₄(bdc)_{9.6}] at 12 K

Formula	Zr ₂₄ O ₁₂₀ C _{153.6} H _{76.8}
Formula weight	6071.881
Density (gcm ⁻³)	1.135
Temperature (K)	12
Wavelength (Å)	0.827154(1)
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>
a (Å)	20.7136(6)
V (Å ³)	8887.2(7)
Z	1
R _p	0.0538
R _{wp}	0.0690
R _F	0.0389
χ ²	3.822
Number of refined parameters	34
Phase fraction (%)	28
Zero point (°)	-0.05235(6)
Gaussian profile coefficients	GU = 176(8), GV = -1.226(0), GW = 1.1(1)
Lorentzian profile coefficients	LX = 1.61(8)
Eta	0
Microstrain broadening coefficients	S400 = 0, S202 = 0

Table 3.3 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for the major phase $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ at 12 K.

Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Zr	0.11955(4)	0	0	0.74(3)	1
O2	0.1726(1)	0	0.0940(1)	0.89(8)	1
O3	0.0583(1)	-0.0583(1)	-0.0583(1)	0.89(8)	1
C4	0.1492(2)	0	-0.1492(2)	4.1(2)	1
C5	0.2043(3)	0	0.2043(3)	4.1(2)	1
C6	0.2677(2)	0	0.1814(2)	4.1(2)	1

Table 3.4 Final atomic coordinates, isotropic thermal parameters ($\text{\AA}^2$) and occupancies for the minor phase $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{9.6}]$ at 12 K

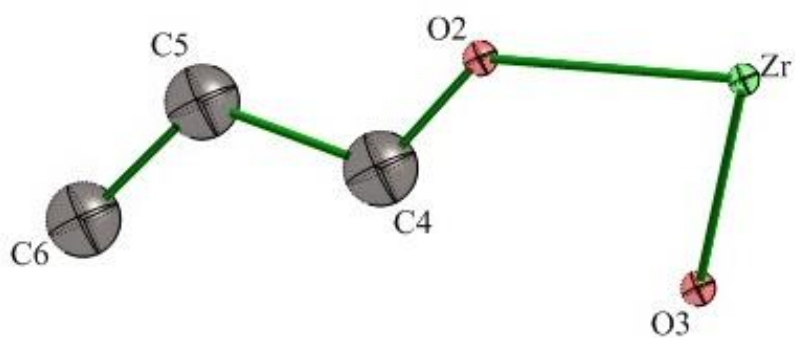
Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Zr	0.12035(13)	0.0	0.0	2.89(9)	1
O2	0.1765(3)	0.0	0.0938(3)	2.3(3)	1
O3	0.0590(3)	-0.0590(3)	-0.0590(3)	2.3(3)	1
C4	0.1467(7)	0.0	-0.1467(7)	2.8(6)	0.796(9)
C5	0.2054(7)	0.0	0.2054(7)	2.8(6)	0.796(9)
C6	0.2642(6)	0.0	0.1793(6)	2.8(6)	0.796(9)

Table 3.5 Selected bond lengths (Å) and bond angles (°) for the major phase [Zr₆O₄(OH)₄(bdc)₁₂] at 12 K

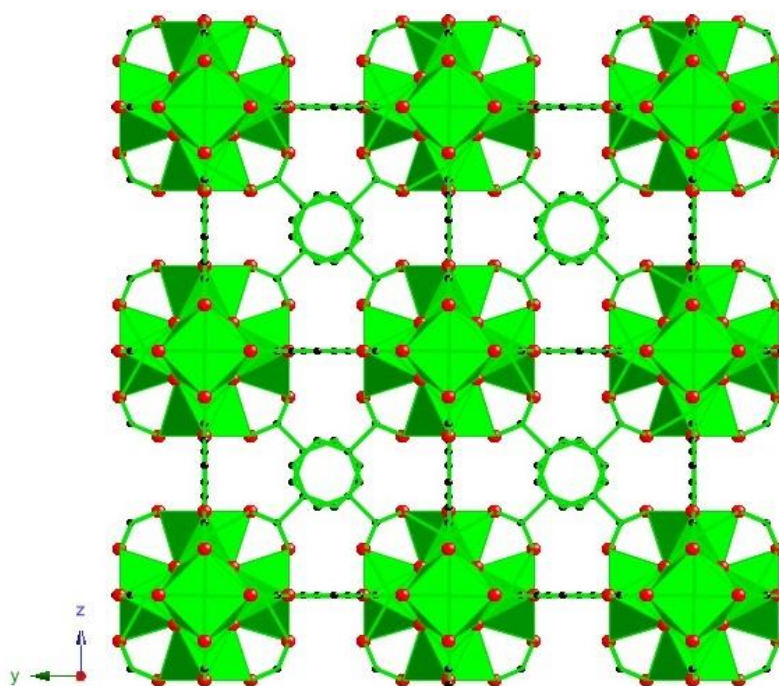
Zr—O2	2.241(3)	O2 ⁵ —Zr—O3 ⁵	141.95(3)
Zr—O3	2.131(1)	O2 ⁵ —Zr—O3 ⁸	78.4(1)
C4—O2 ⁵	1.244(3)	O2 ⁵ —Zr—O3 ⁹	141.95(3)
C4—C5 ⁵	1.618(9)	O2 ⁶ —Zr—O2 ⁷	121.1(1)
C5—C6	1.279(4)	O2 ⁶ —Zr—O3	141.95(3)
C6—C6 ¹²	1.494(8)	O2 ⁶ —Zr—O3 ⁵	141.95(3)
		O2 ⁶ —Zr—O3 ⁸	78.4(1)
O2—Zr—O2 ⁵	121.1(1)	O2 ⁶ —Zr—O3 ⁹	78.4(1)
O2—Zr—O2 ⁶	76.01(6)	O2 ⁷ —Zr—O3 ⁸	141.95(3)
O2—Zr—O2 ⁷	76.01(6)	O2 ⁷ —Zr—O3 ⁹	141.95(3)
O2—Zr—O3	141.95(3)	O2 ⁷ —Zr—O3	78.4(1)
O2—Zr—O3 ⁵	78.4(1)	O2 ⁷ —Zr—O3 ⁵	78.4(1)
O2—Zr—O3 ⁷	141.95(3)	O3—Zr—O3 ⁵	69.1(1)
O2—Zr—O3 ⁹	78.4(1)	Zr—O2—C4 ⁵	127.5(4)
O2 ⁵ —Zr—O2 ⁶	76.01(6)	Zr—O3—Zr ³	110.8(1)
O3—Zr—O3 ⁸	69.1(1)	Zr—O3—Zr ⁴	110.8(1)
O3—Zr—O3 ⁹	106.7(3)	Zr ³ —O3—Zr ⁴	110.8(1)
O3 ⁵ —Zr—O3 ⁸	106.7(3)	O2 ⁵ —C4—O2 ¹⁰	136.1(7)
O3 ⁵ —Zr—O3 ⁹	69.1(1)	O2 ⁵ —C4—C5 ⁵	112.0(4)
O3 ⁸ —Zr—O3 ⁹	69.1(1)	C4 ⁵ —C5—C6	115.1(4)
O2 ⁵ —Zr—O2 ⁷	76.01(6)	C6—C5—C6 ¹¹	129.7(7)
O2 ⁵ —Zr—O3	78.4(1)		

Symmetry transformations used to generated equivalent atoms:

(1) z, x, y ; (2) y, z, x ; (3) $y, -z, -x$; (4) $-z, -x, y$; (5) $x, y, -z$; (6) x, z, y ; (7) $x, -z, y$; (8) $-z, x, y$; (9) $-z, x, -y$; (10) $z, -y, -x$; (11) z, y, x ; (12) $-z+1/2, y, -x+1/2$



(a)



(b)

Figure 3.8 (a) The asymmetric unit of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ (b) The structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ viewed along the $[100]$ direction.

3.2.3 Results and discussion

The unit cell dimension and unit cell volume of the major phase $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ and the minor phase of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{9.6}]$ from 12 - 290 K are listed in **Table 3.6** and **Table 3.7** respectively. The minor phase of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{9.6}]$ shows a random behaviour which is presumably due to low precision of refinements as it is 28 % of sample and peaks are not clearly defined. For this reason, it is not discussed further.

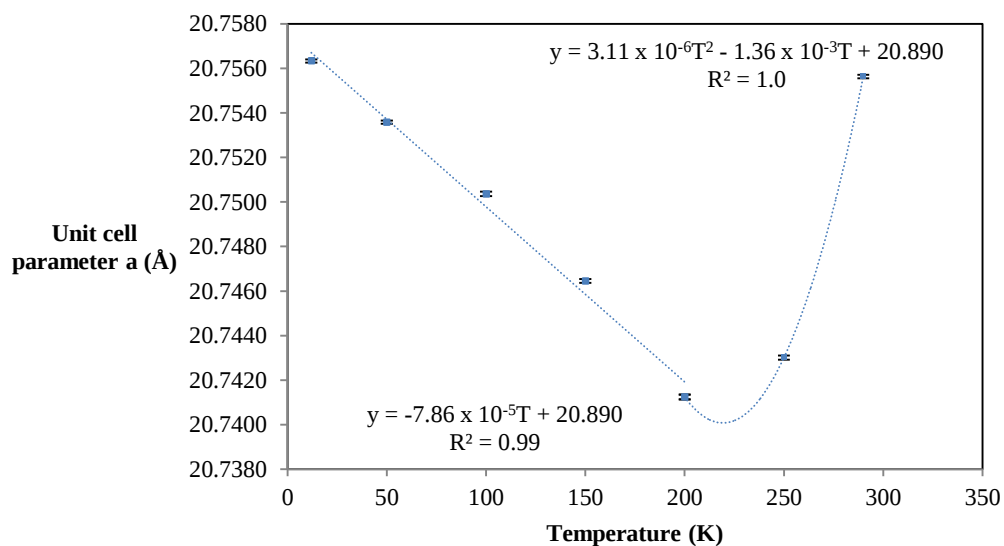
Table 3.6 Unit cell dimensions a (Å), unit cell volume V (Å³), goodness of fit (χ^2), R_p and R_{wp} for the major phase $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ from 12 - 290 K

Temperature (K)	a	V	χ^2	R_p	R_{wp}
12	20.75633(7)	8942.4(1)	3.902	0.054	0.0623
50	20.75358(8)	8938.8(1)	4.618	0.058	0.0751
100	20.75036(10)	8934.6(1)	4.602	0.058	0.0750
150	20.74645(9)	8929.6(1)	3.333	0.049	0.0641
200	20.74124(11)	8922.9(1)	3.305	0.049	0.0638
250	20.74301(9)	8925.1(1)	3.323	0.049	0.0644
290	20.75563(8)	8941.4(1)	4.205	0.054	0.0733

Table 3.7 Unit cell dimensions a (Å), unit cell volume V (Å³), goodness of fit (χ^2), R_p and R_{wp} for the minor phase $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{9.6}]$ from 12 - 290 K

Temperature (K)	a	V	χ^2	R_p	R_{wp}
12	20.7136(6)	8887.2(7)	3.902	0.054	0.0623
50	20.7076(3)	8879.5(3)	4.618	0.058	0.0751
100	20.7125(8)	8885(1)	4.602	0.058	0.0750
150	20.7098(9)	8882(1)	3.333	0.049	0.0641
200	20.707(1)	8879(1)	3.305	0.049	0.0638
250	20.7102(9)	8882(1)	3.323	0.049	0.0644
290	20.7311(6)	8909.2(8)	4.205	0.054	0.0733

$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ shows negative thermal expansion over the temperature range of 12 – 200 K before exhibiting expansion from 200 K to 290 K. No phase transition is observed. The measured variations in lattice parameter and unit cell volume as a function of temperature of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ are shown in **Figure 3.9**.



(a)

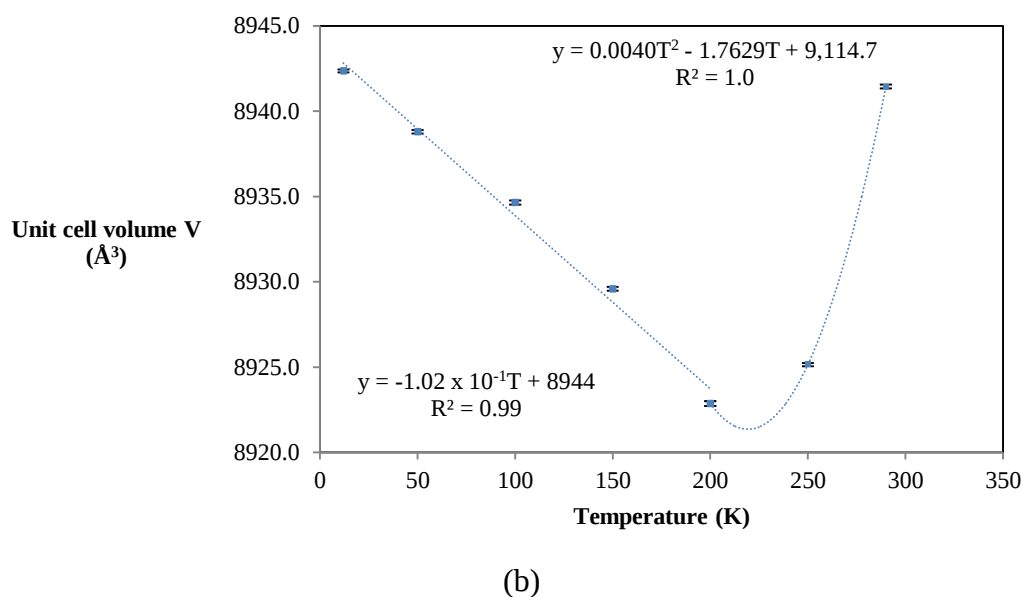
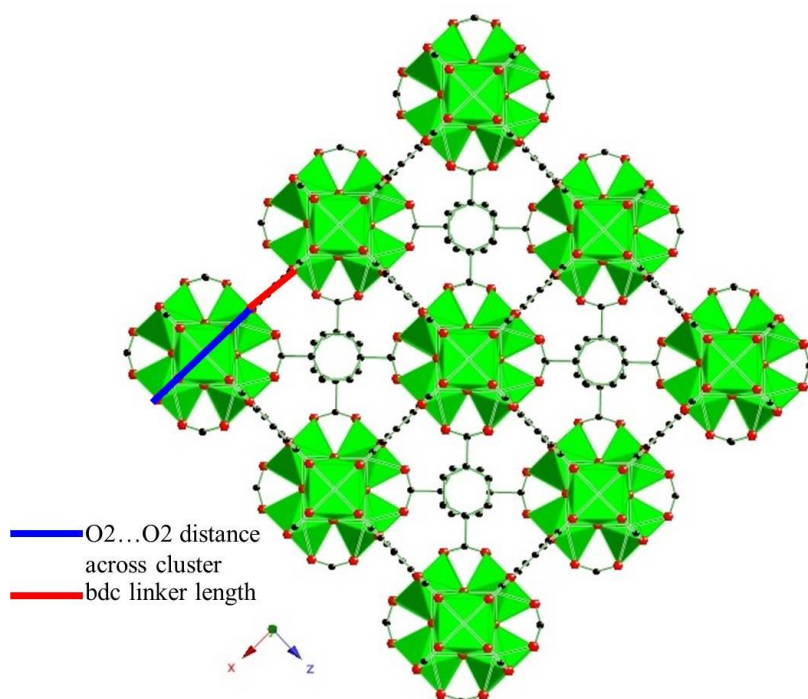


Figure 3.9 (a) The variation of the unit cell parameter a and (b) the unit cell volume V as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

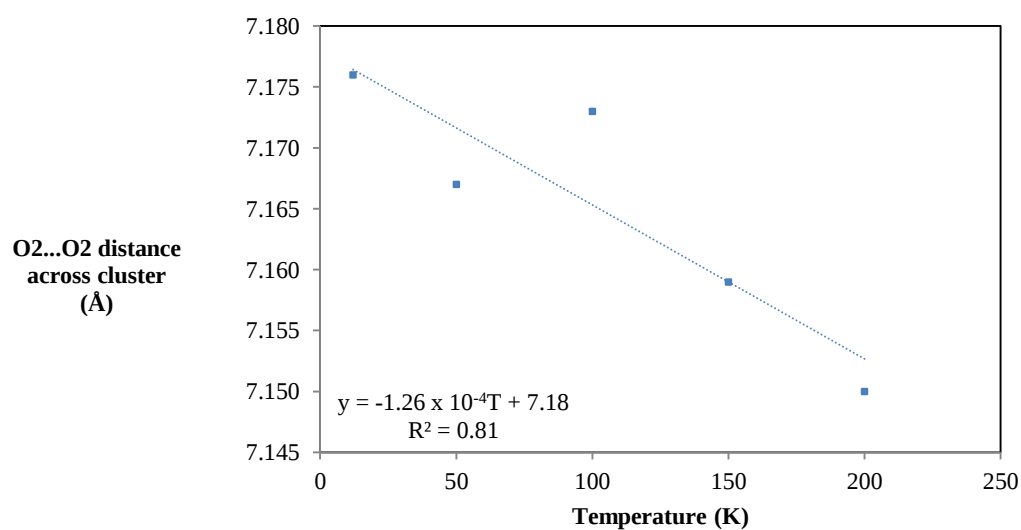
$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ shows zero thermal expansion over the entire temperature range observed. A smooth decrease along the a axis over the temperature range of 12 – 200 K is counteracted by a later non-linear increase from 200 – 290 K. The total decrease of the unit cell over the entire temperature range studied is $0.9 \text{ \AA}^3$. The maximum decrease of the unit cell volume is $19.5 \text{ \AA}^3$ over the temperature range 10 - 200 K. Smooth decreases both in a ($-7.86 \times 10^{-5} \text{ \AA K}^{-1}$) and V ($V = -1.02 \times 10^{-1}T + 8944.1 \text{ \AA}^3 \text{ K}^{-1}$) are observed over the temperature range of 12 – 200 K. The coefficient of thermal expansion α_V is $-1.14 \times 10^{-5} \text{ K}^{-1}$ over this range and is smaller than that of MOF-5 by ~ 3.5 times.

The isotropic contraction exhibited over the temperature range of 12 – 200 K will be rationalised. Detailed structure data from the Rietveld refinement suggest the possible mechanism responsible for the contraction observed in this temperature range. The contraction along the a axis results from a decrease in the linear coefficient of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic clusters ($\alpha = -1.75 \times 10^{-5} \text{ K}^{-1}$) that outweighs an increase of the bdc linker ($\alpha = 8.53 \times 10^{-6} \text{ K}^{-1}$) as defined in **Figure 3.10** (a). The $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster defines the distance from the O2 oxygen atom of the carboxylate group to the adjacent one at the opposite side of

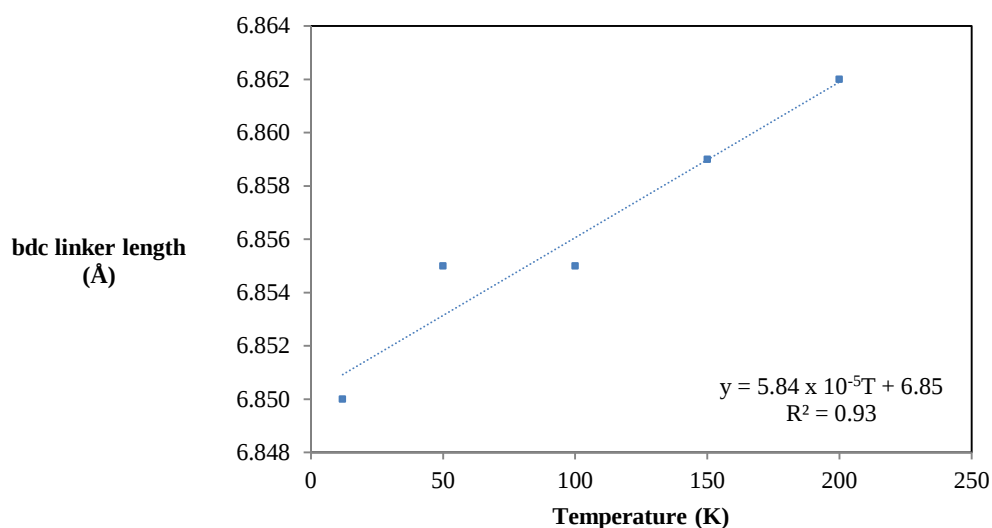
the cluster. The $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster shows a decrease in size as the temperature is increased as shown in **Figure 3.10 (b)** which is found to be the main contributor to the contraction along the a axis. The measured length of the bdc linker, $\text{OC-C}_6\text{H}_4\text{-CO}$ shows a smooth increase as shown in **Figure 3.10 (c)**.



(a)



(b)



(c)

Figure 3.10 (a) The $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster is measured from the oxygen atom of the carboxylate group to the one at the opposite side of the cluster while the length of the bdc linker is measured from the $\text{OC-C}_6\text{H}_4\text{-CO}$ length. The green square antiprism represents the ZrO_8 square antiprism while the red and black balls represent the oxygen and carbon atoms respectively. (b) The variation of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster size as a function of the temperature. And (c) The measured bdc linker length as a function of temperature.

The decrease of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster size might arise from a correlated twisting of the carboxylate groups of the bdc linkers that leads to a concerted rocking motion of the ZrO_8 square antiprism as depicted in **Figure 3.11**. This behaviour is similar to that found in MOF-5 where the correlated twisting of the carboxylate group of the bdc linker causes an individual ZnO_4 tetrahedron unit to twist around the central O atom of the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster and consequently leads to a decrease in its size. The magnitude of the contraction of the inorganic cluster of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ ($\alpha = -1.75 \times 10^{-5} \text{ K}^{-1}$) is found to be comparable with that of MOF-5 ($\alpha = -1.61 \times 10^{-5} \text{ K}^{-1}$).

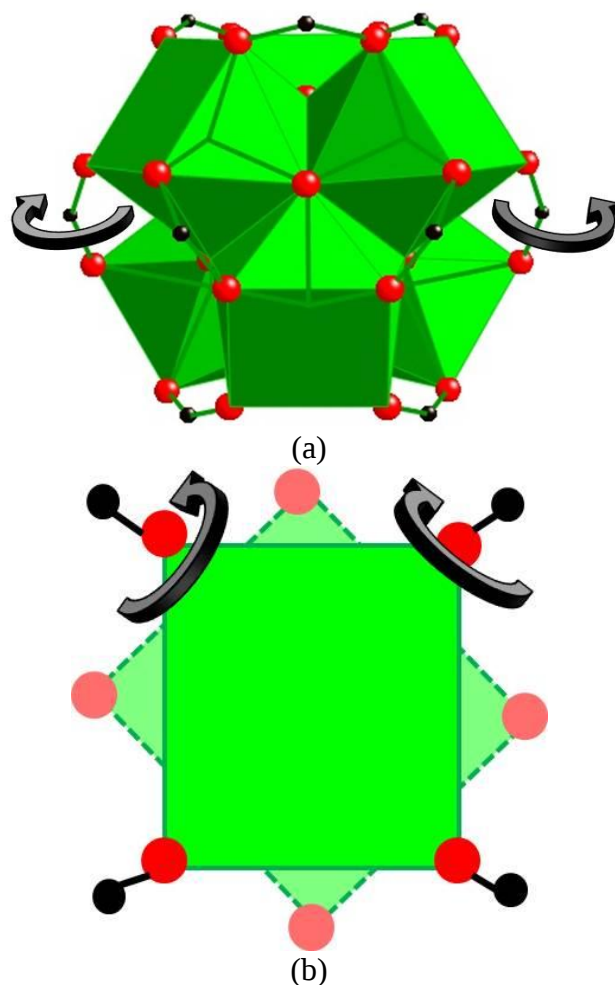
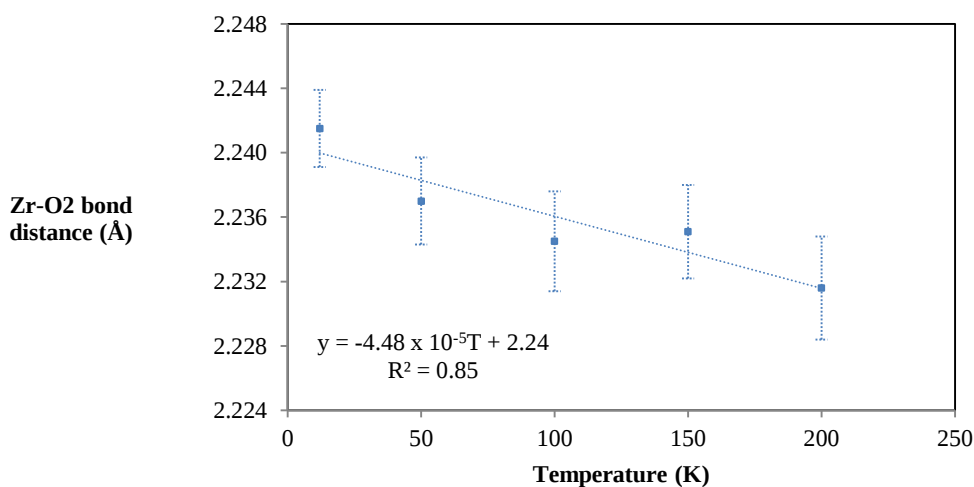


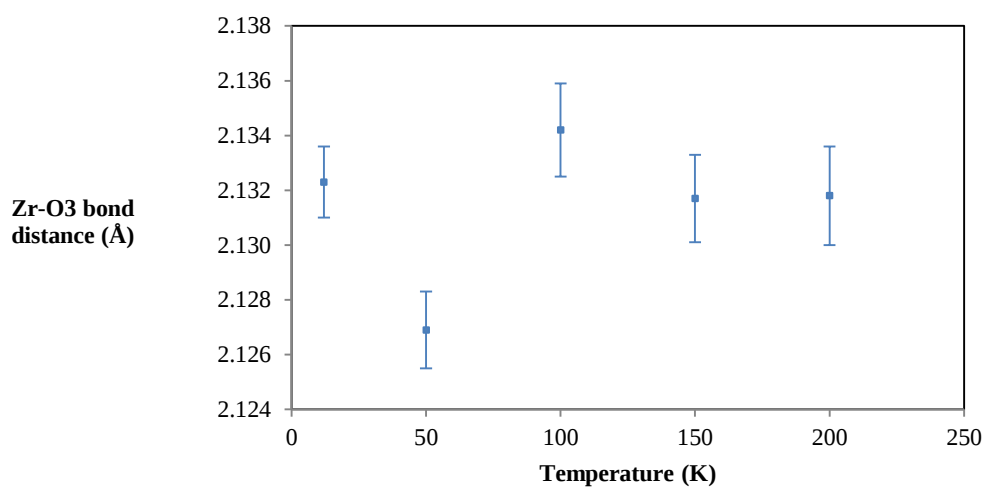
Figure 3.11 A schematic representing the twisting vibrational mode of the carboxylate group of the bdc linker. This mode is found to cause the contraction of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster as it induces a concerted rocking of the ZrO_8 square antiprism. The green cubes represent the ZrO_8 square antiprism while the red and black balls represent the oxygen and carbon atoms respectively. (b) A Top view schematic illustration representing the rocking motion of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster that is introduced by the twisting motion of the carboxylate groups of the bdc linker. The arrows represent the sense of the twisting motion

The decrease in size of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster that arises from the twisting vibration mode of the oxygen atom (denoted as O2) of the carboxylate group is supported by a reduction in the Zr-O2 distance as shown in **Figure 3.12** (a). The $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster contains two different crystallographic oxygen atoms that are the oxygen atom of the carboxylate group and the oxygen atom of the OH group denoted O3, which has coordination of

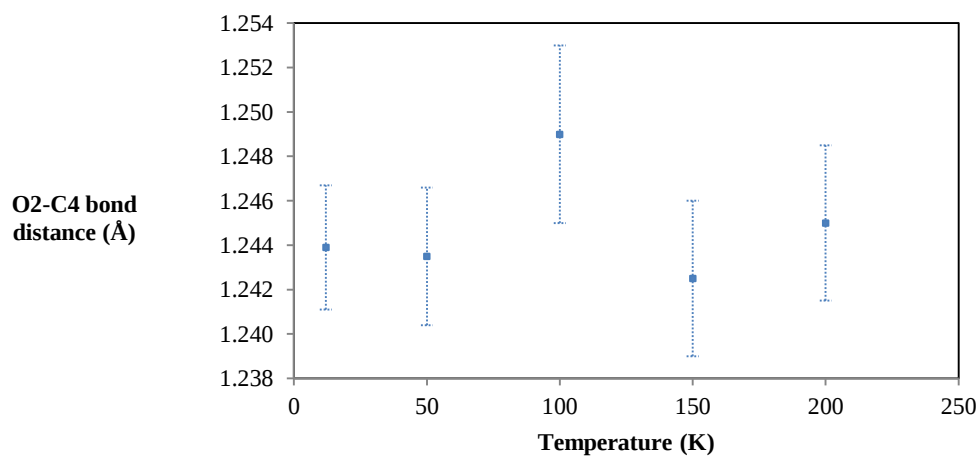
three number. As the O3 oxygen atoms are highly constrained, the Zr-O3 bond distance stays approximate constant over the temperature range studied as shown in **Figure 3.12** (b). In contrast, the O2 oxygen atom is able to vibrate and this vibration is increased upon heating which leads to the apparent decrease of the Zr-O2 distance. The other accompanying geometric parameters that generally support the twisting mode of the carboxylate group of the bdc linker include a near constant value of the C4-O2 bond distances as shown in **Figure 3.12** (c), a non-linear decrease of the O1-C4-O2 bond angles as shown in **Figure 3.12** (d) and a near constant value of the carboxylate O2...O2 non-bonding distance as shown in **Figure 3.12** (e). However, the small magnitude of the changes in the geometric parameters over this temperature range and the precision of the structure refinement limit a more definitive determination of the mechanism of contraction of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster.



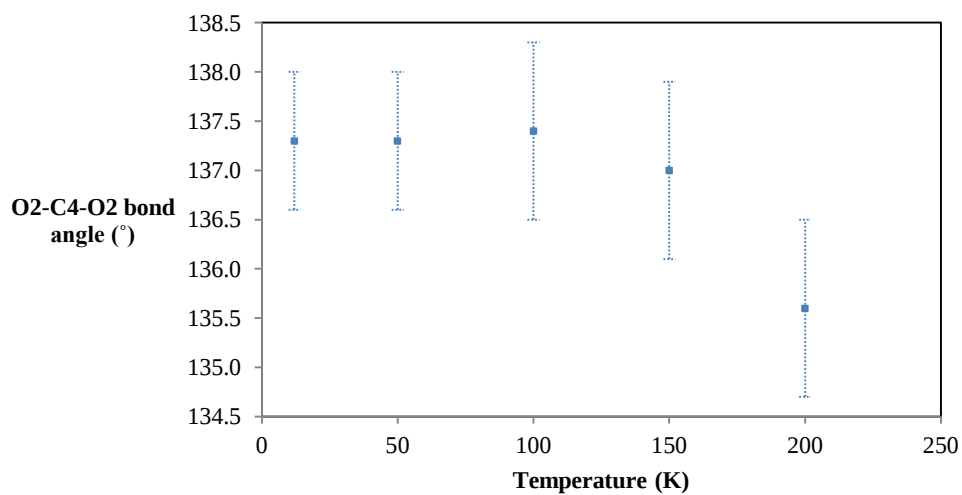
(a)



(b)



(c)



(d)

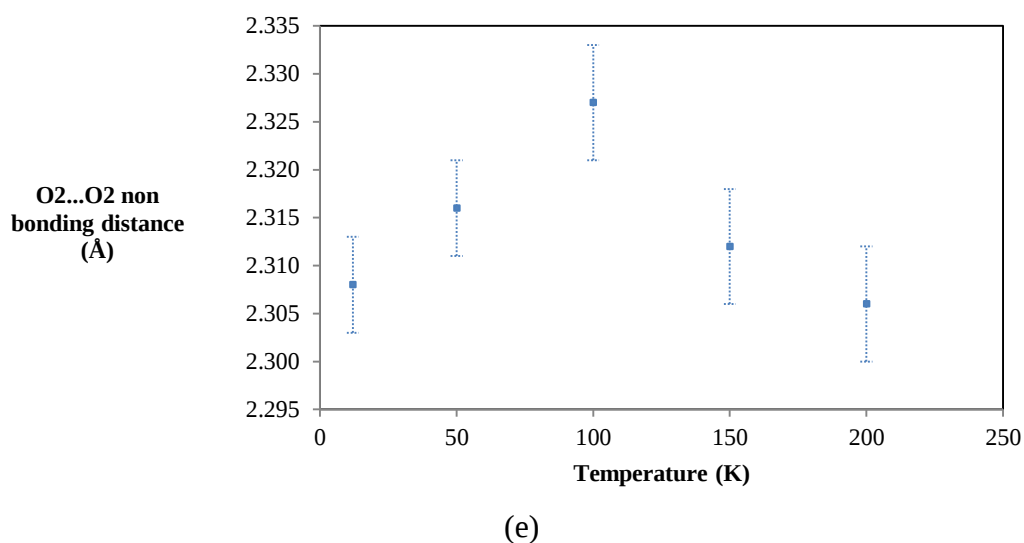


Figure 3.12 The temperature dependence of (a) the Zr-O2 bond distance (b) the Zr-O3 distance (c) the O2-C4 bond distance (d) the O2-C4-O2 bond angle and (e) the carboxylate O2...O2 non-bonding distance. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

The measured variation of the bdc linker, C4...C4 non-bonding distance shows a linear increase in length over the temperature range of 12 – 200 K. This behaviour is as usual and suggests that there is no occurrence of the transverse vibrational modes at the bdc linker like in the case of MOF-5. However, a more definite elucidation of the mechanism of the variation of the bdc linker length cannot be made due to the limitations of the structure refinements. In conclusion, the NTE behaviour of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ over the temperature range of 12 – 200 K is dominated by the twisting motion of the carboxylate groups of the bdc linkers that introduces a rocking motion of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster resulting in a decrease in size of this cluster and hence the overall unit cell volume contraction. The magnitude of the expansivity coefficient of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ is found to be lower than that of MOF-5, although the magnitude of the contraction of the inorganic clusters of both materials is comparable. This is because in MOF-5, the NTE behaviour is not only attributed to the decrease in size of the inorganic cluster but also the decrease of the bdc linker. The latter was found to be caused by the transverse vibrational modes of the bdc linker perpendicular to its C-C₆H₄-C core^[2] which are not evident in this work.

The thermal expansion observed over the temperature range of 200 – 290 K may possibly be due to the incomplete activation of the sample which causes the presence of H₂O, O₂ or N₂ molecules in the framework. The amount of the guest molecules might not be large enough to affect the synchrotron powder X-ray diffraction pattern at low temperature as they might be disordered inside the framework void volume. However, as the temperature is increased, these molecules may vaporize and consequently interfere with the vibrations and volume of the framework (The melting/boiling point of N₂ is 63.15 K/ 77.36 K and of O₂ is 50.5 K/ 90.2 K). Another possible contributor to the expansion over the temperature range of 200 – 290 K are changes of the Zr₆O₄(OH)₄ inorganic cluster itself. For instance, changes in the geometry of the H atoms of the μ_3 -OH groups in the cluster might lead to a geometric change over the temperature range of 200 - 290 K.

3.3 Thermoresponsive behaviour of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$

3.3.1 Syntheses and thermogravimetric analyses of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$

In this section, three hydroxylated forms of the candidate materials were synthesised including $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$. The synthesis procedure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ was identical to that in section 3.2.1.

3.3.1.1 *Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}]$*

All chemicals involved in the synthesis were used without further purification. The synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}]$ is based on that reported previously.^[14] ZrCl_4 (Lancaster Synthesis, 99 %, 0.120 g), H_2bpdc (TCI, 97 %, 0.125 g) and benzoic acid (Sigma-Aldrich, 99 %, 1.883 g) were added to DMF (Sigma-Aldrich, 99.8 %, 20 ml) in a 125 ml glass vial and the mixture was heated at 120 °C for 24 hours. Addition of benzoic acid into the mixture was found to increase the crystallinity of the product. The mixture was cooled down naturally to room temperature prior to filtration. A pale yellow fine powder product was recovered by filtration and washed with 20 ml of DMF followed by 20 ml of acetone. To get rid of the benzoic acid that packs into the pore of the sample, the mixture of 100 mg of the dried product and DMF (10 ml) was placed in a 20 ml Teflon-lined stainless steel autoclave and heated to 150 °C overnight. The product from this treatment was recovered by filtration and washed with DMF (20 ml) and acetone (20 ml).

Calcination of the as-synthesised product was performed in a tube furnace under air at 350 °C for 6 hours in order to remove the solvent molecules such as, water and DMF, that might be present in the pore volume of the as-synthesised

$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{guest})$. The powder patterns of the as-made $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{guest})$ and calcined $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{H}_2\text{O})$ samples are shown in **Figure 3.14** (a) in comparison with the simulated pattern and indicate that a pure phase of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}]$ has been made.

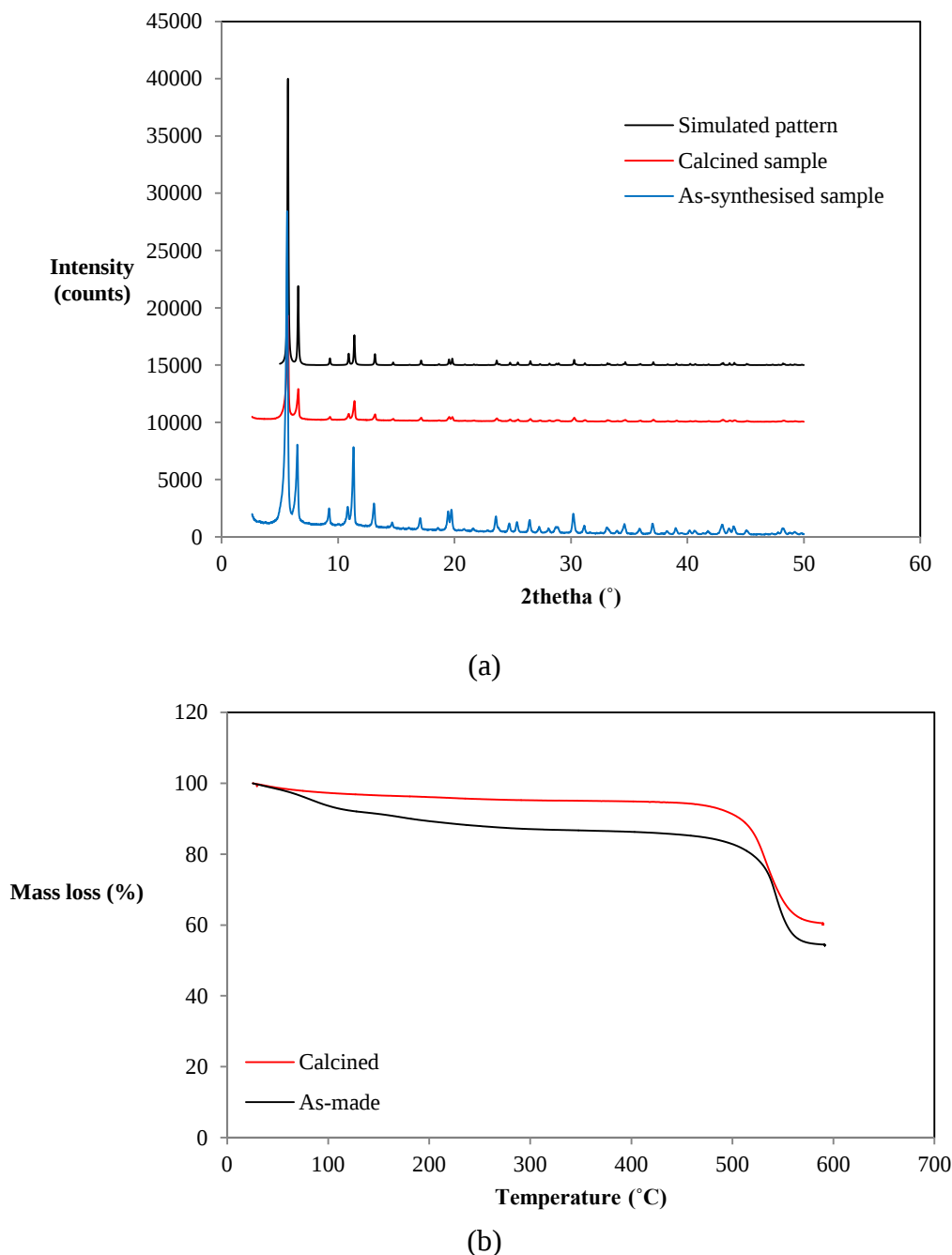


Figure 3.13 (a) The powder patterns of the as-synthesised $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{guest})$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{H}_2\text{O})$ (b) The TGA curves of the as-made $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{guest})$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{H}_2\text{O})$ collected under N_2 atmosphere and a heating of 5°C min^{-1} .

The TGA plots of the as-made $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{guest})$ and the $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}] \cdot (\text{H}_2\text{O})$ are shown in **Figure 3.13** (b). The calcined sample shows two mass losses. The first mass loss shows an infinitesimal gradual change over the temperature range of 100 - ~300 °C. This is due to the dehydroxylation process. It should be noted that the dehydroxylation process was not clearly evident in the TGA data due to the resolution of the equipment. The dehydroxylation process can be investigated by using high resolution TGA and is found to complete when reaching the temperature of ~300 °C.^[9] The second mass loss of 34.5 % starting ~450 °C corresponds to the departure of the bdc linker. This value is found to be lower than the calculated value of 58 %. The discrepancy might arise from incomplete decomposition of the bdc linkers or from missing bpdc linker in the framework as found in the case of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$.^[13]

3.3.1.2 *Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$*

The success of reticular synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(1,4\text{-ndc})_{12}]$ has been reported in 2010.^[15] However, the ndc linker involved in the framework was 1,4-naphthalenedicarboxylic acid. In this work, $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$ where the linker is 2,6-naphthalenedicarboxylic acid was attempted.

The molar ratio used in the synthesis was identical to that reported previously. All chemicals involved in the synthesis were used without further purification. $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$ was synthesised in a 20 ml Teflon-lined stainless steel autoclave by heating a mixture of ZrCl_4 (Lancaster Synthesis, 99 %, 0.204 g), H_2ndc (Sigma-Aldrich, 99 %, 0.1892 g) and DMF (Sigma-Aldrich, 99.8 %, 10 ml) at 120 °C for 24 hours. The powder product was recovered by filtration, washed with 20 ml of DMF followed by 20 ml of acetone. The product was dried overnight before calcining it at 300 °C for 6 hours.

The powder patterns of the as-made $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}] \cdot (\text{guest})$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}] \cdot (\text{H}_2\text{O})$ were collected and compared with the simulated pattern of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ as shown in **Figure 3.14** (a). It can be seen that the powder X-ray diffraction patterns of the products show remarkable similarity with the $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ topology and there were no other phases present in the

patterns which means a phase pure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$ has been made. It is worth mentioning that the reflections from $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}] \cdot (\text{guest})$ are shifted to the left when compared to those from $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ due to the larger unit cell of the $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}] \cdot (\text{guest})$ materials.

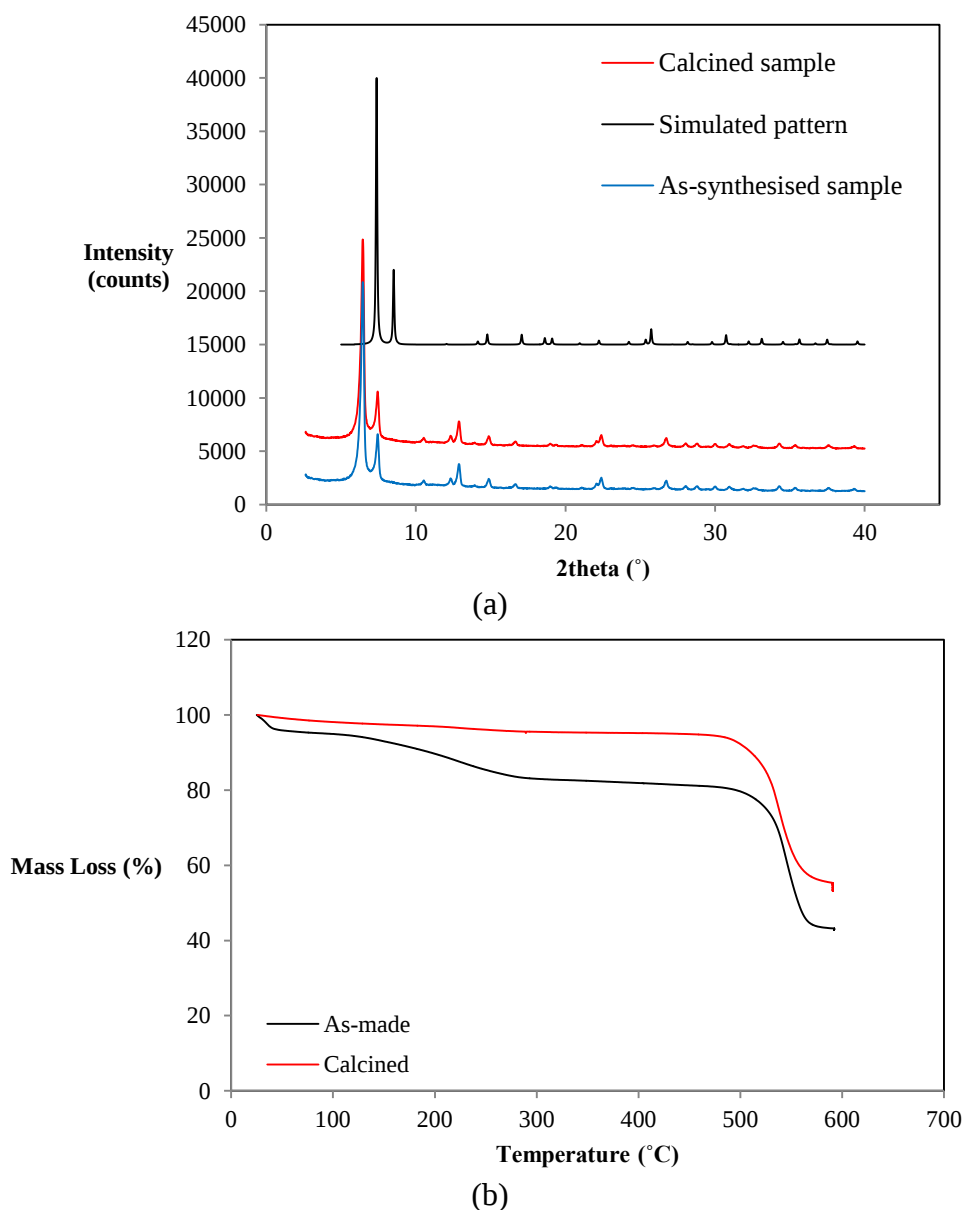


Figure 3.14 (a) The powder X-ray diffraction patterns of as-synthesised $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ndc})_{12}] \cdot \text{guest}$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}] \cdot (\text{H}_2\text{O})$ in comparison with the simulated pattern of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$. (b) The TGA curves of the as-made and calcined $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$ collecting under N_2 atmosphere, flowing rate of 5°C min^{-1} .

The TGA of the as-made sample shows two loss events. The first loss of about 16 % from 25 °C to ~280 °C is due to the loss of any guest molecules, such as DMF and water molecules. The second loss (~38 %) corresponds to the decomposition of the 2,6-ndc linker from the framework that leads to the framework collapse at ~440 °C. On the other hands, the TGA plot of the calcined sample shows two mass losses. The first mass loss shows an infinitesimal gradual change over the temperature range of 100 - ~300 °C. This is due to the dehydroxylation process. It should be noted that the dehydroxylation process was not clearly evident in the TGA data due to the resolution of the equipment. The dehydroxylation process can be investigated by using high resolution TGA and is found to complete when reaching the temperature of ~300 °C.^[9] The second loss of about 40.04 % at ~440 °C correspond to the decomposition of the 2,6-ndc linker from the framework.

3.3.2 Laboratory thermodiffraction study of [Zr₆O₆(bdc)₁₂], [Zr₆O₆(bpdc)₁₂] and [Zr₆O₆(2,6-ndc)₁₂]

The investigation of the thermoresponsive behaviour of [Zr₆O₆(bdc)₁₂], [Zr₆O₆(bpdc)₁₂] and [Zr₆O₆(2,6-ndc)₁₂] was performed using a laboratory-based powder X-ray diffractometer at the University of the Manchester. The investigation procedures were identical for all the three guest-free samples and involved an *in-situ* dehydroxylation process of the sample [Zr₆O₄(OH)₄(bdc)₁₂], [Zr₆O₄(OH)₄(bpdc)₁₂] and [Zr₆O₄(OH)₄(2,6-ndc)₁₂] under vacuum prior to data collection.

3.3.2.1 Data collection

The sample was ground before loading in the sample holder. The sample holder was then inserted into the XRK-900 furnace which was used as a heating

source. The incident X-ray beam was then properly aligned with respect to the sample stage prior to data collection.

The diffraction data were collected under vacuum of 2.11×10^{-5} mbar at 25 °C intervals from 25 °C – 400 °C. The sample was heated to 400 °C and left overnight before thermodiffraction data collection was begun. The temperature of 400 °C was chosen as it was assumed that the dehydroxylation process was complete and that no non-framework species were present inside the framework.

The data were collected upon cooling that means the data were collected from 400 °C to 25 °C with 25 °C intervals. The data were collected from 2° - 80° 2 θ , the step size used was 0.008° and the data collection time was 2 hours per temperature in order to do Le Bail fits at each temperature. In addition, the powder X-ray diffraction data at 300 °C were collected using different scan parameters in order to use this data for Rietveld refinement. The data were collected from 2° - 80° 2 θ , the step size used was 0.008° and the data collection time was 16 hours.

3.3.2.2 *Inspection of dehydroxylation process*

As discussed in section 3.2.2.2, the success of the dehydroxylation process can be indicated by an inspection of the intensity of the (220) reflection. This reflection occurs at 2 θ = 12.1°, 9.5° and 10.6° (if the incident beam wavelength is 1.54056 Å) for [Zr₆O₄(OH)₄(bdc)₁₂], [Zr₆O₄(OH)₄(bpdc)₁₂] and [Zr₆O₄(OH)₄(2,6-ndc)₁₂] respectively. This reflection was found to disappear after the sample of [Zr₆O₄(OH)₄(bdc)₁₂] was heated to 400 °C resulting in [Zr₆O₆(bdc)₁₂] as shown in **Figure 3.15**. In cases of [Zr₆O₆(bpdc)₁₂] and [Zr₆O₆(2,6-ndc)₁₂], this reflection is still present but its intensity decreases upon heating. In [Zr₆O₆(bdc)₁₂], the intensity of this reflection grew when the temperature was decreased below 100 °C. For [Zr₆O₆(bpdc)₁₂] and [Zr₆O₆(2,6-ndc)₁₂], the intensity of this reflection also increased as the temperature is decreased below 100 °C. Therefore, the powder X-ray diffraction patterns at 25 – 75 °C were excluded from the analysis. This was to

assure that only the dehydroxylated phase was being studied. The evolution of the (220) reflection of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ is shown in **Figure 3.16** and **Figure 3.17** respectively.

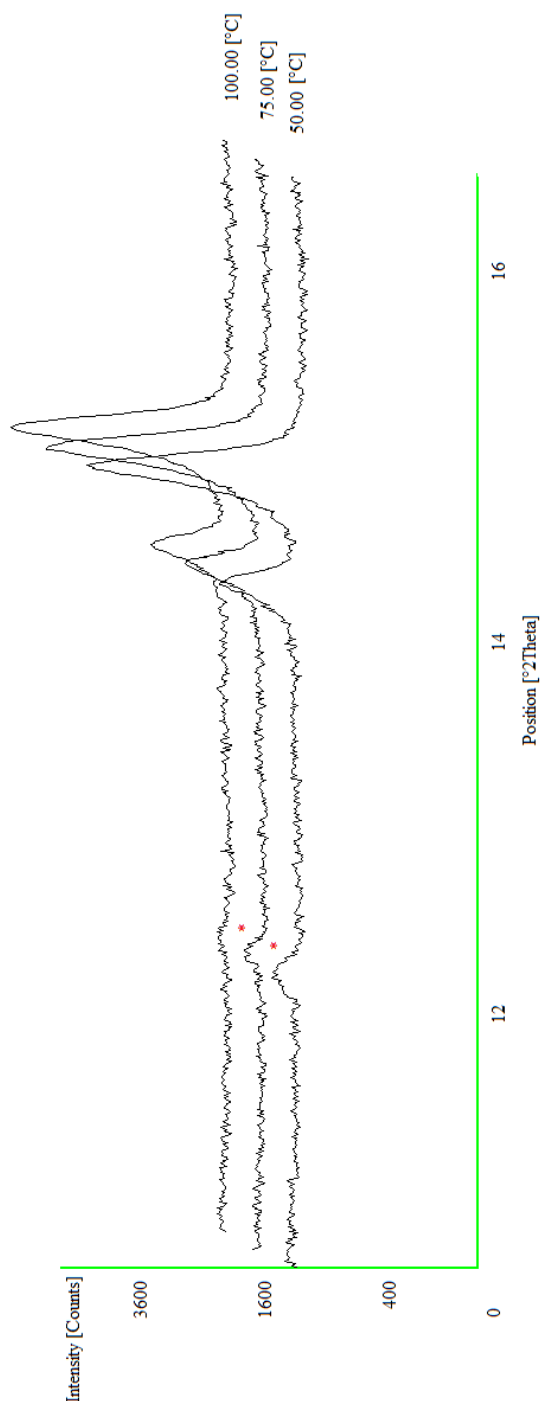


Figure 3.15 The powder X-ray thermodiffraction patterns of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$. The reflection at $2\theta = 12.1^\circ$ is marked by red asterisks.

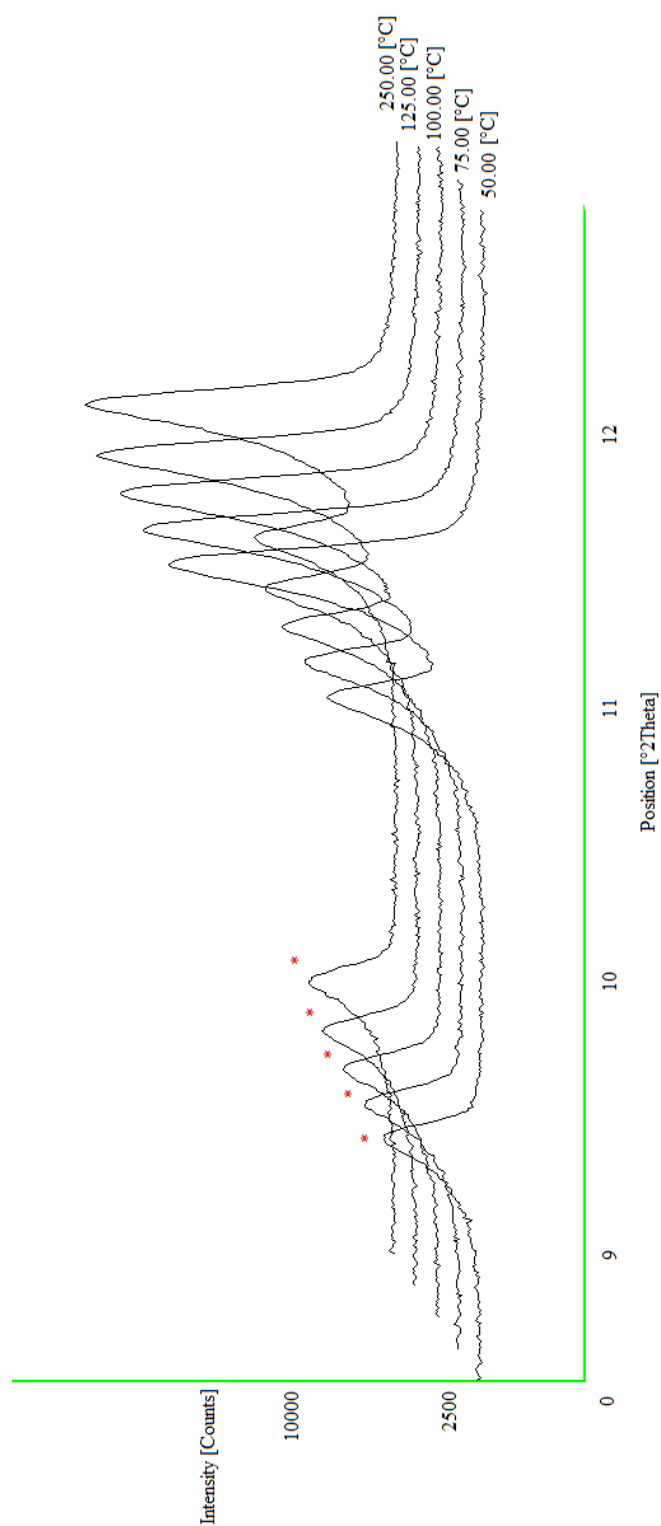


Figure 3.16 (a) The powder X-ray thermodiffraction patterns of $[\text{Zr}_6\text{O}_6(\text{bpdC})_{12}]$. The reflection at $2\theta = 9.5^\circ$ is marked by red asterisks.

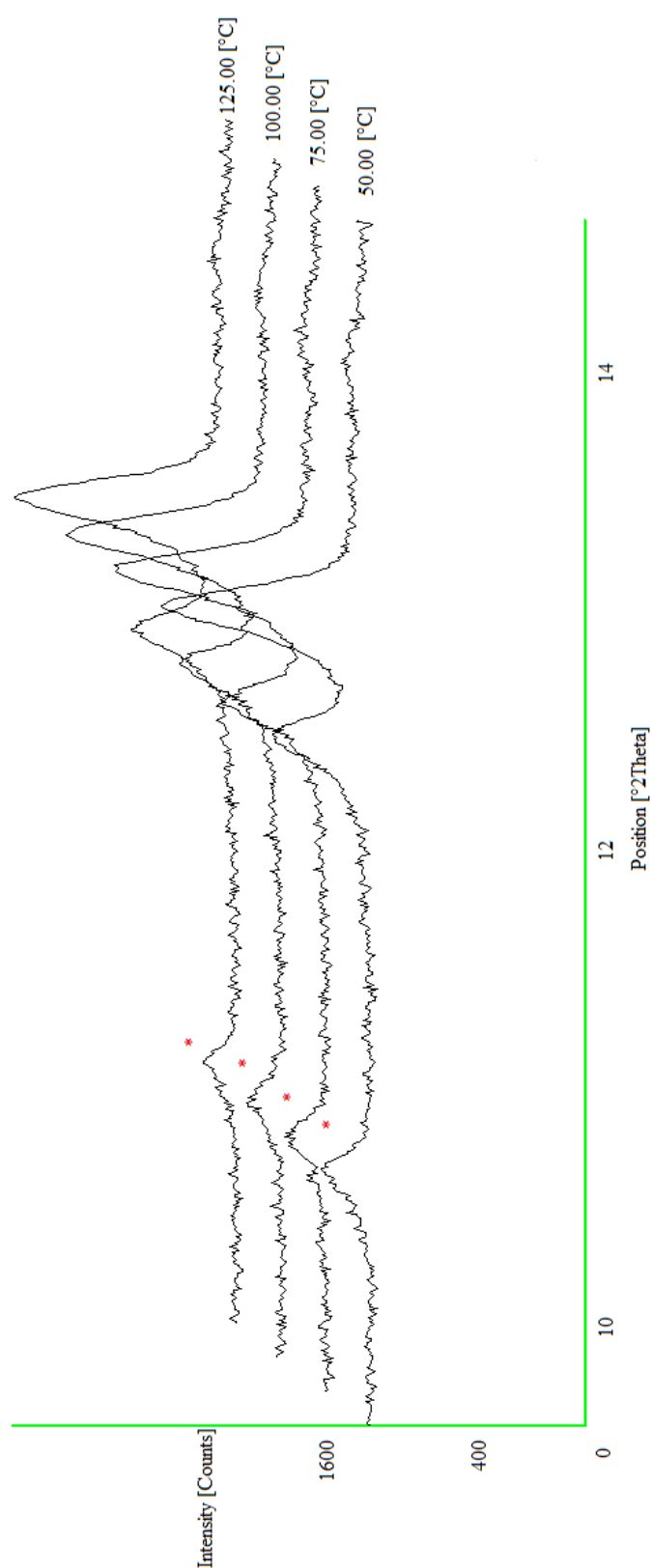


Figure 3.17 (a) The powder X-ray thermodiffraction patterns of $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$. The reflection at $2\theta = 10.6^\circ$ is marked by red asterisks.

3.3.2.3 Data analysis of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$

The data analysis of the three samples was done in the same manner. The Le Bail method was used to fit the unit cell parameters and profile coefficients to the powder X-ray diffraction data. The starting model used in the Le Bail fitting of the synchrotron powder X-ray diffraction of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ was taken from the literature (Cubic, $Fm\bar{3}m$, $a = 20.7004(2)$ Å).^[12]

The powder X-ray diffraction pattern at 25 °C, over the 2θ range of 2° - 80°, was fitted first with the first reflection excluded from the refinement. The background was manually fitted over the refining 2θ range. The instrumental parameters such as the zero point parameter, unit cell parameters, the correction parameters for peak shape asymmetry and the peak shape profile parameters were refined. A pseudo-Voigt function (profile option number 4 in the GSAS program) was chosen to fit the peak shape profile. This profile function accounts the effect of the crystallite size and microstrain broadening. For cubic materials, S400 and S220 are the refined parameter for the microstrain broadening. The diffraction patterns at 50 °C...400 °C were then fitted by the same manner as the diffraction pattern at 25 °C except that the zero point parameter obtained from the first refinement was kept constant and the shift parameter was refined instead.

Rietveld refinements were performed using the powder X-ray diffraction patterns of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ at 300 °C. For $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$, the structure refinement was not performed as the crystal structure of these materials have never been reported before. However, from the similarity of the TGA and thermodiffraction behaviour of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ to $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, they were assumed that the dehydroxylation process of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(2,6\text{-ndc})_{12}]$ were also successful.

The starting structural model used for the Rietveld refinement of the powder X-ray diffraction pattern of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ was taken from the literature.^[12] The difference between the hydroxylated phase and dehydroxylated phase is that the occupancy of the O3 oxygen atom is reduced from 1.0 in the hydroxylated phase to 0.75 in the dehydroxylated phase.^[13]

For $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, the Rietveld refinement was performed on 14250 observations. The final cycle of least-squares refinement comprised of 18 refined parameters including the scale factor, detector zero point, unit cell parameters, peak shape profile parameters, atomic coordinates and isotropic atomic displacement parameters of all six atoms in the asymmetric unit. The isotropic thermal parameters (U_{iso}) of the O atoms were constrained to have the same value, as were those of the C atoms.

The final observed, calculated and difference plot for Rietveld refinement of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ is shown in **Figure 3.18**. The crystallographic data of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ at 573 K are summarized in **Table 3.8**. The final atomic coordinates, occupancies and isotropic atomic displacement parameters of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ is given in **Table 3.9**. Bond lengths and bond angles of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ is given in **Table 3.10**. The asymmetric unit and the crystal structure $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ are shown **Figure 3.19** (a) and (b). This is a representative final result and all the refinements of all data sets are given in the attached appendix of the CD.

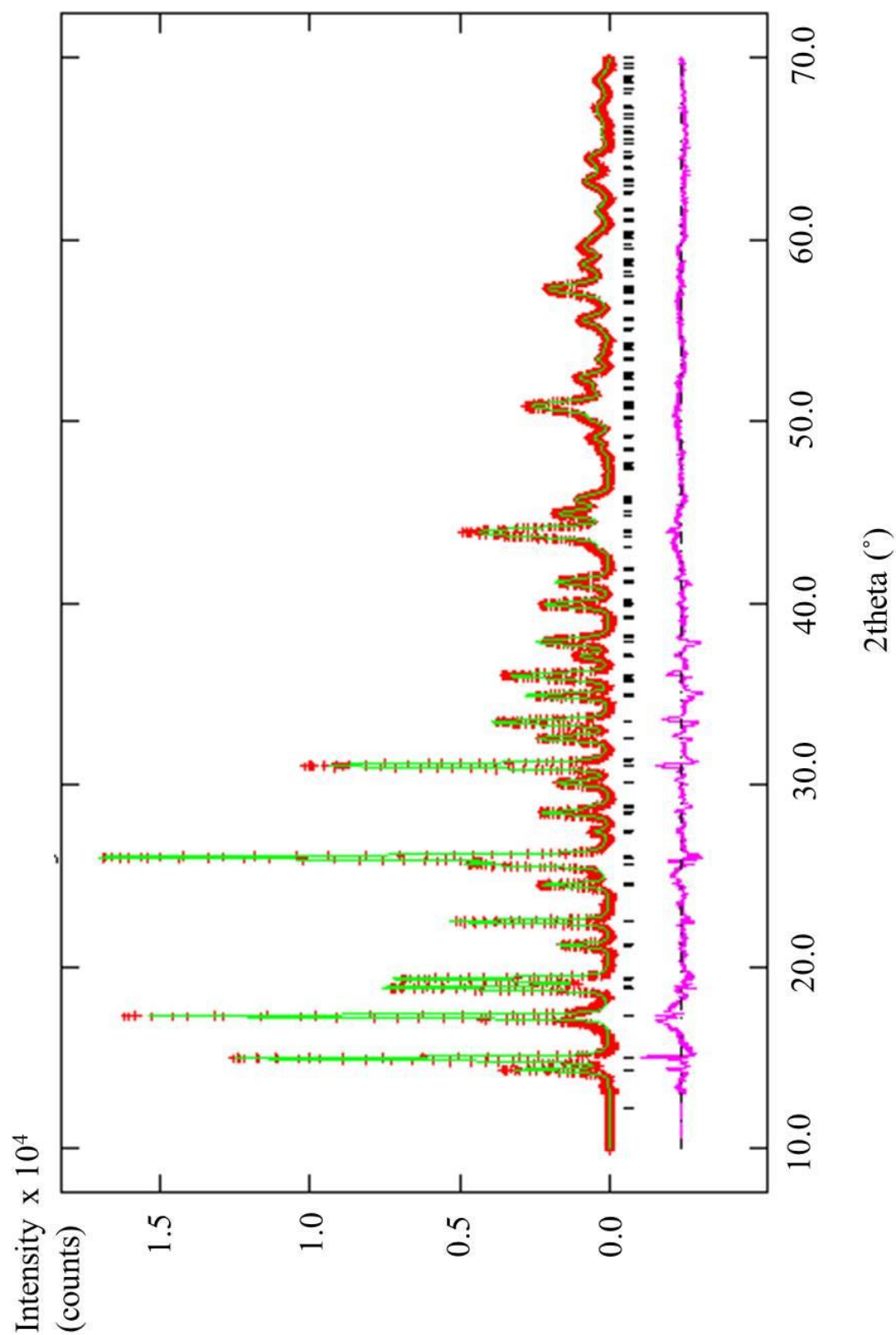


Figure 3.18 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Rietveld refinement of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$. The black tick marks are the calculated 2θ angles for the Bragg peaks.

Table 3.8 Crystal data and structure refinement parameters for [Zr₆O₆(bdc)₁₂] at 573 K

Formula	Zr ₂₄ O ₁₁₄ C ₁₉₂ H ₈₄
Formula weight	6415.272
Density (gcm ⁻³)	1.216
Temperature (K)	573
Wavelength (Å)	K _{α1} = 1.54056, K _{α2} = 1.54439
Space group	<i>Fm</i> $\bar{3}m$
a (Å)	20.6143(1)
V (Å ³)	8759.9(1)
Z	1
R _p	0.0281
R _{wp}	0.0366
R _F	0.0663
χ ²	5.033
Number of refined parameters	18
Scale factor	32.49(8)
Zero point (°)	0.06333
Shift (°)	-0.00725(8)
Gaussian profile coefficients	GU = 1058(45), GV = -97(20), GW = -8(2)
Lorentzian profile coefficients	LX = 7.57(8)
Eta	0
Microstrain broadening coefficients	S400 = 0, S220 = 0.0057(1)

Table 3.9 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ at 573 K

Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Zr	0.12070(5)	0.0	0.0	0.0334(3)	1
O2	0.1718(1)	0.0	0.09367(1)	0.05(1)	1
O3	0.05334(1)	-0.05337(1)	-0.0533(1)	0.05(1)	0.75
C4	0.1477(3)	0.0	-0.1477(3)	0.096(2)	1
C5	0.2065(3)	0.0	0.2065(3)	0.096(2)	1
C6	0.2640(2)	0.0	0.1832(2)	0.096(2)	1

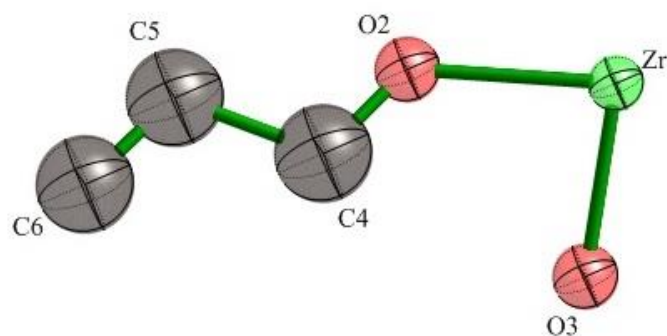
Table 3.10 Bond lengths ($\text{\AA}$) and bond angles ($^\circ$) for $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ at 573 K

Zr—O2	2.199(2)	O2 ⁵ —Zr—O2 ⁷	76.76(6)
Zr—O3	2.085(1)	O2 ⁵ —Zr—O3	81.68(9)
O2—C4 ⁵	1.219 (3)	O2 ⁵ —Zr—O3 ⁵	141.44(4)
C4—O2 ⁵	1.219(3)	O2 ⁵ —Zr—O3 ⁷	81.68(9)
C4—C5 ⁵	1.714(7)	O2 ⁵ —Zr—O3 ⁹	141.44(4)
C5—C6	1.279(4)	O2 ⁶ —Zr—O2 ⁷	122.8(1)
C6—C6 ¹²	1.541(7)	O2 ⁶ —Zr—O3	141.44(4)
		O2 ⁶ —Zr—O3 ⁵	141.44(4)
O2—Zr—O2 ⁵	122.8(1)	O3 ⁵ —Zr—O3 ⁹	63.7(1)
O2—Zr—O2 ⁶	76.76(6)	O3 ⁸ —Zr—O3 ⁹	63.7(1)
O2—Zr—O2 ⁷	76.76(6)	Zr—O2—C4 ⁵	127.4(4)
O2—Zr—O3	141.44(4)	Zr—O3—Zr ³	115.09(8)
O2—Zr—O3 ⁵	81.68(9)	Zr—O3—Zr ⁴	115.09(8)
O2—Zr—O3 ⁸	141.44(4)	Zr ³ —O3—Zr ⁴	115.09(8)
O2—Zr—O3 ⁹	81.68(9)	O2 ⁵ —C4—O2 ¹⁰	138.0(8)
O2 ⁵ —Zr—O2 ⁶	76.76(6)	O2 ⁵ —C4—C5 ⁵	111.0(4)
O2 ⁶ —Zr—O3 ⁸	81.68(9)	O2 ¹⁰ —C4—C5 ¹⁰	111.0(4)

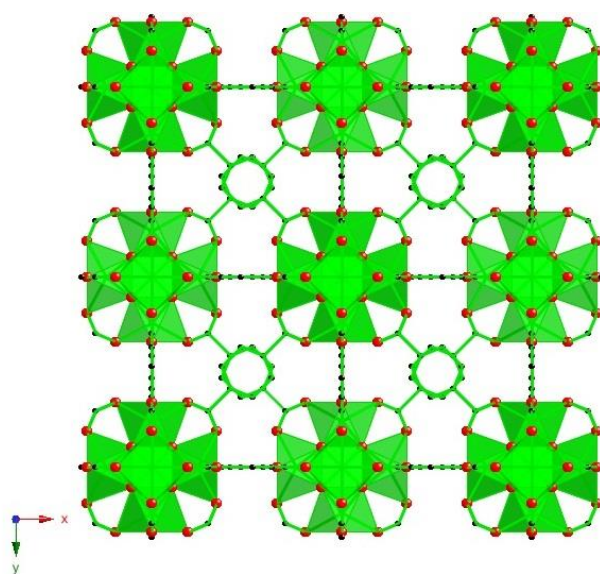
O2 ⁶ —Zr—O3 ⁹	81.68(9)	C4 ⁵ —C5—C6	112.9(5)
O2 ⁷ —Zr—O3	81.68(9)	C4 ^v —C5—C6 ¹¹	112.9(5)
O2 ⁷ —Zr—O3 ⁵	81.68(9)	C6—C5—C6 ¹¹	134.1(1)
O2 ⁷ —Zr—O3 ⁸	141.44(4)	C5—C6—C6 ¹²	112.9(5)
O2 ⁷ —Zr—O3 ⁹	141.44(4)		
O3—Zr—O3 ⁵	63.7(1)		
O3—Zr—O3 ⁸	63.7(1)		
O3—Zr—O3 ⁹	96.5(2)		
O3 ⁵ —Zr—O3 ⁸	96.5(2)		

Symmetry transformations used to generate equivalent atoms:

(1) z, x, y; (2) y, z, x; (3) y, -z, -x; (4) -z, -x, y; (5) x, y, -z; (6) x, z, y; (7) x, -z, y; (8) -z, x, y; (9) -z, x, -y; (10) z, -y, -x; (11) z, y, x; (12) -z+1/2, y, -x+1/2.



(a)



(b)

Figure 3.19 (a) The asymmetric unit of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ (b) The structure of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ viewed along the $[100]$ direction.

3.3.2.4 Data analysis of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$

The starting model used in the Le Bail fitting of the synchrotron powder X-ray diffraction of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ was taken from the literature (Cubic, $Fm\bar{3}m$, $a = 27.0027(1) \text{ \AA}$).^[12] The powder X-ray diffraction pattern at 25°C , over the 2θ range of $2^\circ - 80^\circ$, was fitted first with the first reflection excluded from the refinement. The background was manually fitted over the refining 2θ range. The instrumental parameter such as zero point parameter, unit cell parameters, the

correction parameters for peak shape asymmetry and the peak-shaped profile parameters were refined. A pseudo-Voigt function was chosen to fit the peak shape profile. This profile function accounts the effect of the microstrain broadening. For cubic materials, S400 and S220 are the refined parameter for the microstrain broadening. The diffraction patterns at 50 °C...400 °C were then fitted by the same manner as the diffraction pattern at 25 °C except that the zero point parameter obtained from the first refinement was kept constant and the shift parameter was refined instead.

The final cycle of the Le Bail fitting included the detector zero point, the unit cell parameters and the peak shape profile coefficients. The final observed, calculated and difference plot for Le Bail fitting of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ is shown in **Figure 3.20**. The refined parameters for the Le Bail fitting at 573 K are summarized in **Table 3.11**. This is a representative final result and all the fitting of all data sets are given in the attached appendix of the CD.

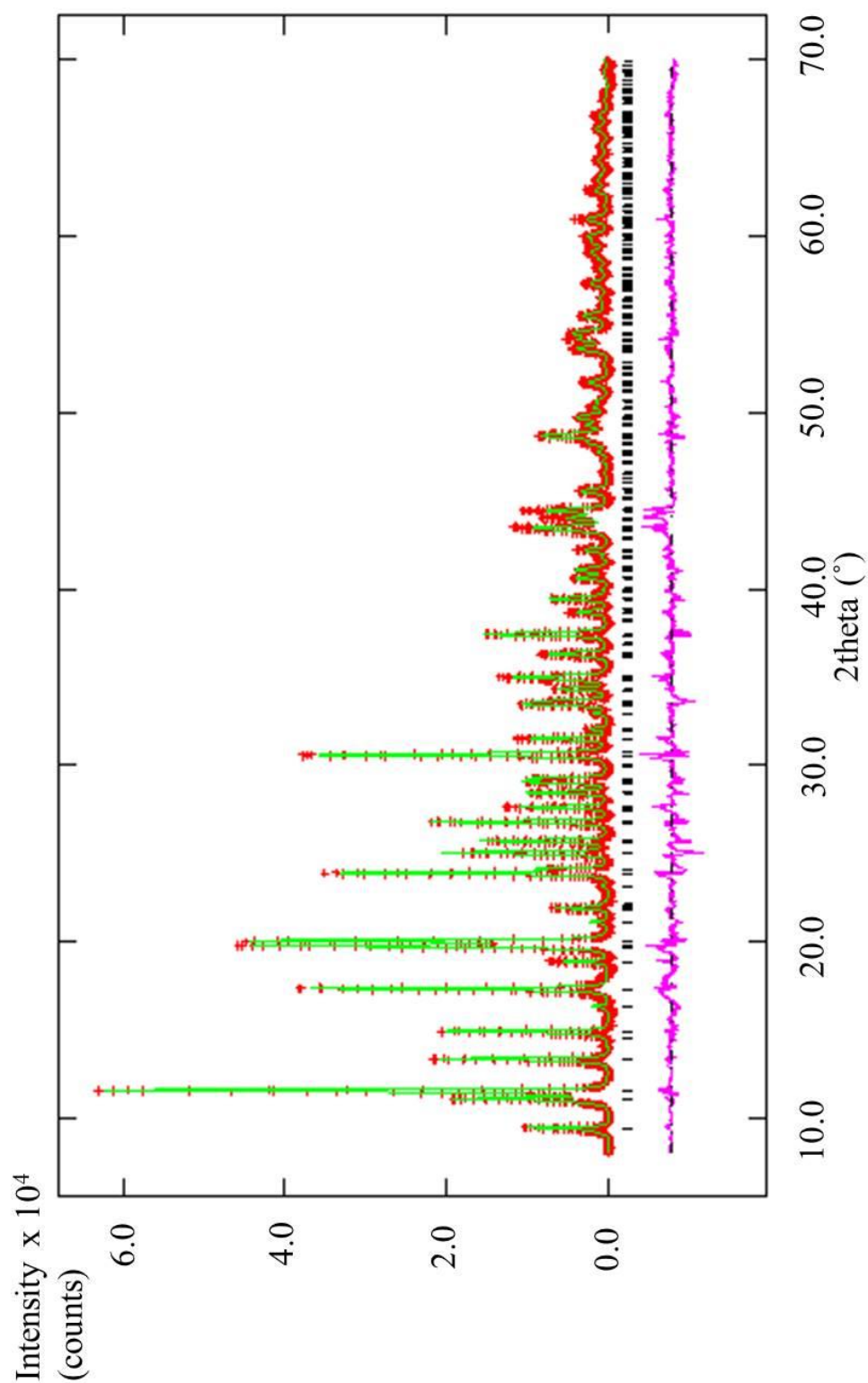


Figure 3.20 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Le Bail fitting of $[\text{Zr}_6\text{O}_6(\text{bpdC})_{12}]$ at 573 K. The black tick marks are the calculated 2θ angles for the Bragg peaks. The plot is scaled by 4x over the 2θ range of $14^\circ - 70^\circ$.

Table 3.11 Crystal data and structure refinement parameters for [Zr₆O₆(bpdC)₁₂] at 573 K

Temperature (K)	573
Wavelength (Å)	K _{α1} = 1.54056, K _{α2} = 1.54439
Space group	<i>Fm3̄m</i>
a (Å)	26.6733(2)
V (Å ³)	18977.0(5)
R _p	0.0282
wR _p	0.0370
χ ²	4.669
Number of refined parameters	6
Zero point (°)	0.00017
Shift (°)	-0.0818(2)
Gaussian profile coefficients	GU = 0, GV = 0, GW = 10.1(1)
Lorentzian profile coefficients	LX = 0
Asymmetric peak profile coefficient	S/L = 0.0307(0), H/L = 0.0.0231(0)
Eta	0.656(5)
Microstrain broadening coefficients	S400 = 0.0025(3), S220 = 0.0014(4)

3.3.2.5 Data analysis of [Zr₆O₆(2,6-ndc)₁₂]

For the Le Bail fitting of [Zr₆O₆(2,6-ndc)₁₂], the X-ray powder diffraction pattern of [Zr₆O₆(2,6-ndc)₁₂] at 25 °C was fitted using the unit cell parameters of [Zr₆O₆(bdc)₁₂]. The first two reflections were excluded from the powder X-ray diffraction pattern and the background over the observed 2θ range was manually fitted. The instrumental parameter such as zero point parameter, unit cell parameters, the correction parameters for peak shape asymmetry and the peak shape profile parameters were refined. A pseudo-Voigt function was chosen to fit

the peak shape profile. This profile function accounts for the effect of the microstrain broadening. For cubic materials, S400 and S220 are the refined parameter for the microstrain broadening. The unit cell parameters of $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ was $a = 23.8002(1) \text{ \AA}$. The obtained unit cell parameters of $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ at 25°C were then used for the Le Bail fitting of the powder X-ray diffraction patterns collected at the other temperatures. The diffraction patterns at $50^\circ\text{C} \dots 400^\circ\text{C}$ were then fitted by the same manner as the diffraction pattern at 25°C except that the zero point parameter obtained from the first refinement was kept constant and the shift parameter was refined instead.

The final cycle of the Le Bail fitting included the detector zero point, the unit cell parameters and the peak shape profile coefficients. The final observed, calculated and difference plot for Le Bail fitting is shown in **Figure 3.21**. The refined parameters for the Le Bail fitting at 573 K are summarised in **Table 3.12**. This is a representative final result and all the refinements of all data sets are given in the attached appendix of the CD.

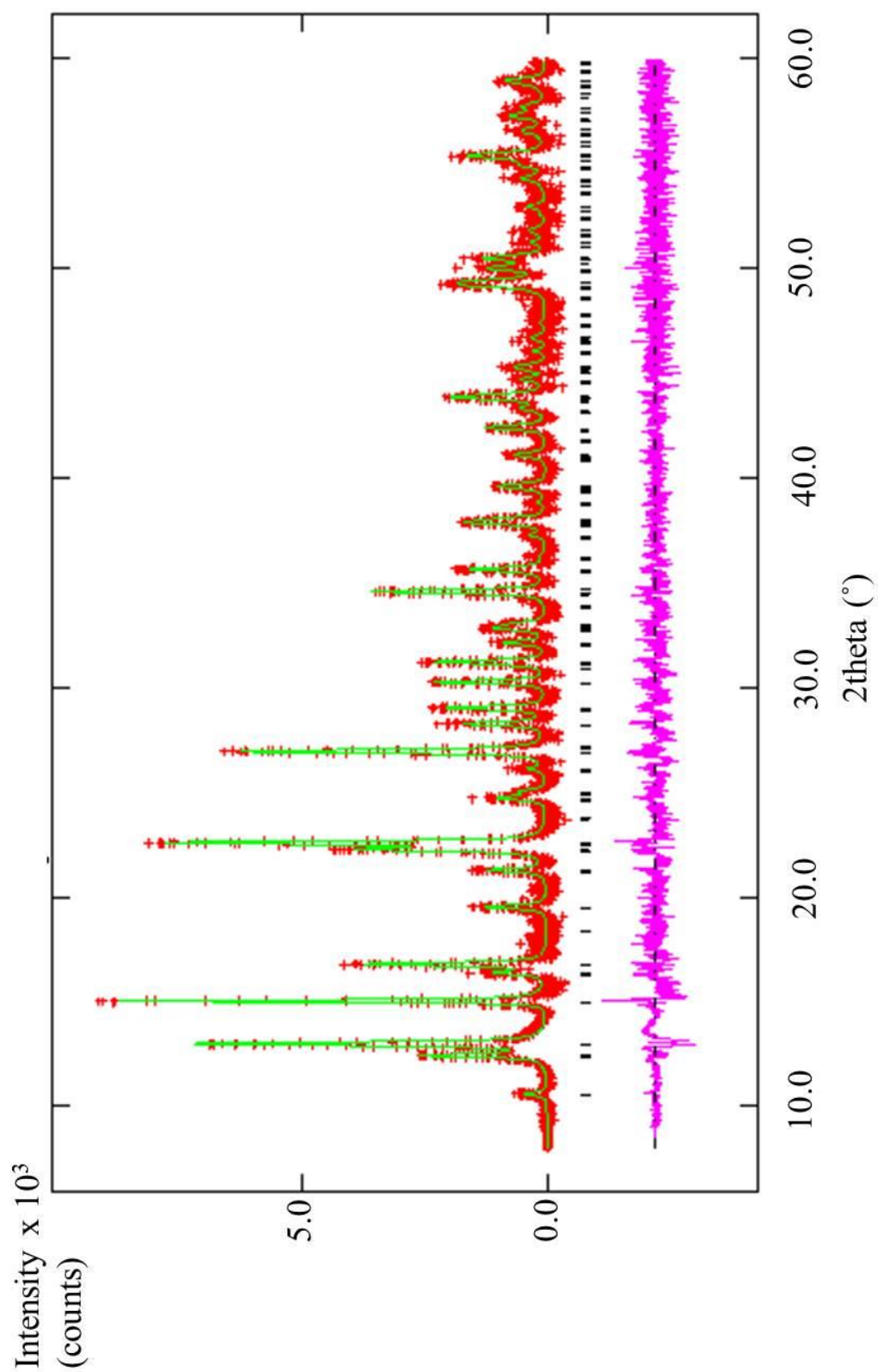


Figure 3.21 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Le Bail fitting of $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ at 573 K. The black tick marks are the calculated 2θ angles for the Bragg peaks. The plot is scaled by 3x and 5x over the 2θ range of $15^\circ - 45^\circ$ and $45^\circ - 60^\circ$ respectively.

Table 3.12 Crystal data and structure refinement parameters for $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ at 573 K

Temperature (K)	573
Wavelength ($\text{\AA}$)	$K_{a1} = 1.54056$, $K_{a2} = 1.54439$
Space group	$Fm\bar{3}m$
a ($\text{\AA}$)	23.6583(5)
V ($\text{\AA}^3$)	13242.0(9)
R_p	0.0206
R_{wp}	0.0270
χ^2	1.503
Number of refined parameters	6
Zero point	0.00198
Shift	-0.00512(5)
Gaussian profile coefficients	GU = 0, GV = -22(4), GW = 27(9)
Lorentzian profile coefficients	LX = 11.2(1)
Eta	0
Microstrain broadening coefficients	S400 = 0, S220 = 0.0021(1)

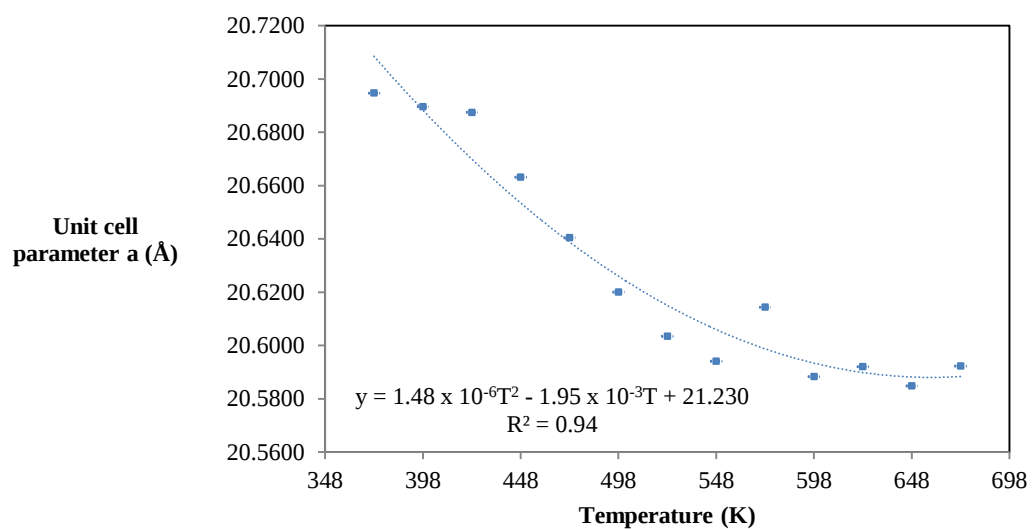
3.3.3 Results and discussion

The unit cell parameter and the unit cell volume of the three candidate materials are listed in **Table 3.13**. The variation of the unit cell parameter and the unit cell volume as a function of temperature are shown in **Figure 3.22**.

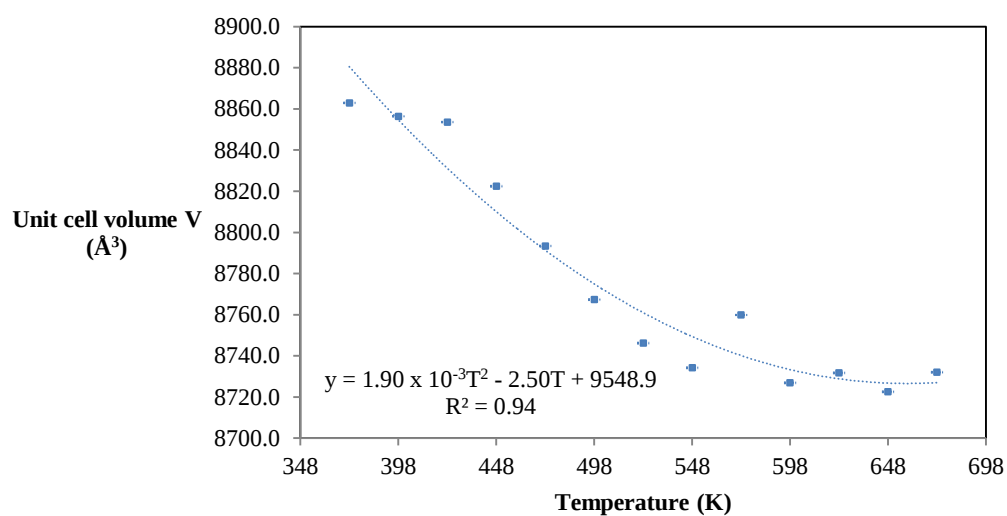
Table 3.13 Unit cell dimensions a (Å), unit cell volume V (Å³), goodness of fit (χ^2), R_{wp} and R_p for [Zr₆O₆(bdc)₁₂], [Zr₆O₆(bpdc)₁₂] and [Zr₆O₆(2,6-ndc)₁₂] from 373 – 673 K.

Temperature (K)	a	V	χ^2	R_p	R_{wp}
[Zr₆O₆(bdc)₁₂]					
373	20.6947(1)	8862.9(2)	1.127	0.031	0.040
398	20.6896(1)	8856.4(2)	1.133	0.031	0.040
423	20.6874(1)	8853.6(2)	1.087	0.031	0.040
438	20.6631(1)	8822.4(2)	1.034	0.030	0.039
473	20.6404(2)	8793.4(2)	0.997	0.029	0.038
498	20.6200(2)	8767.3(2)	1.209	0.032	0.042
523	20.6034(2)	8746.1(2)	1.207	0.030	0.038
548	20.5941(2)	8734.2(2)	1.044	0.030	0.039
573	20.6143(1)	8759.9(1)	5.033	0.028	0.037
598	20.5883(2)	8726.9(2)	1.084	0.030	0.039
623	20.5921(2)	8731.7(2)	0.949	0.029	0.037
648	20.5848(2)	8722.5(2)	1.000	0.030	0.038
673	20.5923(2)	8732.0(2)	0.984	0.029	0.038
[Zr₆O₆(bpdc)₁₂]					
373	26.7906(2)	19228.6(4)	1.693	0.0349	0.044
398	26.7802(2)	19206.2(4)	1.678	0.0346	0.044
423	26.7666(2)	19176.8(4)	1.741	0.0350	0.045
438	26.7458(2)	19132.3(4)	1.871	0.0362	0.047
473	26.7009(2)	19036.0(4)	1.733	0.0347	0.045
498	26.6774(2)	18985.9(4)	1.574	0.0334	0.043
523	26.6622(2)	18953.4(4)	1.656	0.0344	0.044
548	26.6596(2)	18947.9(4)	1.293	0.0303	0.039
573	26.6733(2)	18977.0(5)	4.699	0.0282	0.037
598	26.6529(2)	18933.5(4)	1.385	0.0314	0.041

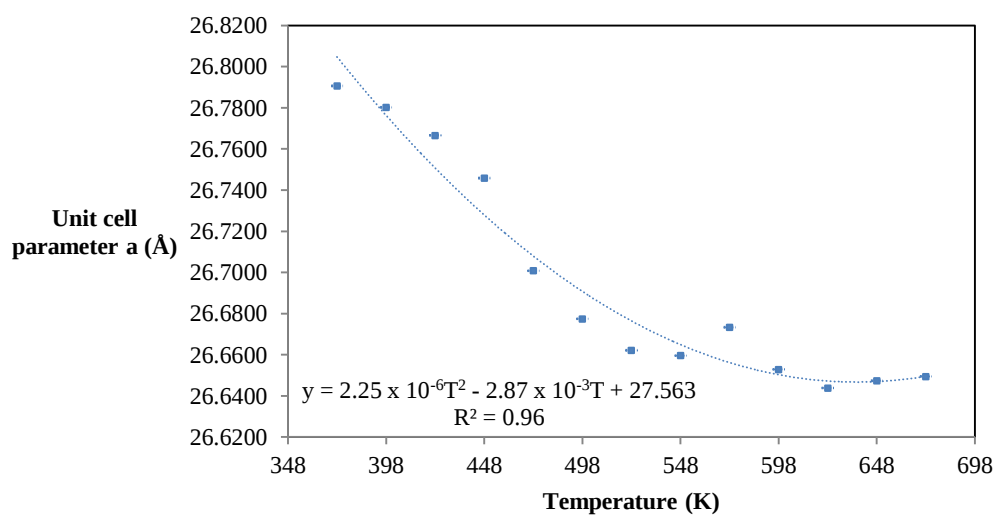
623	26.6438(2)	18914.2(4)	1.344	0.0312	0.040
648	26.6474(2)	18921.8(4)	1.309	0.0306	0.039
673	26.6495(2)	18926.3(4)	1.541	0.0336	0.042
[Zr₆O₆(2,6-ndc)₁₂]					
373	23.7821(5)	13450.9(8)	1.255	0.035	0.045
398	23.7806(5)	13448.3(8)	1.180	0.034	0.044
423	23.7662(5)	13424.0(8)	1.140	0.033	0.042
438	23.7405(4)	13380.5(7)	0.992	0.032	0.040
473	23.7116(4)	13331.7(7)	0.934	0.031	0.039
498	23.6830(4)	13283.5(7)	0.924	0.031	0.039
523	23.6661(4)	13255.0(7)	0.887	0.030	0.038
548	23.6614(5)	13247.1(8)	0.919	0.030	0.038
573	23.6583(5)	13242.0(9)	1.503	0.021	0.027
598	23.6567(3)	13239.3(8)	0.851	0.029	0.037
623	23.6519(5)	13231.2(8)	0.921	0.030	0.038
648	23.6497(5)	13227.5(8)	0.931	0.030	0.039
673	23.6407(5)	13212.3(9)	0.942	0.031	0.039



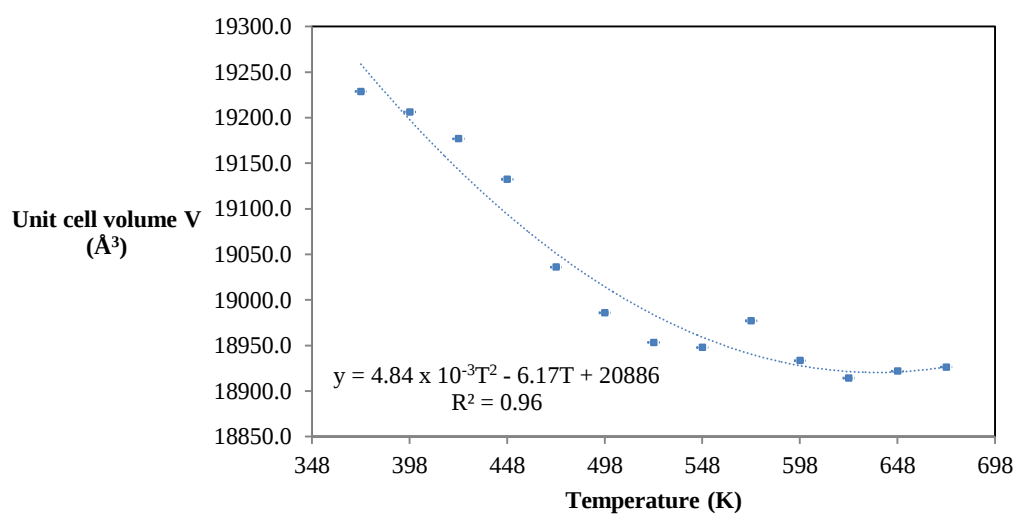
(a)



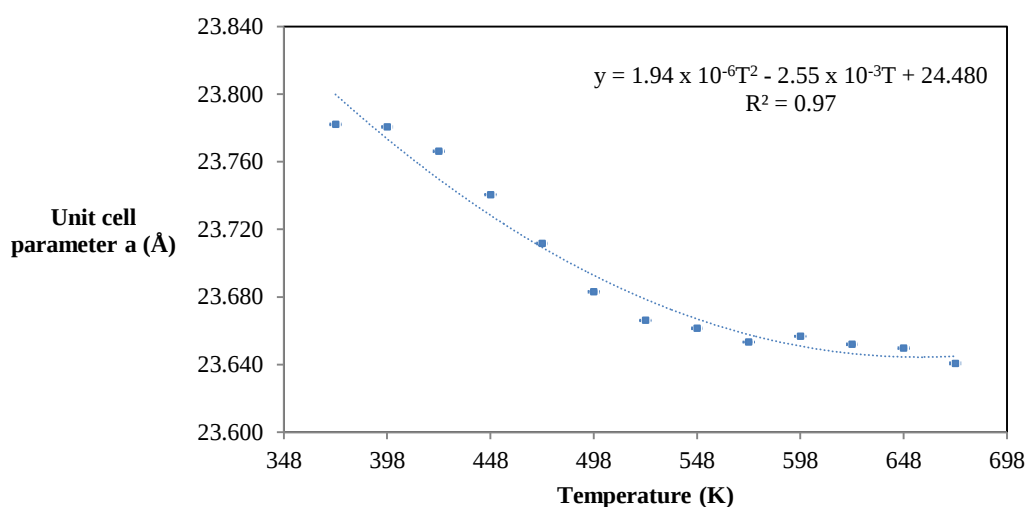
(b)



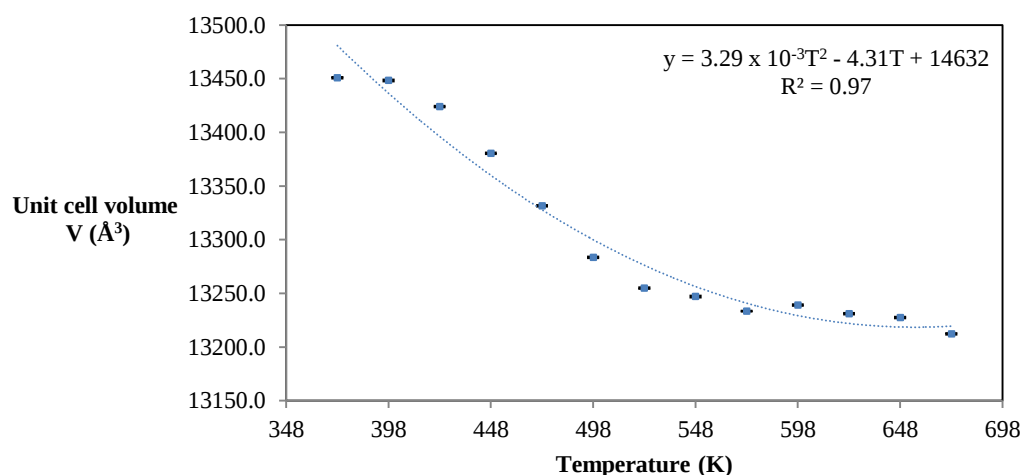
(c)



(d)



(e)



(f)

Figure 3.22 The temperature dependence of (a) the unit cell parameter a of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, (b) the unit cell volume V of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, (c) the unit cell parameter a of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$, (d) the unit cell volume V of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$, (e) the unit cell parameter a of $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ and (f) the unit cell volume of $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$. The estimate standard deviations are superimposed on data point markers.

$[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ show negative thermal expansion over the entire temperature range studied, 373 – 673 K. The polynomial function, as shown in Equation 3.1 is used to represent the temperature dependence of the unit cell parameter and the overall volume contraction of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$. The

coefficient of thermal expansion is calculated using the expression provided in the Equation 3.2. The resulting coefficients are summarised in **Table 3.14**.

$$p = p_0 + p_1T + p_2T^2 \quad \text{Equation 3.1}$$

$$\alpha = \frac{(p_1 + 2p_2T)}{p} \quad \text{Equation 3.2}$$

Table 3.14 The resulting coefficients of the polynomial function of thermal behaviour of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$.

Cell parameter	p_0	p_1	p_2
$[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$			
a	21.230	-1.95×10^{-3}	1.48×10^{-6}
V	9548.9	-2.50	1.90×10^{-3}
$[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$			
a	27.563	-2.87×10^{-3}	2.25×10^{-6}
V	20886	-6.17	4.84×10^{-3}
$[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$			
a	24.4804	-2.55×10^{-3}	1.94×10^{-6}
V	14631.5	-4.31	3.29×10^{-3}

The volumetric coefficient of thermal expansion α_V at each temperature of all three candidate materials are summarised in **Table 3.15** and the variation of these coefficients as a function of temperature are shown in **Figure 3.23**.

Table 3.15 The volumetric coefficients of thermal expansion ($\alpha_V \times 10^{-5} \text{ K}^{-1}$) of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ at each temperature.

Temperature (K)	$[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$	$[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$	$[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$
373	-12.21	-13.31	-13.80
398	-11.15	-12.07	-12.58
423	-10.08	-10.82	-11.37
438	-9.47	-10.09	-10.67
473	-7.99	-8.36	-8.98
498	-6.93	-7.11	-7.78
523	-5.86	-5.84	-6.56
548	-4.78	-4.57	-5.32
573	-3.68	-3.29	-4.078
598	-2.61	-2.01	-2.83
623	-1.52	-0.74	-1.59
648	-0.43	0.54	-0.35
673	0.66	1.82	0.90

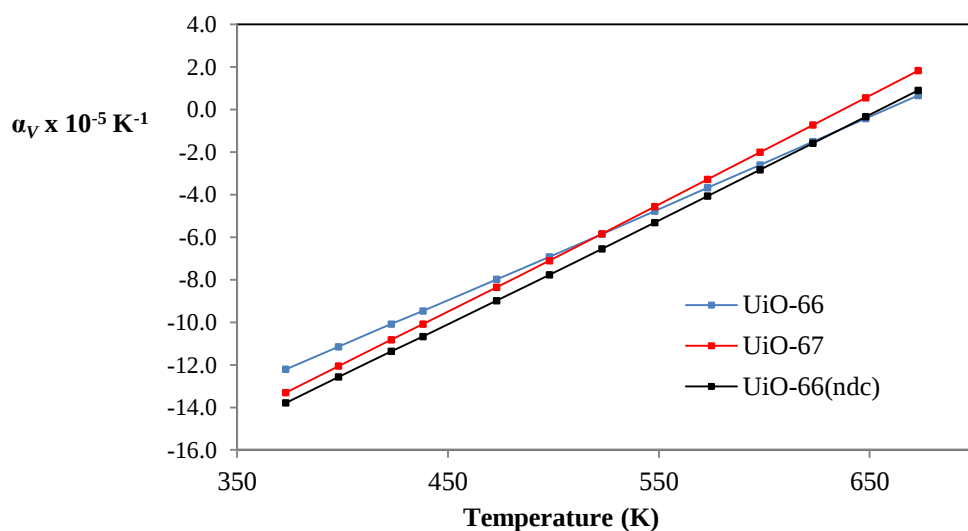


Figure 3.23 The variation of the volumetric coefficient of thermal expansion of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ denoted UiO-66, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ denoted UiO-67 and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ denoted UiO-66 (ndc) as a function of temperature.

Figure 3.23 indicates that $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ has the greatest magnitude of the coefficient of thermal contraction over the entire range of the temperature studied. While the coefficient of $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ is greater than $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ over the temperature range of 373 – 523 K and is found to be smaller than that of $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ over the remaining temperature range. The expansivity coefficients of all three materials are found to be larger than that observed in MOF-5 (α_V at 376 K = $-39.3(1) \times 10^{-6} \text{ K}^{-1}$).^[16] If comparing the magnitude of contraction at ~ 373 K between $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ and MOF-5, both of which contain the bdc linkers, it is evident that $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ has a greater magnitude of contraction by ~ 3.30 times. This might possibly due to the greater amount of contraction at the Zr_6O_6 inorganic cluster as the size of this cluster is bigger than the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster of MOF-5.

The variation of the coefficient of thermal contraction of the three materials having isorecticular topology but containing different dicarboxylate linker length is found to partially depend on the organic linker length. The linker length if measured from the carbon atom of the carboxylate group to the carbon atom of the carboxylate group at the other end has a trend as follows: bdc ($\sim 6 \text{ \AA}$) < ndc ($\sim 8 \text{ \AA}$) < bpdc ($\sim 10 \text{ \AA}$) while the trend of the coefficient of thermal contraction is $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}] \leq [\text{Zr}_6\text{O}_6(\text{bpdc})_{12}] < [\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$. This result is not quite in accordance to the trend that has been predicted for the IRMOF members whose magnitude of contraction was predicted to be directly dependent on the linker length.^[17] In this work, it is more likely that the effect of the organic linker on the coefficient of thermal contraction is dependent on the intrinsic nature of such a linker rather than only the linker length. The greater magnitude of contraction in $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ therefore might arise from some other possible transverse vibrational modes such as an out of plane butterfly mode and an out of plane chair modes as shown in **Figure 3.24**.

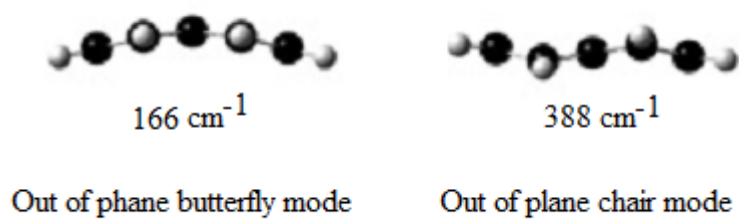


Figure 3.24 Schematic illustration of the possible vibrational modes of the 2,6-ndc linker.^[18]

However, the organic linker species are found to have a small effect on the magnitude of the coefficient of thermal expansion when compared to the effect of the inorganic cluster on this coefficient.

3.4 Conclusion

In this work, a new family of MOFs containing zero-dimensional inorganic clusters, $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$ and its isoreticular members: $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ has been revealed to show negative thermal expansion over a selection of temperature ranges. The presence of a different inorganic cluster, but an identical linker is found to have a profound effect on the thermoresponsive behaviour of such a material as the decrease in size of the inorganic cluster is found to be the main contributor to the thermal contraction. This means the size of the inorganic cluster dominates the NTE behaviour in these materials. In the case of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, the presence of three coordination sphere oxygen atom stiffens the inorganic cluster and inherently inhibits any possible rocking mode of the polyhedra. The twisting motion of the carboxylate groups of the bdc linker is found to play a major role in introducing the rocking motion of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster resulting in an apparent decrease in size of this cluster.

The nature of the organic linker is also found to have an effect on the thermal behaviour of the materials although their effect is small when compared to the effect of the inorganic cluster on the thermal behaviour. The magnitude of the coefficient of thermal expansion is dependent on the intrinsic nature of the linker rather than the linker length as has been predicted by molecular simulation.^[4]

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4. Thermoresponsive behaviour of the MIL-53 family

4.1 Introduction

The MIL-53 family is one of the most well-known MOF families because of its distinctive properties, one of which is its framework “breathing effect”. Their members have been studied widely both experimentally and theoretically with much focus on their behaviour toward external stimuli such as heat,^[1] pressure^[1-2] and various types of guest molecules.^[3-4] Owing to their interesting properties, they have been tested for use in many applications such as gas adsorption,^[5-15] gas separation,^[16-17] gas storage,^[18] catalysis,^[19-20] drug delivery,^[21] and as electrode materials.^[22]

To date, there are nine members within the MIL-53 family which adopt a similar structure. Their three-dimensional framework contains a one-dimensional diamond-shaped channel which consists of chains of trans-corner sharing infinite chain of MO_4X_2 octahedra cross-linked by the organic linker 1, 4-benzenedicarboxylate anion (bdc). As shown in **Figure 4.1**, the chain of octahedra is made from corner-sharing metal centred octahedra linked in a zigzag fashion with four infinite chains of octahedra being connected by bdc molecules to generate a channel running along the crystallographic x axis. Accessibility along the y and z axes is generally not possible since adjacent bdc molecules form a non-permeable wall at ambient conditions. The general chemical formula of the members of this family is $[\text{MX}(\text{bdc})]\cdot\text{guest molecule}$ where M is V^{4+} , V^{3+} , Cr^{3+} , Al^{3+} , Ga^{3+} , Fe^{3+} , In^{3+} , and Sc^{3+} and X is OH^- , O^{2-} or F^- . The single metal containing materials reported to date are $[\text{VO}(\text{bdc})]$,^[23] $[\text{V}(\text{OH})(\text{bdc})]$,^[24] $[\text{Cr}(\text{OH})(\text{bdc})]$,^[25-26] $[\text{Al}(\text{OH})(\text{bdc})]$,^[27] $[\text{Ga}(\text{OH})(\text{bdc})]$,^[28] $[\text{Fe}(\text{OH})(\text{bdc})]$,^[29] $[\text{In}(\text{OH})(\text{bdc})]$,^[30] $[\text{AlF}(\text{bdc})]$,^[31] and $[\text{Sc}(\text{OH})(\text{bdc})]$.^[32]

Apart from varying the metal cations that leads to the aforementioned isostructural materials, an alteration of the organic linker from the bdc molecule to other dicarboxylate organic linkers also generates isostructural materials. Aiming

to enhance and engineer the properties of such materials e.g. surface area, pore size and adsorption ability, many isostructural materials of the MIL-53 family have been reported. The ligands used cover a great variety of functionalization ranging from bdc-X (where X = NH₂, COOH, Cl, Br, CH₃, NO₂, OH, (OH)₂)^[33-35] to ndc (2, 6- naphthalene dicarboxylate) and bpdc (4, 4'-biphenyldicarboxylated).^[36]

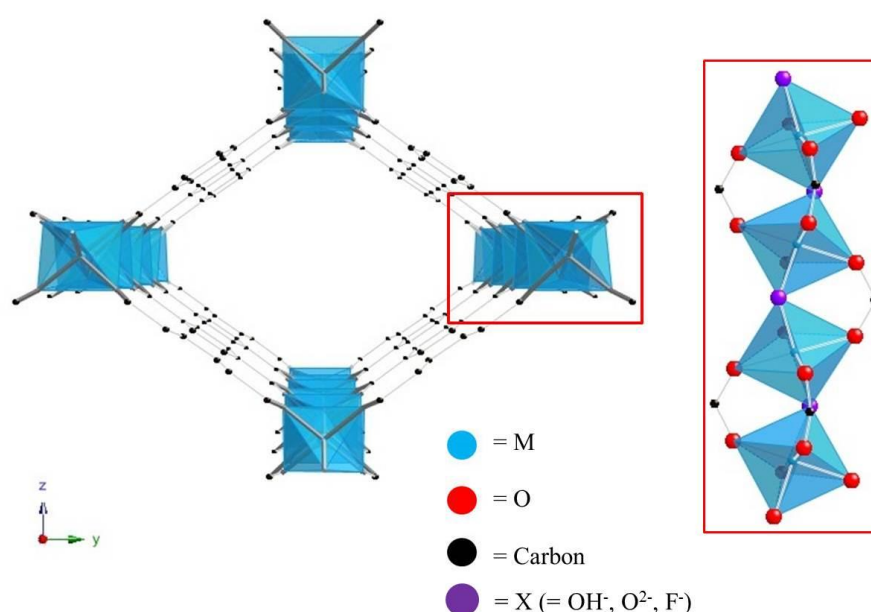


Figure 4.1 A diagram of the MIL-53 framework viewed along the one-dimensional lozenge shape channel. Inset shows a magnified view of the chain of metal centred corner-sharing octahedra.

The first member of the MIL-53 family to be reported was made in 2002 by hydrothermal synthesis. The as-prepared sample has the chemical formula of [Cr(OH)(bdc)]•0.75(H₂bdc). The structure (orthorhombic, *Pnam*, *a* = 17.340(1) Å, *b* = 12.718(1) Å and *c* = 6.822(1) Å, *V* = 1504.45(1) Å³) contains disordered unreacted H₂bdc molecules inside the pore which can be removed by heating the sample to 300 °C for a certain period of time giving an empty large pore structure [Cr(OH)(bdc)], labelled the **lp** phase according to the literature. When the **lp**-[Cr(OH)(bdc)] (orthorhombic, *Imcm*, *a* = 16.733(1) Å, *b* = 13.038(1) Å and *c* =

6.812(1) Å, $V = 1486.14(1) \text{ Å}^3$) is left at room temperature a narrow pore structure, $[\text{Cr}(\text{OH})(\text{bdc})] \cdot (\text{H}_2\text{O})$ (monoclinic, $C2/c$, $a = 19.685(4) \text{ Å}$, $b = 7.849(1) \text{ Å}$ and $c = 6.782(1) \text{ Å}$, $\beta = 104.90(2)^\circ$ $V = 1047.87(1) \text{ Å}^3$), is obtained and is labelled the **np** phase. This process was found to be reversible by heating the **np** phase above 100 °C to retrieve the **lp** phase. The ability to reversibly change its framework structure is called the “*breathing effect*” as illustrated in Figure 4.2.

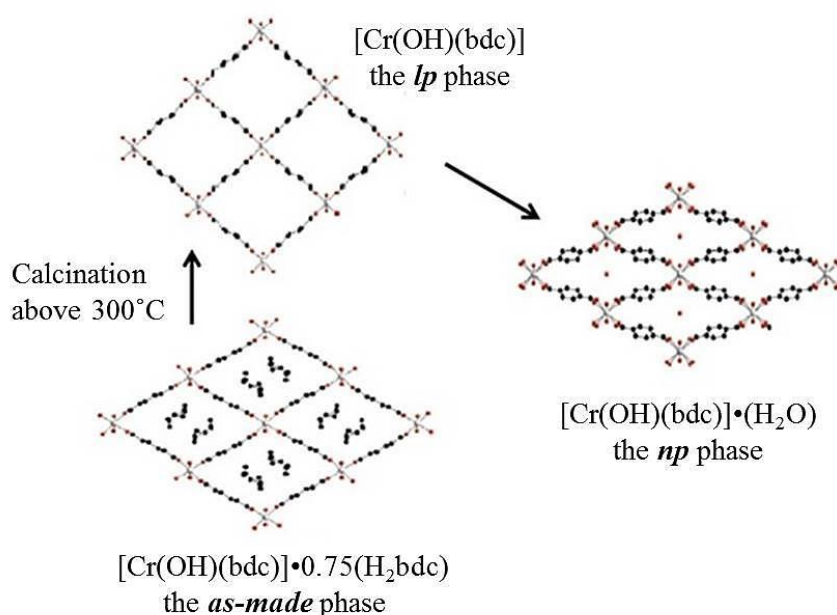


Figure 4.2 A schematic showing $[\text{Cr}(\text{OH})(\text{bdc})] \cdot 0.75(\text{H}_2\text{bdc})$ with residual bdc inside the channels. bdc molecules can be removed by calcination giving an open-pored structure of $[\text{Cr}(\text{OH})(\text{bdc})]$, called the **lp** phase. A closed-pore structure of $[\text{Cr}(\text{OH})(\text{bdc})] \cdot (\text{H}_2\text{O})$, called **np** phase, is achieved through rehydration of the framework when left under atmospheric condition. The grey, red and black dots represent the chromium, oxygen and carbon atoms respectively.^[26]

By replacing the chromium salt with an aluminium salt in the synthesis, $[\text{Al}(\text{OH})(\text{bdc})]$ was formed instead. It is isostructural with $[\text{Cr}(\text{OH})(\text{bdc})]$ and also exhibits a similar breathing effect. The causes of the breathing effect have been investigated thoroughly. Originally, it was believed that the breathing effect occurs due to guest molecule inclusion. It was found that framework shrinkage upon guest molecule insertion was caused by hydrogen bonding between the hydrogen atoms of water molecules and the oxygen atoms of the carboxylate

linkers and hydrogen bonding between the OH group of the chain of octahedra and the water molecules with the latter being more energetically favourable.^[37] This hydrogen bonding scheme is shown in **Figure 4.3**.

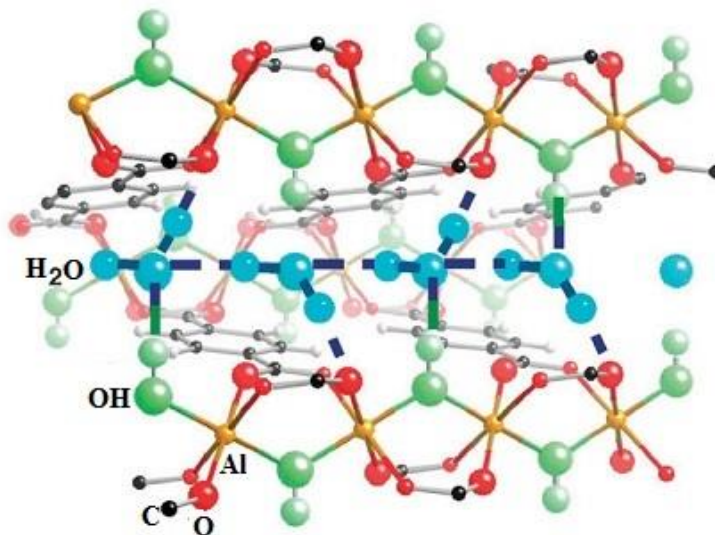


Figure 4.3 The causes of the framework transformation to the **np** phase upon guest molecule inclusion. Two types of hydrogen bonding occur including between water molecules and oxygen atoms of the carboxylate bridge and between the water molecules and the OH⁻ group of the (MO₄(OH₂))_∞ chain. The orange, green, red and black balls indicate the aluminium cation, the OH⁻ group, the oxygen atoms and the carbon atoms while the blue balls represent water molecule. The hydrogen bonding is indicated by the blue dashed line.^[37]

However, later in 2008 Lui *et al.* discovered that the phase transition of [Al(OH)(bdc)] can occur without any assistance of the guest molecule. The observation was conducted on guest-free [Al(OH)(bdc)] by heating the sample from 77 K to 450 K and cooling back to 77 K. Upon cooling, they found that the structural transition of [Al(OH)(bdc)] from the **lp** to the **np** phase occurred at 125 K to 150 K while the structure changed from the **np** phase to the **lp** phase at 325 K to 375 K upon heating to 450 K as shown in **Figure 4.4**. Thus, the phase transition of [Al(OH)(bdc)] is considered to have a large hysteresis.^[38] The origin of the structural transition was suggested to be the low-energy librational mode of the benzene ring. In the **lp** phase this vibrational mode was evident at the energy level of 5 meV which decreased significantly upon structural transition to the **np** phase.

Further explanation from computational methods suggested that the **np**-[Al(OH)(bdc)] is more stable at low temperature because of dispersive interactions involving the benzene ring whilst the **lp** form is entropically stabilised at high temperatures.^[39] A similar result was also observed for guest-free [Cr(OH)(bdc)] with the low-energy librational modes of benzene ring being observed at $E = 5.1$ meV which is in close agreement to that measured in **lp**-[Al(OH)(bdc)].^[40] Based on the behaviour of [Al(OH)(bdc)] and [Cr(OH)(bdc)], one factor that has a profound effect on the breathing process appears to be the presence of the OH group.

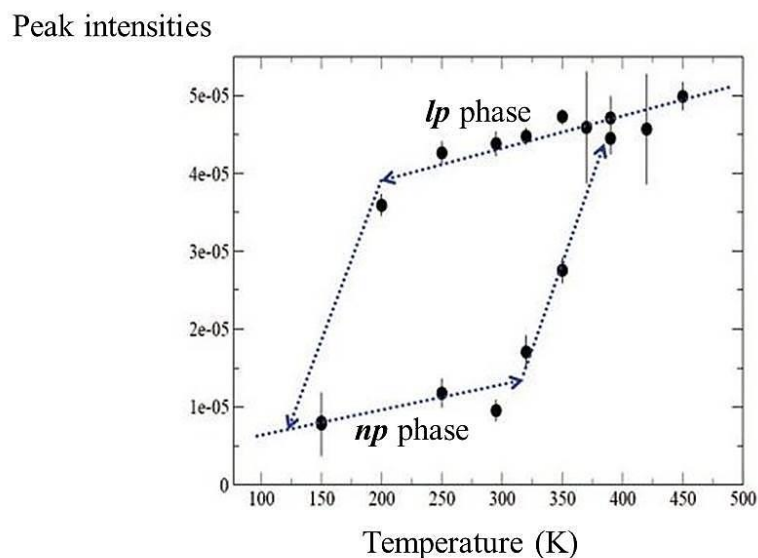


Figure 4.4 The structural hysteresis of [Al(OH)(bdc)] determined from neutron powder diffraction data.^[38]

[Ga(OH)(bdc)] was synthesised hydrothermally and was found to exhibit a slightly different thermal behaviour from [Al(OH)(bdc)]. Below 333 K, [Ga(OH)(bdc)]·(H₂O) exists in the **np** form but with different crystallographic details compared to [Al(OH)(bdc)], (monoclinic, $P2_1/c$, $a = 19.7053(2)$ Å, $b = 15.1642(4)$ Å and $c = 6.6812(9)$ Å, $\beta = 103.7936(8)^\circ$ and $V = 1938.56(7)$ Å³). Once the temperature was increased to 493 K, a very narrow pore structure labelled the **vnp** phase (monoclinic, $C2/c$, $a = 21.2693(2)$ Å, $b = 6.7589(4)$ Å and

$c = 6.8838(2) \text{ \AA}$, $\beta = 114.625(9)^\circ$ and $V = 886.28(5) \text{ \AA}^3$) was observed. However, from 493 K to its decomposition temperature at 653 K, the **lp** phase existed with a trace of **vnp** phase. **Figure 4.5** illustrates the thermal behaviour of $[\text{Ga}(\text{OH})(\text{bdc})]$ in comparison with $[\text{Al}(\text{OH})(\text{bdc})]$.

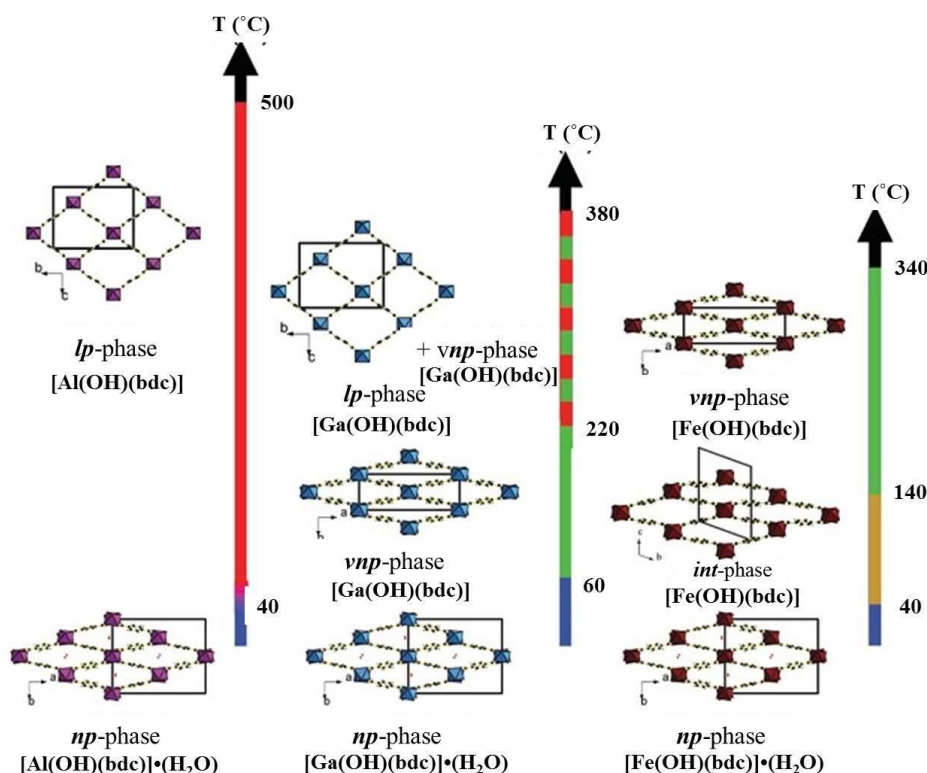


Figure 4.5 A diagram comparing the thermal behaviour of the $[\text{Al}(\text{OH})(\text{bdc})]$, $[\text{Ga}(\text{OH})(\text{bdc})]$ and $[\text{Fe}(\text{OH})(\text{bdc})]$ with respect to the loss of non-framework species, and later thermally induced phase transformation.^[41]

$[\text{Fe}(\text{OH})(\text{bdc})]$ was synthesised hydrothermally and was also found to show a breathing effect but its structural evolution is completely different from $[\text{Cr}(\text{OH})(\text{bdc})]$, $[\text{Al}(\text{OH})(\text{bdc})]$ and $[\text{Ga}(\text{OH})(\text{bdc})]$. Upon dehydration of the **np** phase (monoclinic, $C2/c$, $a = 19.3197(2) \text{ \AA}$, $b = 15.0362(2) \text{ \AA}$ and $c = 6.8351(6) \text{ \AA}$, $\beta = 96.305(1)^\circ$, $V = 1973.55(3) \text{ \AA}^3$), its framework did not change to the **lp** phase but closed further to form the **vnp** phase (monoclinic, $C2/c$, $a = 21.2693(3) \text{ \AA}$, $b = 6.7589(1) \text{ \AA}$ and $c = 6.8838(2) \text{ \AA}$, $\beta = 114.625(2)^\circ$, $V = 899.59(3) \text{ \AA}^3$) via an empty phase labelled the **int** phase (triclinic, $P-1$, $a = 6.8865(2) \text{ \AA}$, $b =$

10.5579(2) Å and $c = 13.4662(3)$ Å, $\alpha = 88.058(2)^\circ$, $\beta = 96.305(2)^\circ$ and $\gamma = 103.967(2)^\circ$, $V = 892.41(3)$ Å³)^[42] as shown in **Figure 4.5**.

The structural evolution of hydrothermally synthesised [Sc(OH)(bdc)] was reported to be similar to [Fe(OH)(bdc)] except that structures of the various phases had different specific crystallographic details. The desolvated form exists as a **np** phase (monoclinic, $P2_1/c$, $a = 20.2983(2)$ Å, $b = 7.3308(8)$ Å, $c = 11.6912(2)$ Å, $\beta = 104.958(2)^\circ$ and $V = 1680.8(3)$ Å³). As the temperature is increased to 523 K the **np** form slightly changes in structure by rotation of the chains of the ScO₄(OH)₂ octahedra about the -Sc-OH-Sc- chain running through the core of the ScO₄(OH)₂ core. As the temperature is increased to 623 K, the **vnp** phase (monoclinic, $C2/c$, $a = 21.5050(3)$ Å, $b = 6.6301(8)$ Å, $c = 7.2743(2)$ Å, $\beta = 113.543(2)^\circ$ and $V = 950.83(3)$ Å³) was obtained. In addition, rehydration of the **np** phase will give the **int** phase (monoclinic, $P2_1/c$, $a = 20.5382(3)$ Å, $b = 7.2992(1)$ Å and $c = 12.5604(3)$ Å, $\beta = 106.551(2)^\circ$ and $V = 1804.95(5)$ Å³). The structure evolution diagram of [Sc(OH)(bdc)] is shown in **Figure 4.6**.^[32]

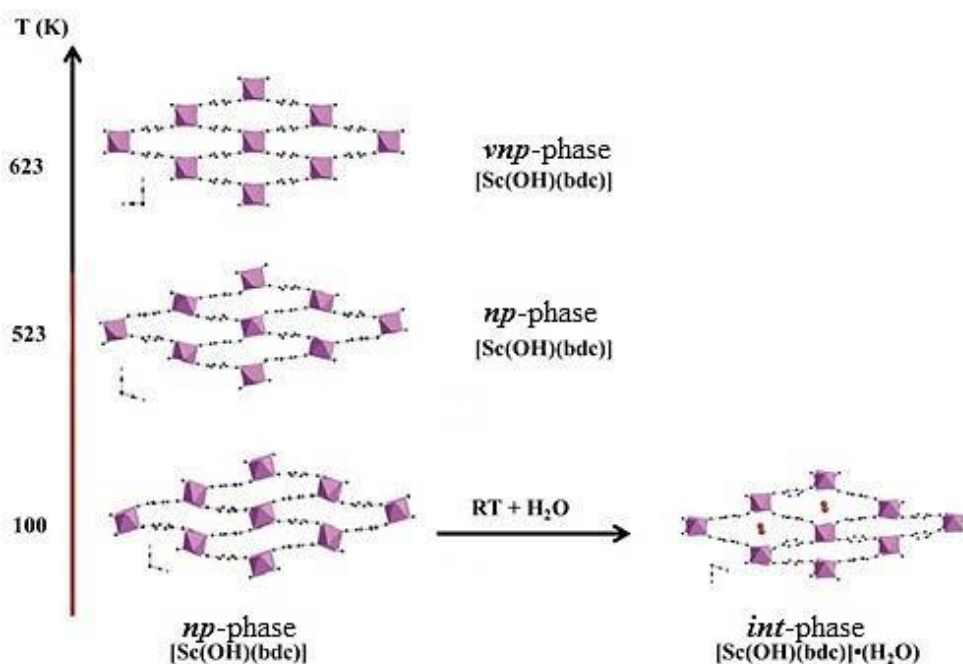


Figure 4.6 A diagram showing the thermal behaviour of [Sc(OH)(bdc)]. At room temperature the **np** form undergoes rehydration resulting in **int** phase. Once the temperature is increased, the **np** phase changes gradually until the **vnp** phase is obtained.^[32]

$[\text{In}(\text{OH})(\text{bdc})]\cdot 0.75(\text{H}_2\text{bdc})$, (monoclinic, $P2_1/c$, $a = 18.228(3) \text{ \AA}$, $b = 11.970(2) \text{ \AA}$, $c = 34.062(6) \text{ \AA}$, $\beta = 122.4(1)^\circ$ and $V = 6278(2) \text{ \AA}^3$) forms an isostructural framework to $[\text{Al}(\text{OH})(\text{bdc})]$ but the H_2bdc cannot be removed from the pores without framework collapse.^[30]

$[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ was recently synthesised. The as-made $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{bdc})$ had the residual bdc inside the pores which can be exchanged with DMF to give $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]\cdot(\text{DMF})$. When $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]\cdot(\text{DMF})$ is calcined at 423 K and then 523 K under vacuum, $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ is obtained. This phase was found to display varied thermoresponsive behaviour. If $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ is left under ambient conditions, the structure converts to the **np** form, $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$ (monoclinic, $C2/c$, $a = 19.808(3) \text{ \AA}$, $b = 7.5931(4) \text{ \AA}$, $c = 6.8159(3) \text{ \AA}$, $\beta = 104.29(1)^\circ$ and $V = 993.5(1) \text{ \AA}^3$). The activation of $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$ leads to a phase transition from the **np** form to the **int** form, $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ (triclinic, $P\bar{1}$, $a = 6.9(2) \text{ \AA}$, $b = 10.7(2) \text{ \AA}$, $c = 13.7(3) \text{ \AA}$, $\alpha = 111(2)^\circ$, $\beta = 89(2)^\circ$, $\gamma = 104(2)^\circ$ and $V = 914(3) \text{ \AA}^3$) at 400 K before transforming to the **np** form $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ (monoclinic, $C2/c$, $a = 21.2(3) \text{ \AA}$, $b = 6.9(4) \text{ \AA}$, $c = 6.8(3) \text{ \AA}$, $\beta = 115(1)^\circ$ and $V = 908(1) \text{ \AA}^3$) at 450 K and finally changing to the **lp** form $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ (orthorhombic, $Pm\bar{c}n$ or $Im\bar{c}m$, $a = 16.515(2) \text{ \AA}$, $b = 13.647(2) \text{ \AA}$ and $c = 6.860(1) \text{ \AA}$, $V = 1546.1(3) \text{ \AA}^3$). As can be seen the thermoresponsive behaviour of the previous materials is dependent on the trivalent metal ions in the structure. The thermoresponsive behaviour of $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ is summarised in **Figure 4.7**.

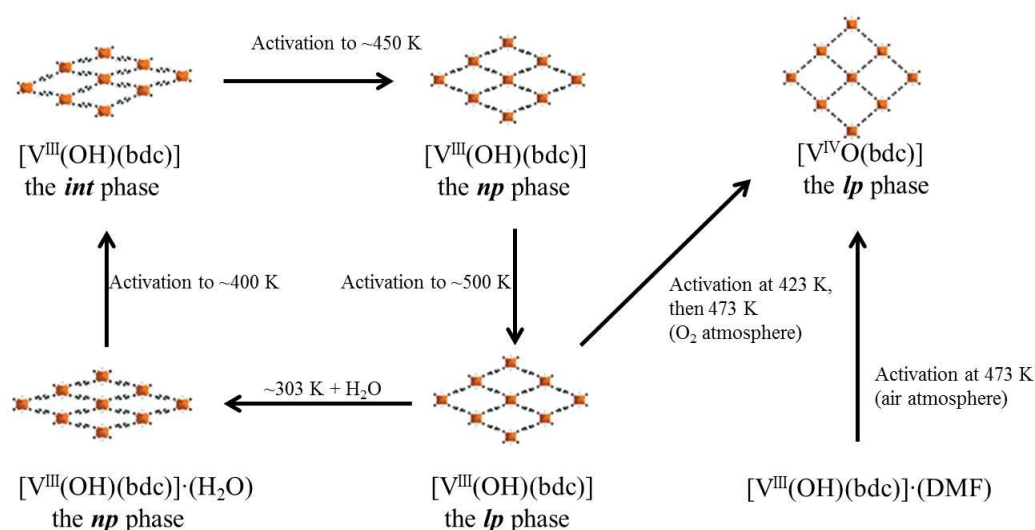


Figure 4.7 A diagram showing thermal behaviour of $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ and $[\text{V}^{\text{IV}}\text{O}(\text{bdc})]$ upon activation at various conditions.

If *lp*- $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})]$ is activated under O_2 atmosphere at 423 K and then 473 K, $[\text{V}^{\text{IV}}\text{O}(\text{bdc})]$ is achieved and this process is found to be irreversible. Moreover, $[\text{VO}(\text{bdc})]$ that is isostructural to MIL-53 but named MIL-47, $[\text{V}^{\text{IV}}\text{O}(\text{bdc})]$ can also be obtained by calcination of $[\text{V}(\text{OH})(\text{bdc})] \cdot \text{DMF}$ at 473 K under air condition. The structure exists in the *lp* phase (orthorhombic, *Pmcn*, $a = 16.070(1)$ Å, $b = 13.960(1)$ Å and $c = 6.818(1)$ Å, $V = 1529.5(1)$ Å³) from 100 – 500 K under vacuum and the framework does not adsorb atmospheric H_2O or undergo a phase transition to the *np* phase under atmospheric conditions.^[24] Inelastic neutron scattering was used to determine that $[\text{V}^{\text{IV}}\text{O}(\text{bdc})]$ did not undergo structural hysteresis over the temperature range of 100 – 500 K, but the main peak of INS spectrum corresponding to the low-energy librational modes of the benzene ring was observed at 5.2 meV which is closed to that found for $[\text{Al}(\text{OH})(\text{bdc})]$ and $[\text{Cr}(\text{OH})(\text{bdc})]$.^[40]

Recently the aluminium fluoride terephthalate was reported which is isostructural to MIL-53 and displays a similar behaviour to $[\text{V}^{\text{IV}}\text{O}(\text{bdc})]$. As-synthesised $[\text{AlF}(\text{bdc})] \cdot (\text{Me}_2\text{NH}_2\text{F})$ converts to the *lp* phase (orthorhombic, *Imma*, $a = 6.550(1)$ Å, $b = 16.250(1)$ Å and $c = 13.378(1)$ Å, $V = 1424.1(2)$ Å³) when it was calcined at 350 °C to remove the guest species. Under ambient conditions the

lp-[AlF(bdc)] material exists without any structural transformation due to adsorption of atmospheric H₂O.^[31] As can be seen from the disappearance of a breathing effect or H₂O adsorption under ambient conditions for [VO(bdc)] and [AlF(bdc)], the thermoresponsive behaviour of these MIL-53 family of materials is also dependent on the atom connecting the metal-centred octahedra and the oxidation state of the metal ion in the structure.

In this work, the drastically different thermoresponsive behaviour of four members of the MIL-53 family [Al(OH)(bdc)], [AlF(bdc)], [Cr(OH)(bdc)] and [VO(bdc)] will be studied to specifically determine the thermal expansion behaviour of the *lp* phase which has not been reported in detail for any of these compounds and how varying the metal type, metal oxidation state and atom X influence this behaviour. The *lp* phase was chosen to be studied as it tends to have the largest thermal stability range and the correct characteristic to exhibit NTE behaviour. This is done with particular emphasis on finding new NTE materials, controlling the NTE behaviour and determining how one-dimensional extended inorganic components with linked octahedra may affect the NTE behaviour in contrast with MOFs with zero dimensional clusters such as HKUST-1, MOF-5 and UiO-66. The study will also determine whether the [VO(bdc)] and [AlF(bdc)] undergo any breathing effect transformation at low temperature for which neither material has been studied, below 300 K for [AlF(bdc)] and 100 K for [VO(bdc)]. Other members of the MIL-53 family were neglected from this study due to the inability to successfully calcine [In(OH)(bdc)]·0.75(H₂bdc), the lack of the *lp* form of [Fe(OH)(bdc)] and [Sc(OH)(bdc)], and the narrow thermal range over which *lp*-[Ga(OH)(bdc)] exists and the difficulty in form producing phase pure *lp*-[Ga(OH)(bdc)].

4.2 Thermoresponsive behaviour of [Al(OH)(bdc)]

4.2.1 Synthesis and activation

All chemicals involved in the synthesis were used without further purification. $[\text{Al}(\text{OH})(\text{bdc})]\cdot 0.75(\text{H}_2\text{bdc})$ was synthesised by following the procedure reported previously.^[27] $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 98 %, 5.2 g) was dissolved in deionized water (20 ml) followed by addition of H_2bdc (Sigma-Aldrich, 98 %, 1.112 g) into the mixture which was then placed into a 40 ml Teflon-lined stainless steel autoclave. The mixture was heated to 220 °C for 3 days and cooled down naturally to room temperature. The white solid powder product was recovered by filtration and washed with deionized water. The powder pattern of the as-made material is shown in **Figure 4.8** and suggests that phase pure $[\text{Al}(\text{OH})(\text{bdc})]\cdot 0.75(\text{H}_2\text{bdc})$ has been achieved.

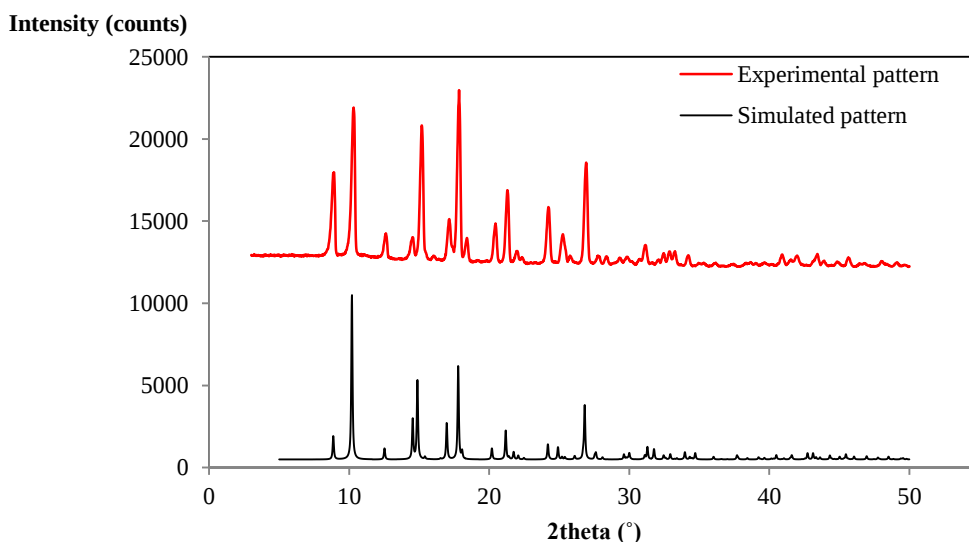
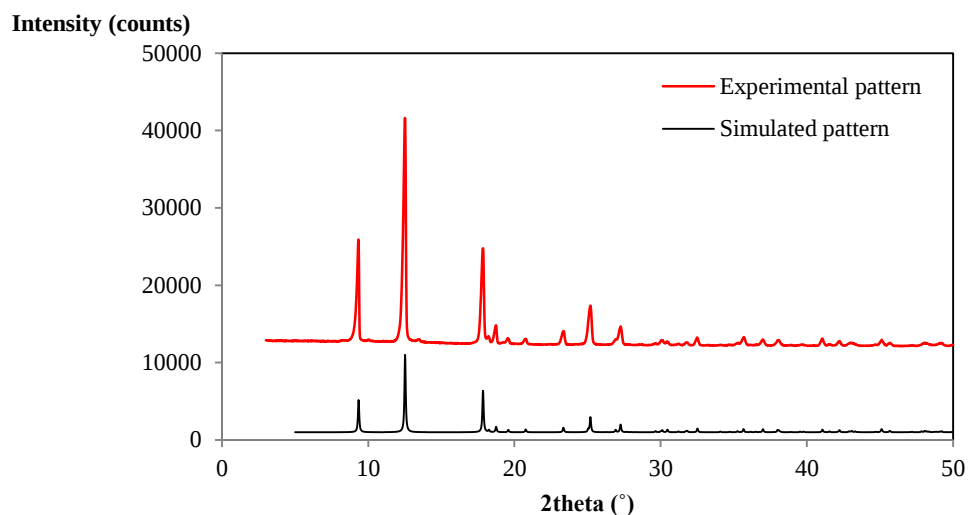


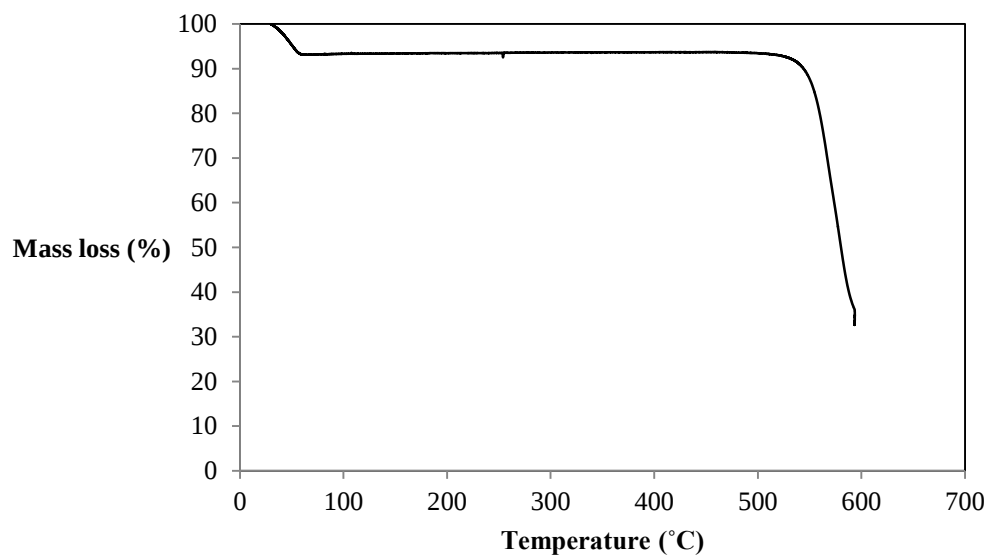
Figure 4.8 The powder pattern of $[\text{Al}(\text{OH})(\text{bdc})]\cdot 0.75(\text{H}_2\text{bdc})$ in comparison with the simulated powder pattern.

The dried product was calcined in a tube furnace under air at 300 °C for 3 days in order to remove the unreacted H_2bdc molecules packed in the pores of the

[Al(OH)(bdc)]·0.75(H₂bdc). The success of the calcination was confirmed by the powder pattern of the calcined sample in comparison with the simulated powder pattern as shown in **Figure 4.9** (a) and the thermogravimetric analysis data of [Al(OH)(bdc)]·(H₂O) that was collected under flowing air with a heating rate of 5 °Cmin⁻¹ that is as shown in **Figure 4.9** (b).



(a)



(b)

Figure 4.9 (a) The powder pattern of [Al(OH)(bdc)]·(H₂O) in comparison with the simulated powder pattern. (b) Thermogravimetric analysis data of [Al(OH)(bdc)]·(H₂O).

The TGA curve of $[\text{Al}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$ shows two mass losses. The first loss of approximately 6.60 % (calculated to be 7.96 %) within the temperature range of 25 - ~60 °C indicates a dehydration process where one equivalent of water molecule is leaving the framework. The second event from ~520 - 600 °C corresponds to the partial mass loss of the bdc molecule ~57.4 %, calculated to be 72.6 %. The discrepancy between the calculated and the experimental mass loss may arise from the incomplete decomposition of the bdc molecules.

A sample of $[\text{Al}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$ was packed in a 0.5 mm diameter borosilicate capillary tube to a length of 4 centimetres and evacuated at 2.1×10^{-1} mbar at 150 °C for 48 hours to obtain a fully desolvated sample. The degassed sample was sealed under vacuum, ready for the data collection at the synchrotron.

4.2.2 Synchrotron powder thermodiffraction study

4.2.2.1 *Data collection*

The diffraction data were collected at 25 K intervals in the temperature range of 100 - 500 K. The diffractometer was operated to collect the data from 3 to 140° 2 θ and the mean wavelength used was 0.825993(3) Å. The data collection time was 30 minutes per sample per temperature with a 2 θ step size of 0.001°. The powder patterns were rebinned with a 2 θ step size of 0.003° and were analysed using the Rietveld structural refinement in the GSAS software package.

4.2.2.2 *Data analysis*

The synchrotron powder X-ray diffraction data were initially fitted using the Le Bail method to obtain accurate lattice parameters and starting peak shape profile coefficients. The starting model for the **lp** form of $[\text{Al}(\text{OH})(\text{bdc})]$ was taken from the literature.^[27] Profile analysis was performed on 11308 data points in the range of 5° to 40° 2 θ and the first highly asymmetrical peak was excluded

from the pattern. The background was fit using linear interpolation between manually designated background points. Peak shape fitting was conducted by using the fourth profile option in the GSAS program suite which is a modified pseudo-Voigt function that accounts for the effect of microstrain broadening.

The lattice parameters and profile coefficients obtained from the Le Bail fit were subsequently used in Rietveld refinement. The final cycle of least-squares refinement in the Rietveld refinement comprised of 28 refined parameters including the scale factor, detector zero point, unit cell parameters, peak profile parameters, atomic coordinates and isotropic atomic displacement parameters of all six atoms in the asymmetric unit. The isotropic atomic displacement parameters (U_{iso}) of the O atoms were constrained to have the same value, as were those of the C atoms. Soft constraints were not included in the refinement in this work as these would influence the structures obtained which would introduce bias to this work. All the data sets from 500 – 150 K were refined using an identical procedure.

In the diffraction pattern at 100 K and 125 K, there was evidence of *np*-[Al(OH)(bdc)] as shown in **Figure 4.10**, so two phases refinements were performed. A Rietveld refinement was used for the major *lp*-[Al(OH)(bdc)] phase and a Le Bail fitting for the minor *np*-[Al(OH)(bdc)]. The initial unit cell parameters for the *np*-[Al(OH)(bdc)] phase were taken from the literature.^[27]

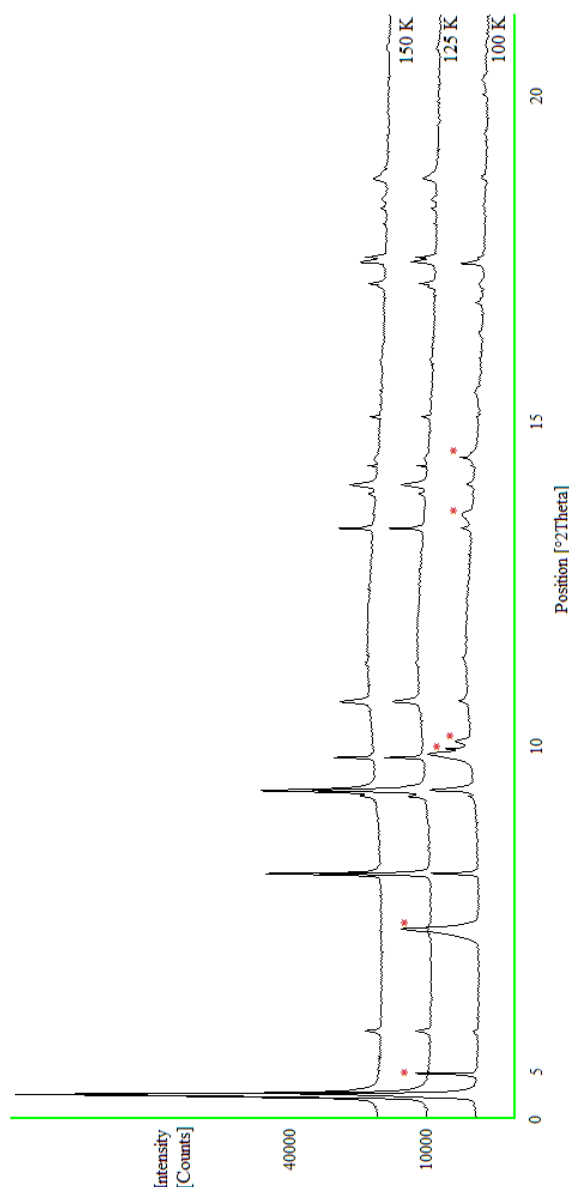


Figure 4.10 The synchrotron powder X-ray diffraction patterns of [Al(OH)(bdc)] at 100 K, 125 K and 150 K. The red asterisks indicate the reflections from an empty *np*-[Al(OH)(bdc)].

The crystallographic data for a representative refinement (300 K) are summarized in **Table 4.1**. The final atomic coordinates, occupancies and isotropic atomic displacement parameters are given in **Table 4.2**. Selected bond lengths and bond angles are given in **Table 4.3**. The asymmetric unit and the full structure are shown in **Figure 4.11** (a) and (b). The final observed, calculated and difference plot for the Rietveld refinement at 300 K is shown in **Figure 4.12**. This is a

representative final result and all the refinements of all data sets are given in the attached appendix of the CD.

Table 4.1 Crystal data and structure refinement parameters for *lp*-[Al(OH)(bdc)] at 300 K

Formula	[AlC ₈ H ₅ O ₅]
Formula weight	208.11
Density (gcm ⁻³)	0.949
Temperature (K)	300
Wavelength (Å)	0.825993(3)
Space group	<i>Imma</i>
a (Å)	6.62946(6)
b (Å)	16.7579(2)
c (Å)	12.7936(2)
V (Å ³)	1421.32(3)
Z	4
R _p	0.0354
R _{wp}	0.0471
R _F	0.2390
χ ²	4.132
Number of refined parameters	28
Scale factor	9.60(3)
Zero point (°)	-0.00909(9)
Gaussian profile coefficients	GU = 0.000, GV = 0.000, GW = 0.48(2)
Lorentzian profile coefficients	LX = 0.03(5)
Eta	0.759(9)
Microstrain broadening coefficients	S400 = 0.000, S040 = 0.0229(7), S004 = 0.244(6) S200 = 0.0007(7), S202 = 0.012(3), S022 = -0.050(1)

Table 4.2 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for *lp*-[Al(OH)(bdc)] at 300 K

Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Al	0.25	0.25	0.75	2.2(1)	1
O1	0.0	0.25	0.685(4)	1.7(8)	1
O2	0.167(3)	0.168(1)	0.844(2)	1.7(8)	1
C1	0.0	0.138(4)	0.870(6)	3.7(1)	1
C2	0.0	0.062(4)	0.945(5)	3.7(1)	1
C3	-0.192(4)	0.035(3)	0.968(4)	3.7(1)	1

Table 4.3 Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) for *lp*-[Al(OH)(bdc)] at 300 K

Al—O1 (x 4)	1.908(2)	O2 ⁵ —Al—O1 ⁵	91.39(12)
Al—O2 (x 2)	1.856(3)	O2 ⁵ —Al—O1 ⁶	91.39(12)
C1—O1 (x 2)	1.258(3)	O1—Al—O1 ¹	92.57(17)
C1—C2	1.593(6)	O1—Al—O1 ⁵	180.0
C2—C3 (x 2)	1.382(3)	O1—Al—O1 ⁶	87.43(17)
C3—C3 ⁴ (x 2)	1.445(7)	O1 ¹ —Al—O1 ⁵	87.43(17)
		O1 ¹ —Al—O1 ⁶	180.0
O2—Al—O2 ⁴	180.0	O1 ⁵ —Al—O1 ⁶	92.57(17)
O2—Al—O1	91.39(12)	Al1—O2—Al1 ²	126.5(3)
O2—Al—O1 ¹	91.39(12)	O1—C1—O1 ²	122.9(6)
O2—Al—O1 ⁵	88.61(12)	C2—C1—O1	118.5(3)
O2—Al—O1 ⁶	88.61(12)	C3 ³ —C3—C2	112.8(4)
O2 ⁵ —Al—O1	88.61(12)	C3—C2—C3 ²	134.5(7)
O2 ⁵ —Al—O1 ¹	88.61(12)	C3—C2—C1	112.7(3)

Symmetry transformations used to generate equivalent atoms:

(1) $x, -y+1/2, z$; (2) $-x, y, z$; (3) $x, -y, -z+2$; (4) $-x+1/2, -y-1/2, -z+3/2$; (5) $-x+1/2, -y+3/2, -z+3/2$; (6) $-x+1/2, y+1, -z+3/2$.

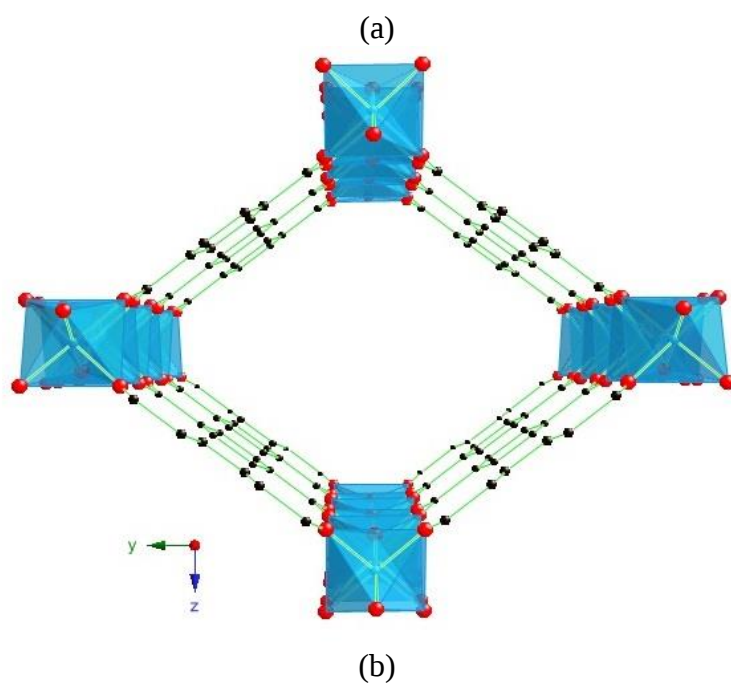
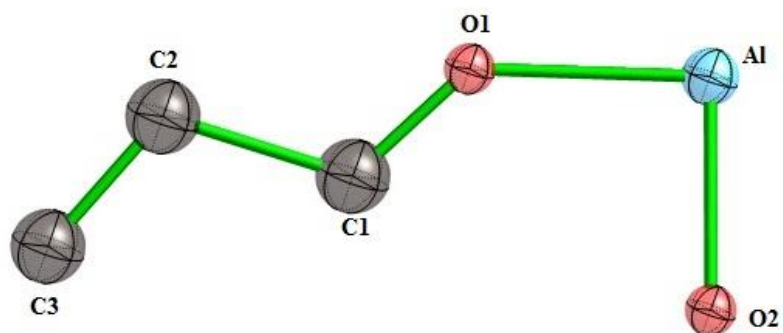


Figure 4.11 (a) Asymmetric unit of lp -[Al(OH)(bdc)]. (b) The perspective viewing of the structure of lp -[Al(OH)(bdc)] viewed along the [100] direction.

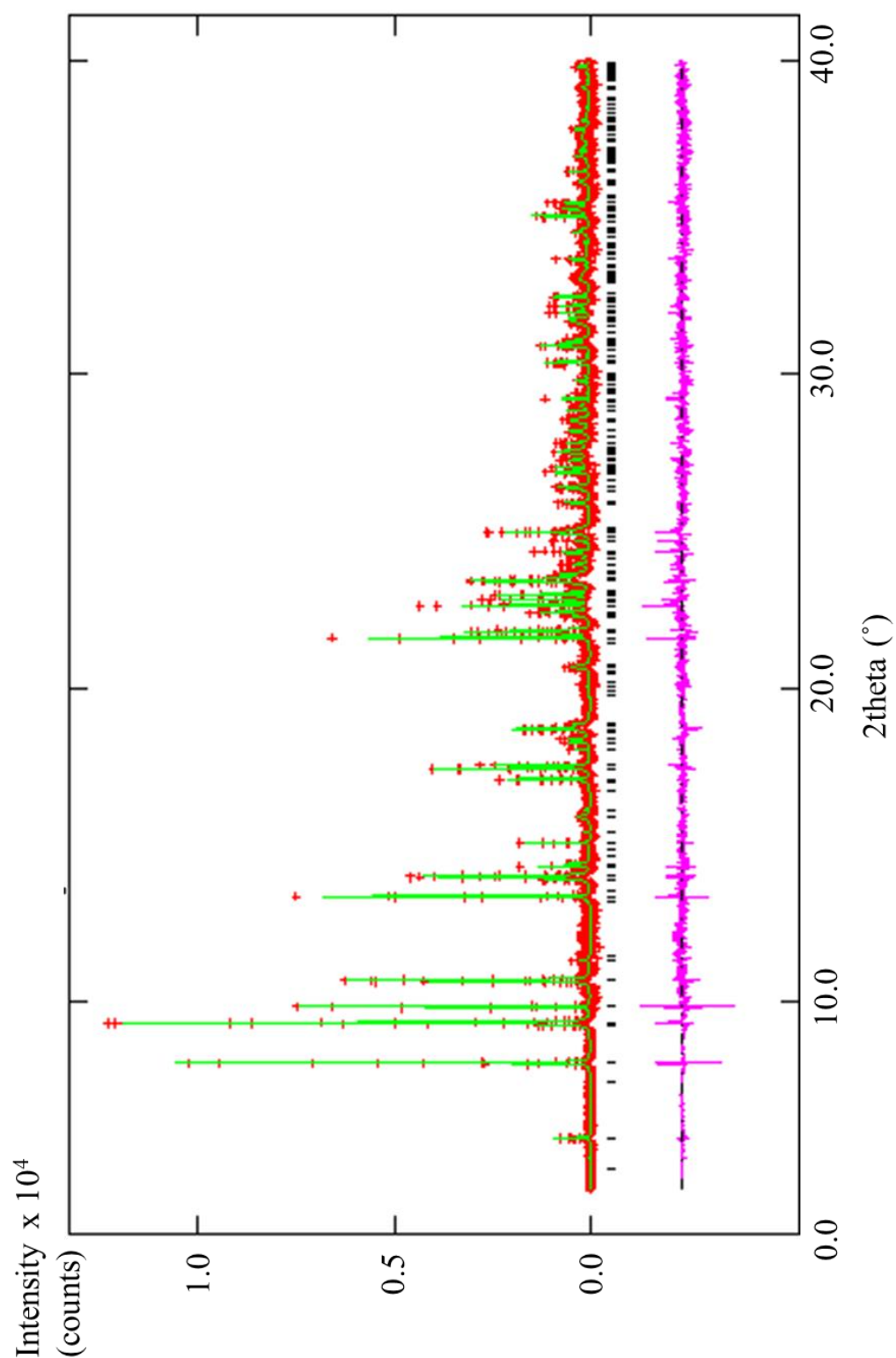


Figure 4.12 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Rietveld refinement of *lp*-[Al(OH)(bdc)] at 300 K. The tick marks are the calculated 2θ angles for the Bragg peaks. The plot is scaled by 4x and 8x over the 2θ range of 10° - 25° and 25° - 40° respectively.

4.2.3 Results and discussion

Unit cell dimensions and unit cell volume of [Al(OH)(bdc)] from 100 - 500 K are listed in **Table 4.4**.

Table 4.4 Unit cell dimensions ($\text{\AA}$), unit cell volume ($\text{\AA}^3$), goodness of fit (χ^2), R_{wp} and R_p for **lp**-[Al(OH)(bdc)] from 100 - 500 K.

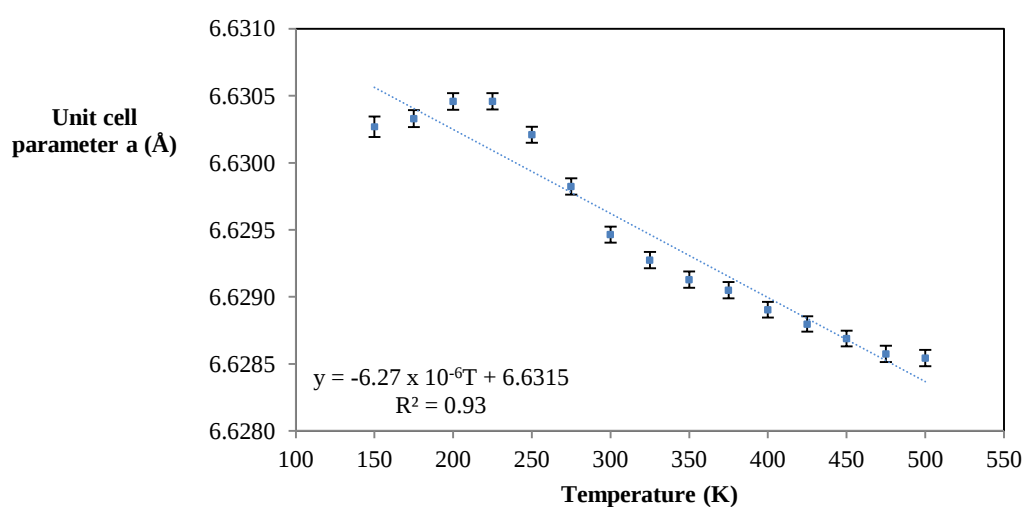
Temperature (K)	a	b	c	V	χ^2	R_{wp}	R_p
100 ^a	6.59388(3)	16.840(2)	12.606(1)	1399.8(1)	9.116	0.0800	0.0553
125	6.63071(8)	16.8072(2)	12.7381(3)	1419.58(4)	6.130	0.0464	0.0350
150	6.63027(6)	16.7974(2)	12.7469(2)	1419.64(3)	4.352	0.0447	0.0341
175	6.63033(6)	16.7902(2)	12.7537(2)	1419.80(3)	4.045	0.0450	0.0341
200	6.63046(6)	16.7832(2)	12.7618(2)	1420.14(3)	4.184	0.0457	0.0345
225	6.63046(6)	16.7759(2)	12.7703(2)	1420.47(3)	4.094	0.0453	0.0342
250	6.63021(6)	16.7700(2)	12.7778(2)	1420.75(3)	4.191	0.0460	0.0346
275	6.62982(6)	16.7638(2)	12.7858(2)	1421.03(3)	4.122	0.0456	0.0343
300	6.62947(6)	16.7579(2)	12.7936(2)	1421.32(3)	4.132	0.0471	0.0354
325	6.62928(6)	16.7515(2)	12.8019(2)	1421.66(3)	4.154	0.0472	0.0356
350	6.62913(6)	16.7457(2)	12.8099(2)	1422.02(3)	4.228	0.0476	0.0358
375	6.62905(6)	16.7400(2)	12.8172(2)	1422.33(3)	4.242	0.0465	0.0346
400	6.62891(6)	16.7338(2)	12.8254(2)	1422.68(3)	4.277	0.0467	0.0348
425	6.62880(6)	16.7276(2)	12.8336(2)	1423.04(3)	4.481	0.0478	0.0358
450	6.62869(6)	16.7224(2)	12.8406(2)	1423.35(3)	4.674	0.0488	0.0362
475	6.62857(6)	16.7168(2)	12.8473(2)	1423.58(3)	4.601	0.0485	0.0359
500	6.62854(6)	16.7120(2)	12.8530(2)	1423.81(3)	4.739	0.0493	0.0365

^a The unit cell parameters of **np**-[Al(OH)(bdc)]: $a = 20.801(1) \text{ \AA}$, $b = 6.9687(2) \text{ \AA}$, $c = 6.5861(3) \text{ \AA}$, $\beta = 113.691(4)^\circ$ and $V = 874.25(6) \text{ \AA}^3$.

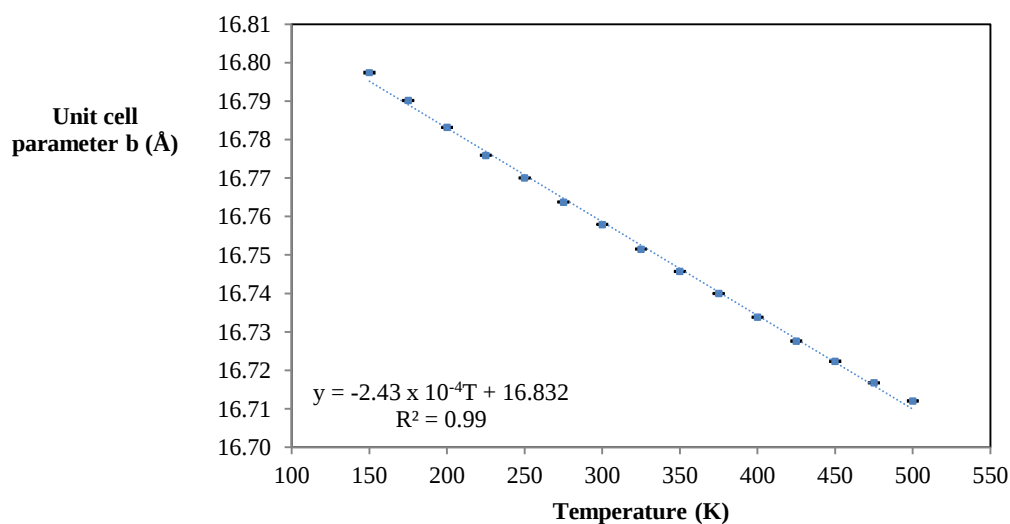
[Al(OH)(bdc)] was found to remain solely in the **lp** form as it was cooled from 500 K to 150 K. At 125 K, small signs of the presence of the **np** form

became evident and at 100 K significant amounts of the **lp** and **np** form coexist within the sample. This behaviour reflects that reported previously.^[38]

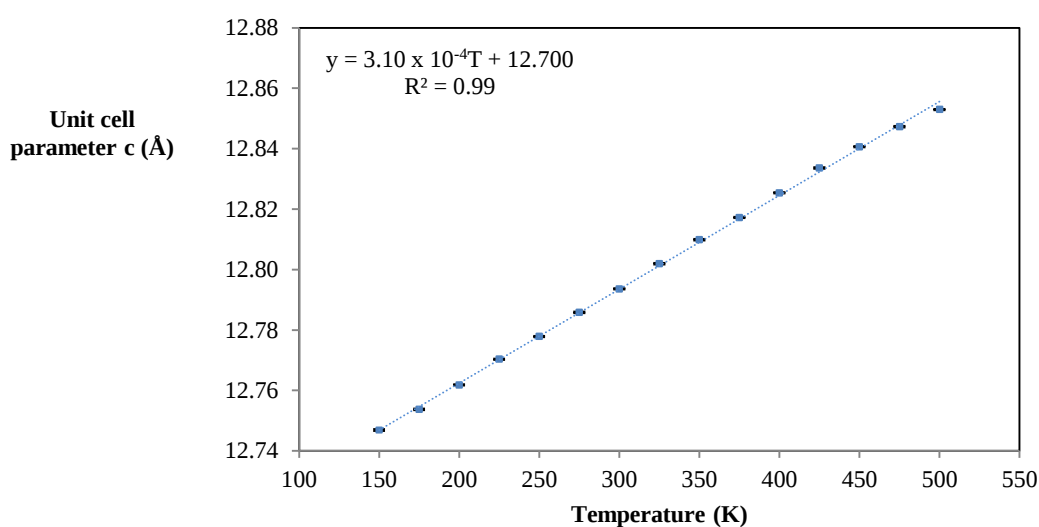
The thermoresponsive behaviour of phase pure **lp**-[Al(OH)(bdc)] will only be discussed as these structural results will not be influenced by the presence of the minor **np** impurity. The measured variations in lattice parameters and unit cell volume as a function of temperature of the pure **lp** form are shown in **Figure 4.13**.



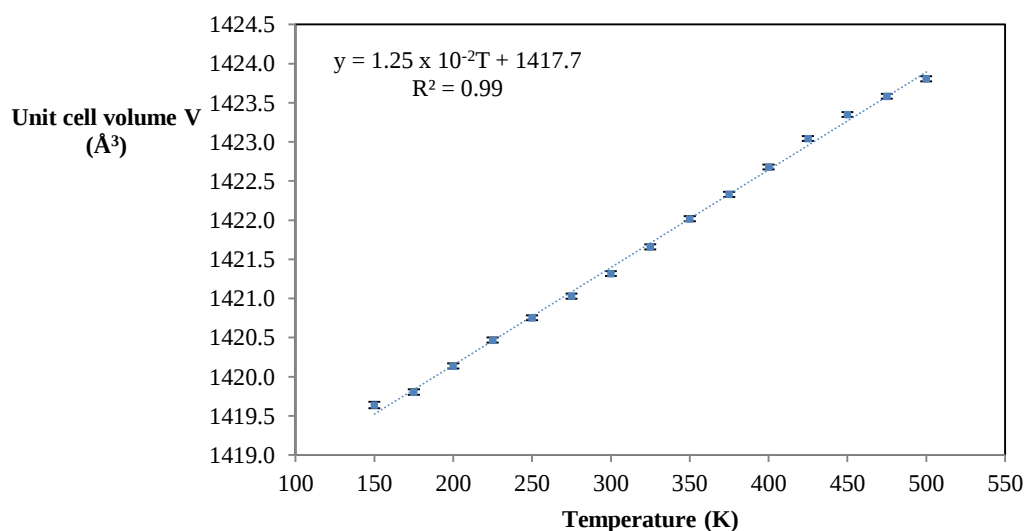
(a)



(b)



(c)



(d)

Figure 4.13 (a), (b) and (c) Plots of the unit cell dimension (a) a , (b) b , (c) c and (d) unit cell volume V as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

A relatively linear decrease in a ($-6.27 \times 10^{-6} \text{ Å K}^{-1}$) and b ($-2.43 \times 10^{-4} \text{ Å K}^{-1}$) and a linear increase in c ($3.10 \times 10^{-4} \text{ Å K}^{-1}$) is observed over the entire temperature range. Overall the positive expansion in the c direction outweighs the contraction in the a and b directions to give an overall linear positive volume expansion represented by $V = 1.25 \times 10^{-2}T + 1417.7$ with a constant value of a volume expansion coefficient $\alpha_V = 8.55 \times 10^{-6} \text{ K}^{-1}$.

Structure refinements at each temperature provide some insight into the mechanism of the thermoresponsive behaviour of the *lp* form. The chain of corner-sharing $\text{AlO}_4(\text{OH})_2$ lying along the *a* axis contracts upon heating. A plausible mechanism for contraction along the *a*-axis is shown in **Figure 4.14** and involves a correlated rocking of the carboxylate groups about the axis of the bdc linker that introduces a twisting motion about the Al-OH-Al linkage of the relatively rigid $\text{AlO}_4(\text{OH})_2$ octahedra. The magnitude of the rocking and twisting motions will increase with temperature resulting in contraction of the structure along the *a*-axis. Such aspects of this mechanism have previously been deduced from single crystal studies for other dicarboxylate-based MOFs.^[43]

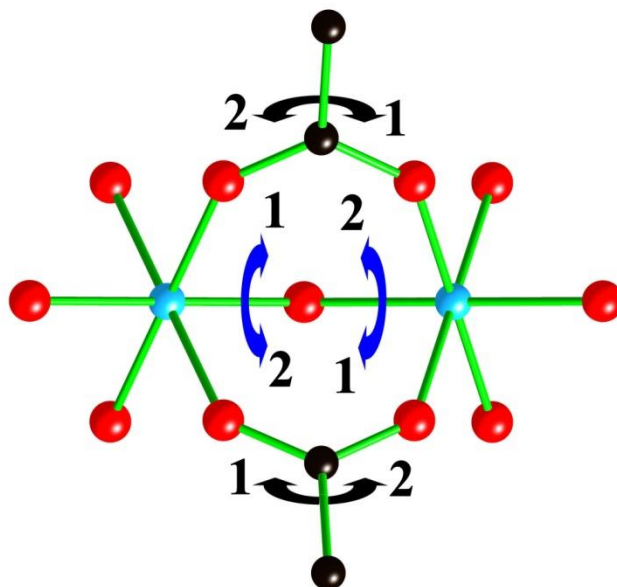
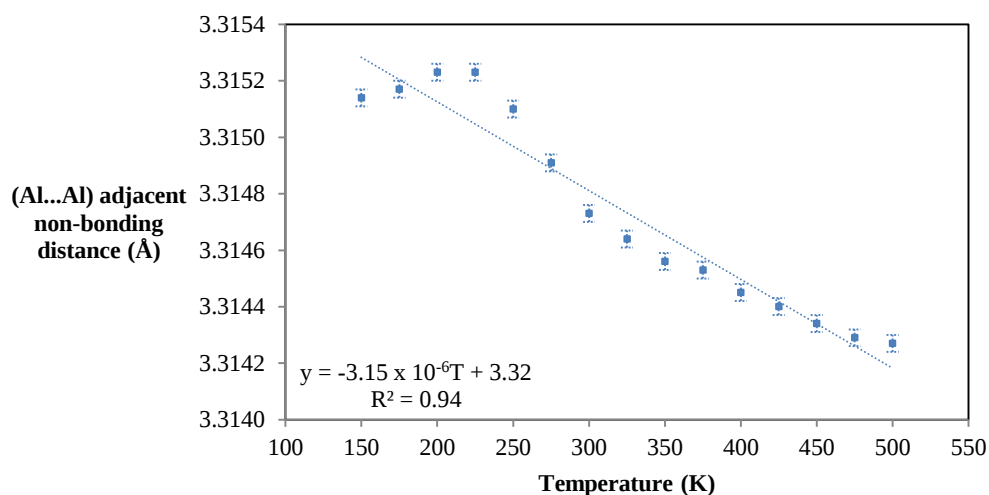


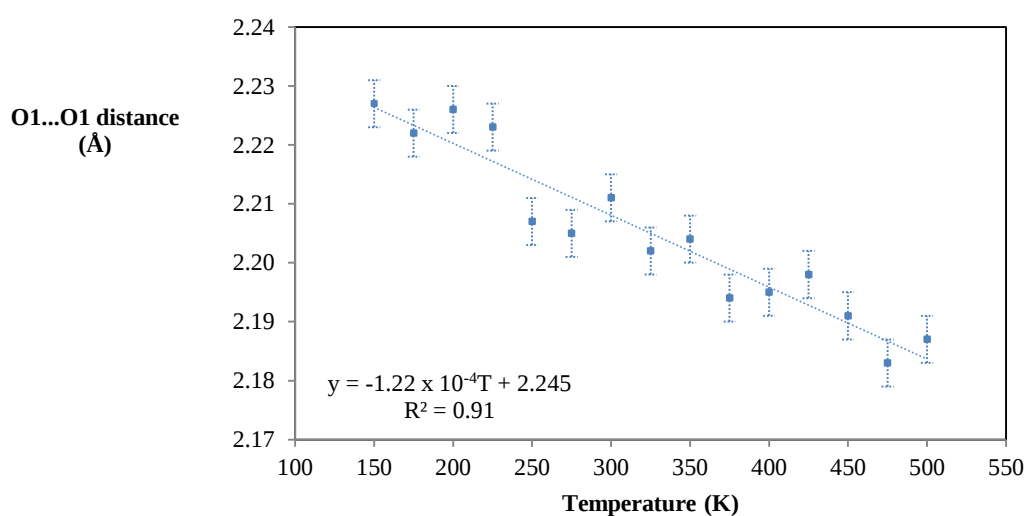
Figure 4.14 A schematic representing the possible mechanism for contraction along the *a*-axis which is a correlated rocking motion of the carboxylate groups about the axis of the bdc linker, illustrated by black arrows. The rocking mode of the carboxylate group causes a twisting motion of the Al-OH-Al linkage, as illustrated by the blue arrows. The numbers on the arrows represent the different sense of twisting.

The expected accompanying decreases in non-bonding adjacent Al...Al (**Figure 4.15(a)**) and carboxylate O1...O1 distances (**Figure 4.15 (b)**) along the $[\text{AlO}_4(\text{OH})]_\infty$ chain support this mechanism, as do the near constant values of the Al-O2, C1-O1 bond distances (**Figure 4.15 (c)** and (d) respectively) and Al-O2-

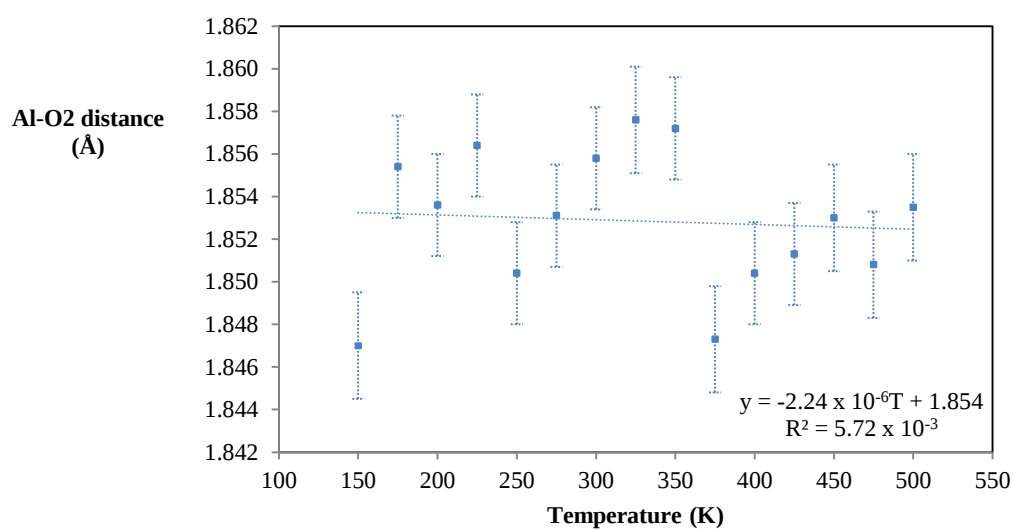
Al bond angle (**Figure 4.15 (e)**), and the slight decrease in the Al-O1 distance and O1-C1-O1 angle (**Figure 4.15 (f) and (g)** respectively). The variation in the latter geometric parameters would be expected as the magnitude of the rocking or twisting motions of the carboxylate and Al-centred octahedra, and associated transverse vibrations of the O species, increase. However, the small magnitude of the changes in geometric parameters over the temperature range and the precision of the structure refinements limit a more definitive determination of the mechanism of contraction along the *a* axis.



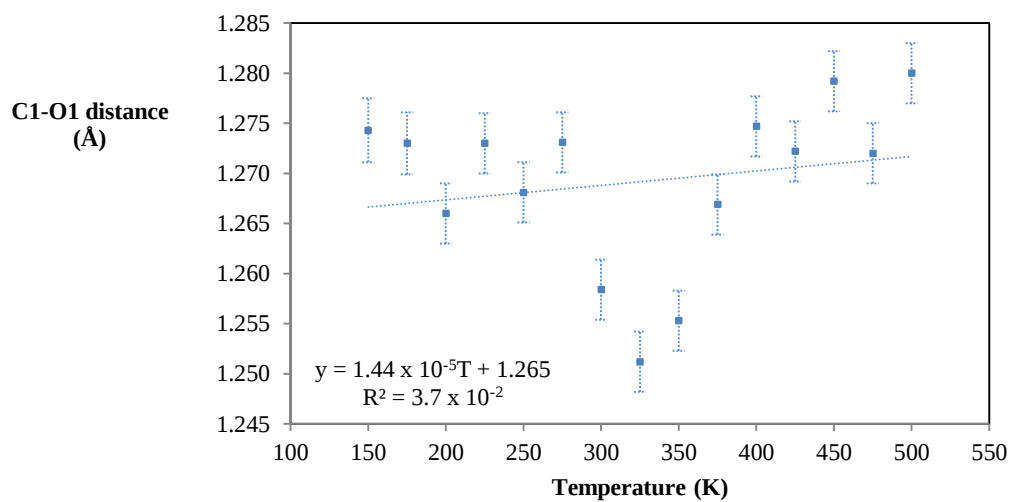
(a)



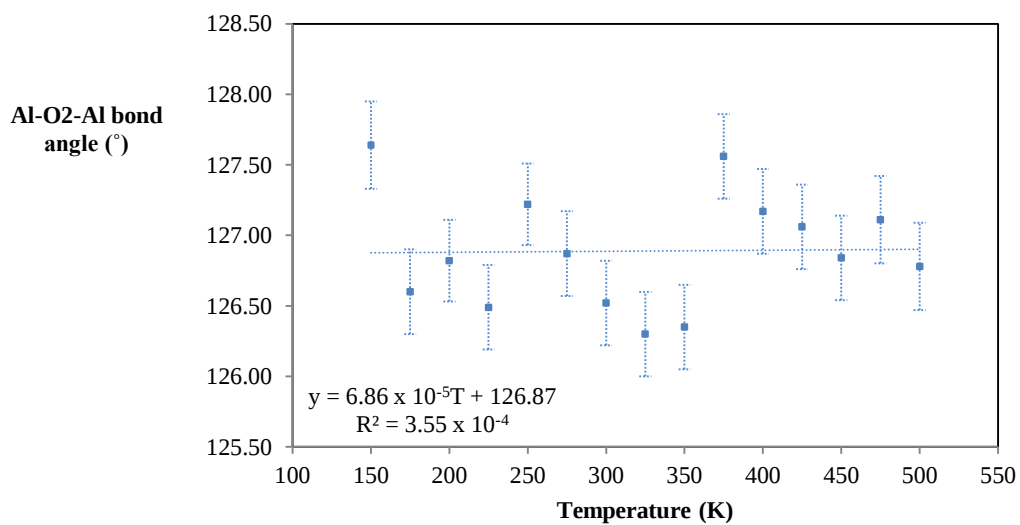
(b)



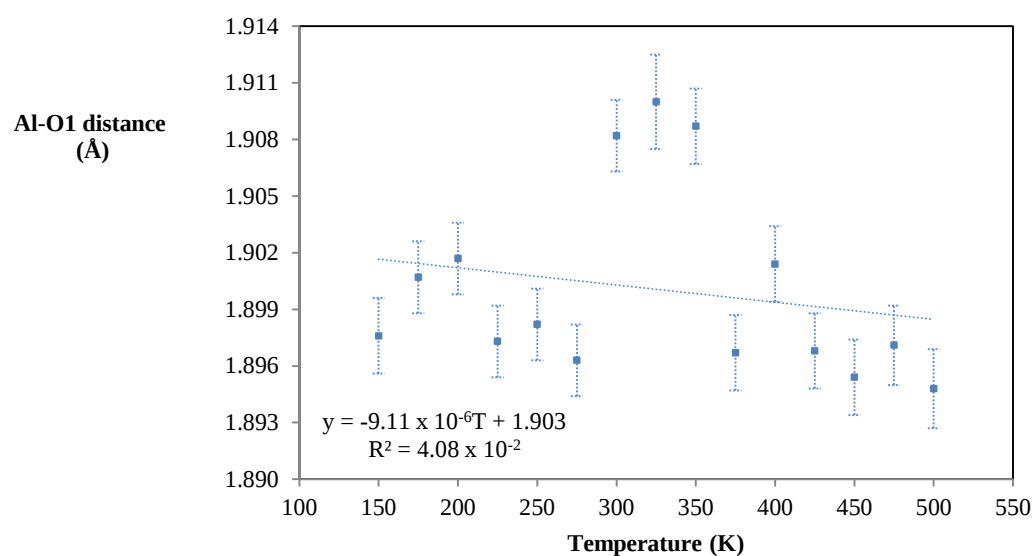
(c)



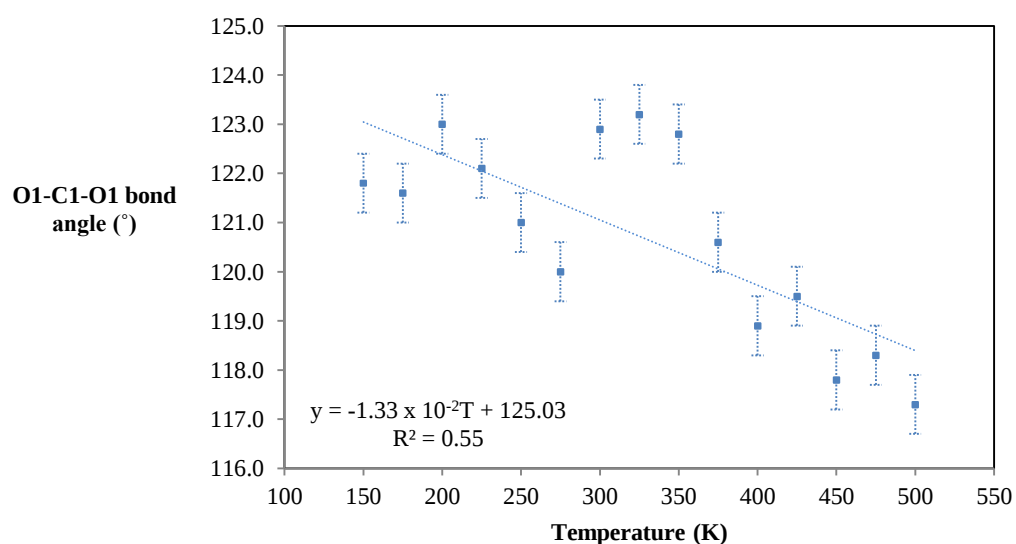
(d)



(e)



(f)



(g)

Figure 4.15 The variation of the observed geometric parameters as a function of temperature (a) the Al...Al adjacent non-bonding distance (b) the O1...O1 non-bonding distance (c) the Al-O2 distance (d) C1-O1 distance (e) Al-O2-Al bond angle (f) Al-O1 distance (g) O1-C1-O1 bond angle. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

Thermal expansion of the structure along the *c*-axis direction and contraction along the *b*-axis direction is observed over the temperature range studied. The mechanism behind this behaviour may be explained by considering one of the rhombus-shaped channels in the (100) plane, as shown in **Figure 4.16**

(a), that is bounded by four bdc ligands with Al atoms at the vertices of the rhombus.

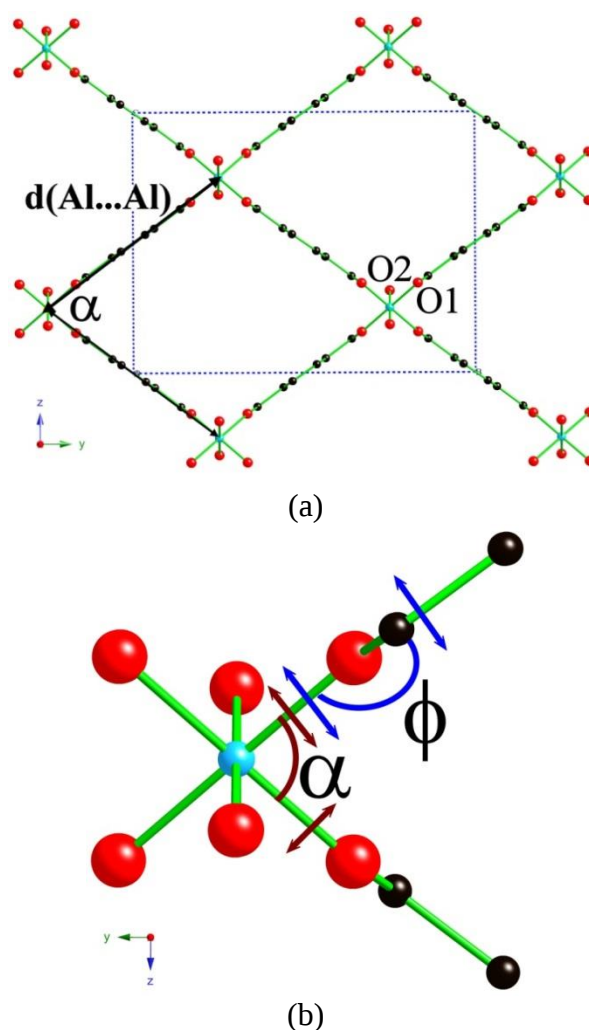
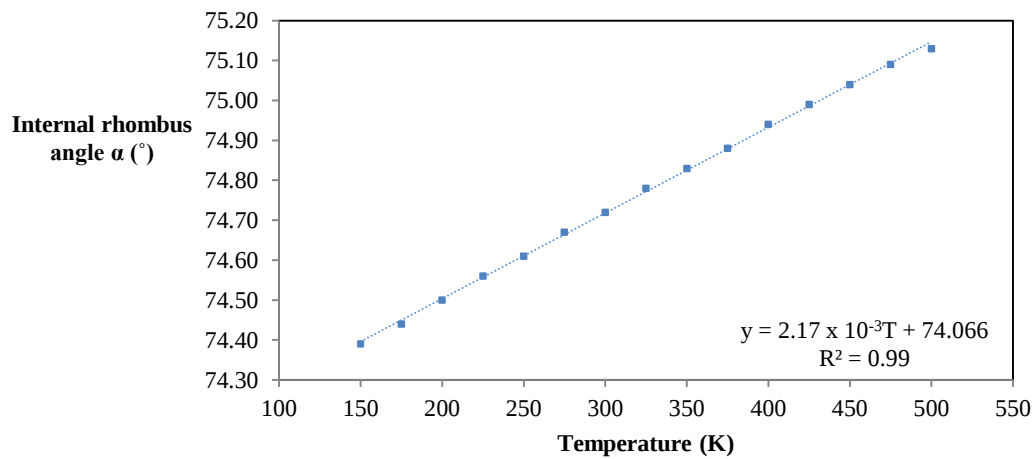


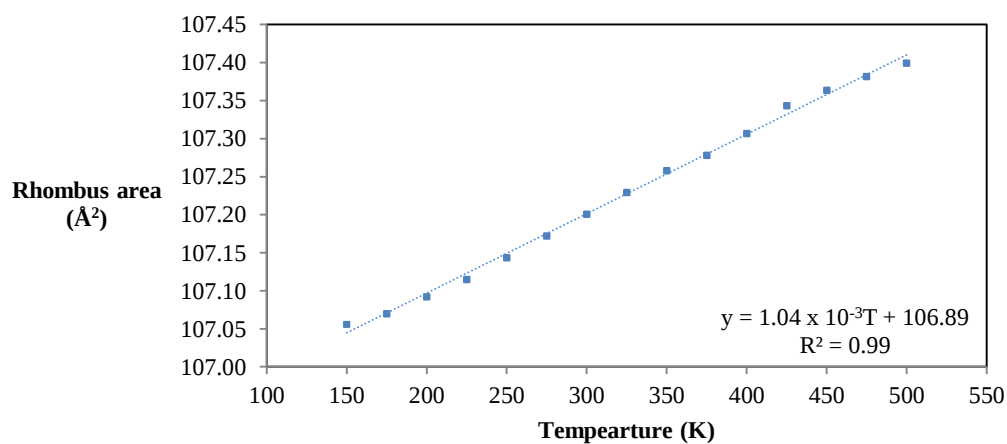
Figure 4.16 (a) A schematic illustrating rhombus-shaped channel viewed in the (100) plane. A rhombus is made by four bdc ligands linked by the aluminium atom at each vertex. The non-bonding distance $\text{Al}\dots\text{Al}$, $d(\text{Al}\dots\text{Al})$ corresponds to the distance from the aluminium atom at a vertex to the adjacent one. (b) A schematic showing the internal rhombus angle, α and the bending angle about the O...O vector, ϕ . The blue, red and black balls represent aluminium, oxygen and carbon atoms respectively.

The bdc linkers rotate around the $-\text{Al}-\text{OH}-\text{Al}-$ chain running through the core of the corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra as the temperature increases and as shown schematically in **Figure 4.16** (b). This process is reflected in the linear decrease of the internal rhombus angle, α , defined in **Figure 4.16** (a), (b) and as shown graphically in **Figure 4.17** (a), the linear increase of the rhombus area as

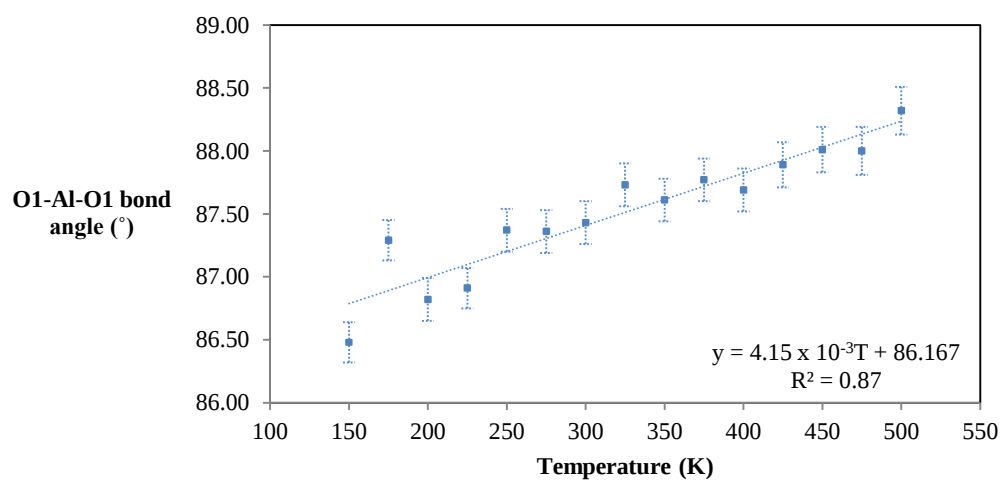
shown in **Figure 4.17 (b)** and the change of the internal O1-Al-O1 angles as shown in **Figure 4.17 (c)**.



(a)



(b)



(c)

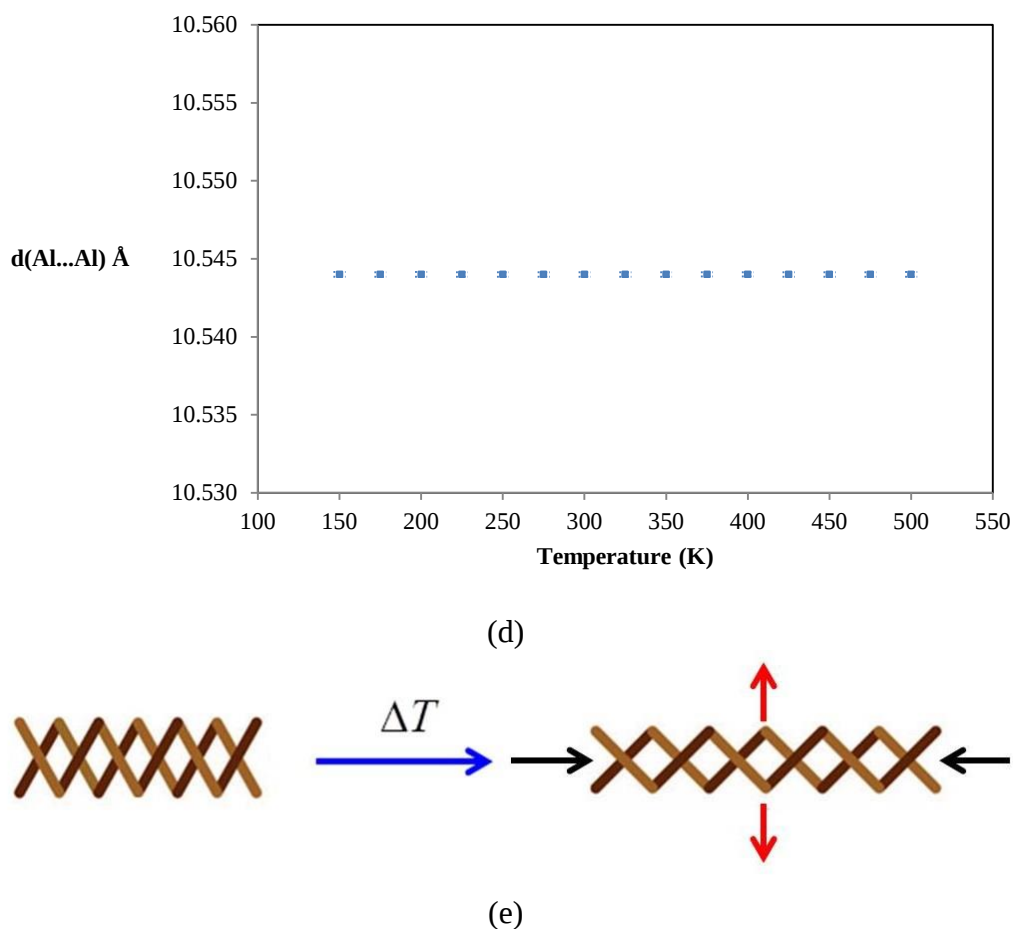


Figure 4.17 (a) The variation of the internal rhombus angle α as a function of temperature. (b) The linear increase of the rhombus area as a function of temperature (c) The decrease of the O1-Al-O1 bond angle as a function of the temperature (d) The variation of $d(\text{Al}\dots\text{Al})$ non-bonding distance as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point. (e) An illustration of the “wine rack” thermo-mechanical mechanism. The red and black arrows indicate the direction of expansion and contraction respectively.^[44]

The sides of the rhombus remain constant in length during this process with a distance, $d(\text{Al}\dots\text{Al})$ as defined in **Figure 4.16** (a), of 10.544(1) Å and is shown graphically in **Figure 4.17** (d). The connectivity of the framework means that these structural factors are coupled to give a “wine rack” thermo-mechanical mechanism of expansion for $[\text{Al}(\text{OH})(\text{bdc})]$ in the (100) plane, similar to that reported for other non-carboxylate containing MOFs.^[45] The “wine rack” thermo-mechanical mechanism is illustrated in **Figure 4.17** (e). The observation of such a mechanism demonstrates that the $\text{AlO}_4(\text{OH})_2$ octahedra are not rigid octahedra in

terms of angular deformation and rotation of the bdc linkers around the -Al-OH-Al- chain running through the core of the corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra is a lower energy process relative to the “knee cap”^[46] bending mode of the carboxylate group and the Al-OH-Al unit about the O-O vector of the carboxylate group by an angle ϕ as shown schematically in **Figure 4.16** (b).

The $[\text{Al}(\text{OH})(\text{bdc})]$ becomes a more open structure over the full temperature range from its *np* to *lp* form and to a more open *lp* form. This change is driven by a reduction in internal energy as the internal O1-Al-O1 angles converge towards the more favourable regular values of 90° and possible associated energetic gains in the framework as the $\text{AlO}_4(\text{OH})_2$ octahedra become more regular in the AlO_4 plane. These results indicate that the thermo-mechanical behaviour of $[\text{Al}(\text{OH})(\text{bdc})]$ can be deconstructed into mechanical building units (XBUs) consisting of rigid bdc linker struts and $\text{Al}_2(\text{OH})(\text{CO}_2)_2$ hinges in a manner described recently^[47] providing possibilities to design the mechanical properties of MOFs.

4.3 Thermoresponsive behaviour of [AlF(bdc)]

4.3.1 Synthesis and activation

The synthesis of [AlF(bdc)] was developed from the previously reported method^[31] with replacement of the DMF (*N,N*-dimethylformamide) solvent by DEF (*N,N*-diethylformamide). All chemicals involved in the synthesis were used without further purification. AlF₃ (Sigma-Aldrich, 99.9 %, 0.0084 g) was dissolved in DEF (TCI, 99 %, 10 ml) followed by addition of H₂bdc (Sigma-Aldrich, 98 %, 0.996 g). The mixture was then placed into a 23 ml Teflon-lined stainless steel autoclave. The mixture was heated to 220 °C for 4 days and cooled down naturally to room temperature. The mother liquor was filtered off leaving a white fine powder product. The product was washed with 20 ml of DMF and then stirred overnight with 15 ml of methanol. The powder was recovered by filtration and dried at 70 °C before calcination. The calcination was performed in air at 300 °C for 24 hours in order to remove any guest molecules from the pore of the framework. The powder pattern of the calcined sample is shown in **Figure 4.18** and confirmed that a phase pure [AlF(bdc)] has been made.

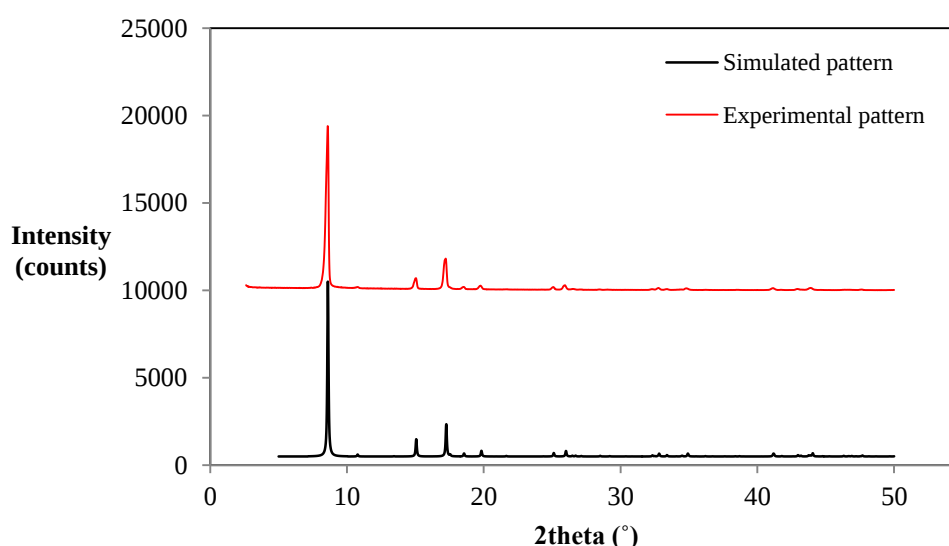


Figure 4.18 The powder pattern of [AlF(bdc)] plotted in comparison with the simulated powder pattern.

4.3.2 Thermogravimetric analysis of [AlF(bdc)]

The TGA curve of [AlF(bdc)] shows one significant mass loss at ~ 500 °C as shown in **Figure 4.19** which suggests that [AlF(bdc)] does not adsorb any water molecules from the atmosphere. The mass loss observed is ~ 42 % (calculated 78.04 %). This corresponds to partial decomposition of the bdc molecules resulting framework collapse. The difference between the observed and the calculated mass loss is due to the incomplete decomposition of the framework which is aided by the relatively low final temperature point in the TGA experiment.

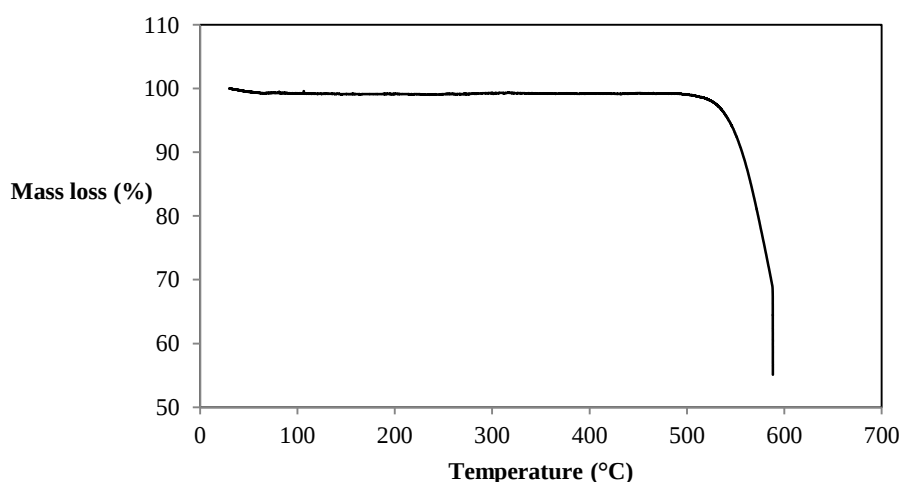


Figure 4.19 Thermogravimetric analysis data of [Al(F)(bdc)] performed under air at a heating rate of $2^{\circ}\text{Cmin}^{-1}$.

4.3.3 Solid state NMR studies of [AlF(bdc)]·(guest molecule) and [AlF(bdc)]

The solid state NMR (SSNMR) spectra for ^{19}F and ^{27}Al were collected using a Bruker 400 spectrometer. An operating frequency of 376.50 MHz, a sample spinning speed of 13 kHz and recycle delays of 5 seconds were used while collecting the ^{19}F SSNMR spectrum. In the case of ^{27}Al SSNMR, an operating frequency of 104.26 MHz, a sample spinning speed of 12 kHz and recycle delays of 5 seconds were used.

The ^{19}F SSNMR spectrum of the $[\text{AlF}(\text{bdc})]\cdot(\text{guest molecule})$ is shown in **Figure 4.20**. One broad peak positioned at -151.74 ppm is evident while spinning sidebands are denoted by asterisks. The chemical shift is in agreement with the other systems containing fluorinated aluminium. For instance, the ^{19}F chemical shift of $\text{AlF}_x\text{O}_{6-x}$ ($1 < x < 5$) lies between -130 ppm to -160 ppm,^[48] and in a similar system such as $\text{Al}_2[\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3](\text{H}_2\text{O})_2\text{F}_2\cdot\text{H}_2\text{O}$, the ^{19}F chemical shift is -144.2 ppm.^[49]

The ^{27}Al SSNMR spectrum is shown in **Figure 4.21** and shows two significant broad peaks situated over the range of -1.76 to -6.44 ppm and at -52.10 ppm. The broadening of the peak is due to the effect of the quadrupole nature of the ^{27}Al nuclear. The ^{27}Al chemical shifts of first broad peak over the range of -1.76 - -6.44 ppm are attributed to octahedrally coordinated alumina as the ^{27}Al chemical shift is intermediate between those for octahedral AlO_6 and AlF_6 whose chemical shifts lie in the range of 3 ppm to -9 ppm.^[50] A small singlet at -52.10 ppm possibly belongs to an unidentified impurity.

The ^{19}F SSNMR spectrum of $[\text{AlF}(\text{bdc})]$ is shown in **Figure 4.22** and shows a peak positioned at -153.89 ppm with the spinning sidebands marked by asterisks. This confirms the presence of one crystallographically independent fluorine site which agrees well with the crystal structure of $[\text{AlF}(\text{bdc})]$. The chemical shift found is similar to that found for other similar systems. Also, a small singlet positioned at 158.51 ppm, integrated to be 0.6 % was also present in the spectrum. The presence of a small singlet may possibly from the presence of a minor phase impurity in the sample or from slightly distorted coordination containing Al-F bond octahedra.^[51]

The ^{27}Al SSNMR spectrum as shown in **Figure 4.23** shows a broad peak situated over the range of -1.76 to -6.44 ppm. This suggests only one crystallographically independent aluminium site, in a good agreement with the reported crystal structure. The chemical shift found is also similar to that reported for other octahedrally coordination AlO_6 units.^[52]

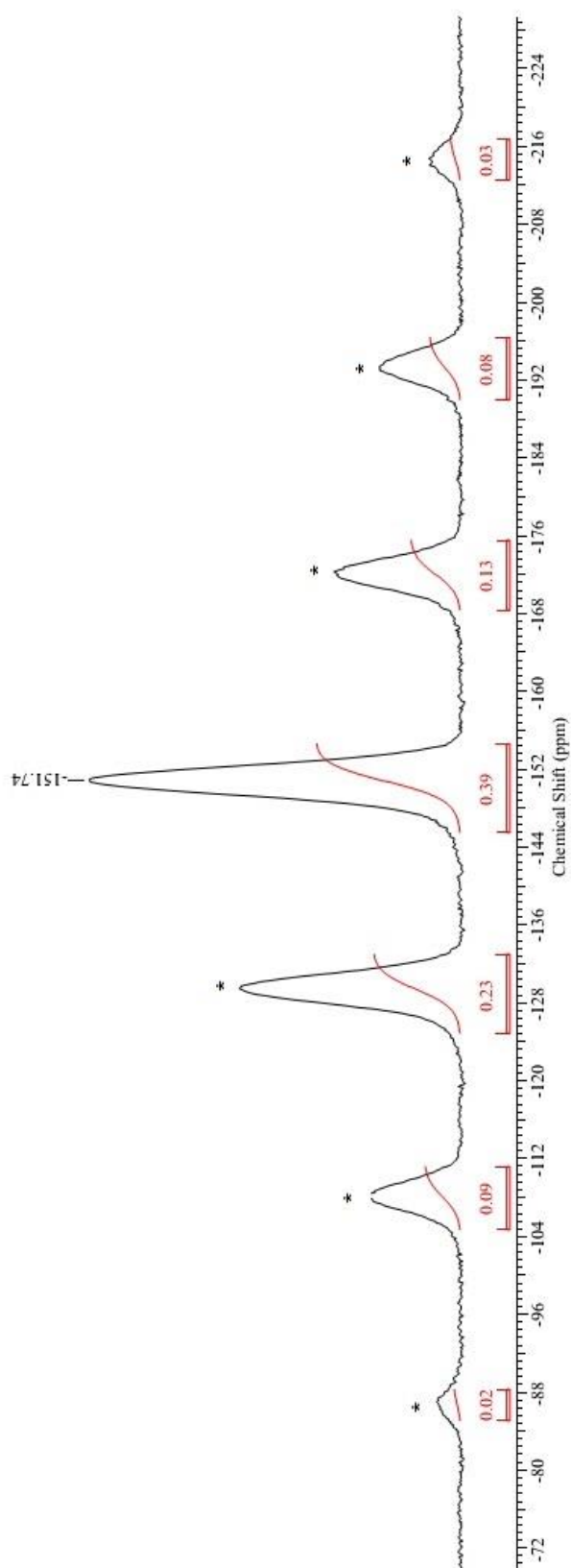


Figure 4.20 The ^{19}F SSNMR spectrum of the $[\text{AlF}(\text{bdc})]\cdot(\text{guest molecule})$. Spinning sidebands are marked by asterisks.

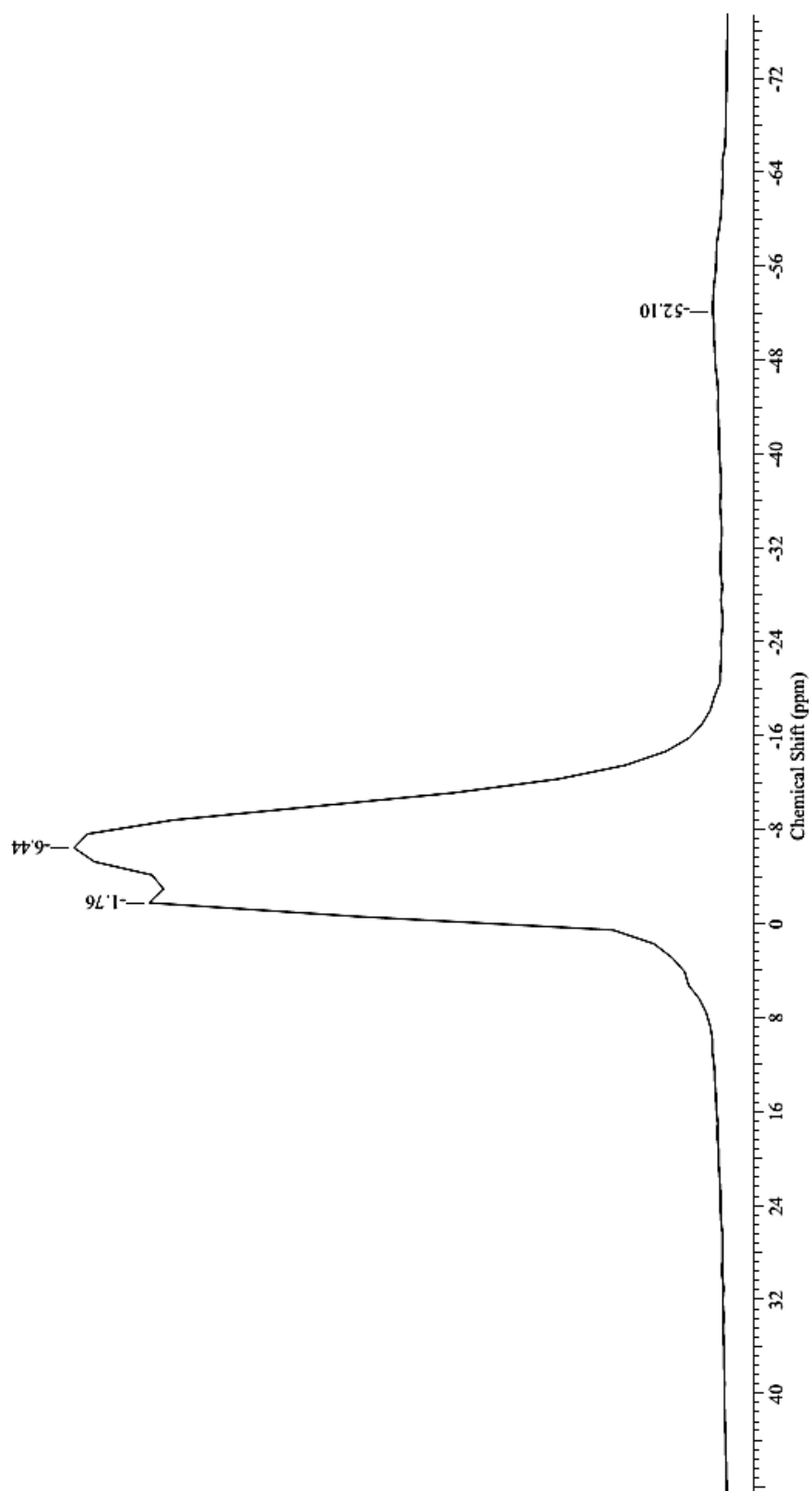


Figure 4.21 The ^{27}Al SSNMR spectrum of the $[\text{AlF}(\text{bdc})]\cdot(\text{guest molecule})$.

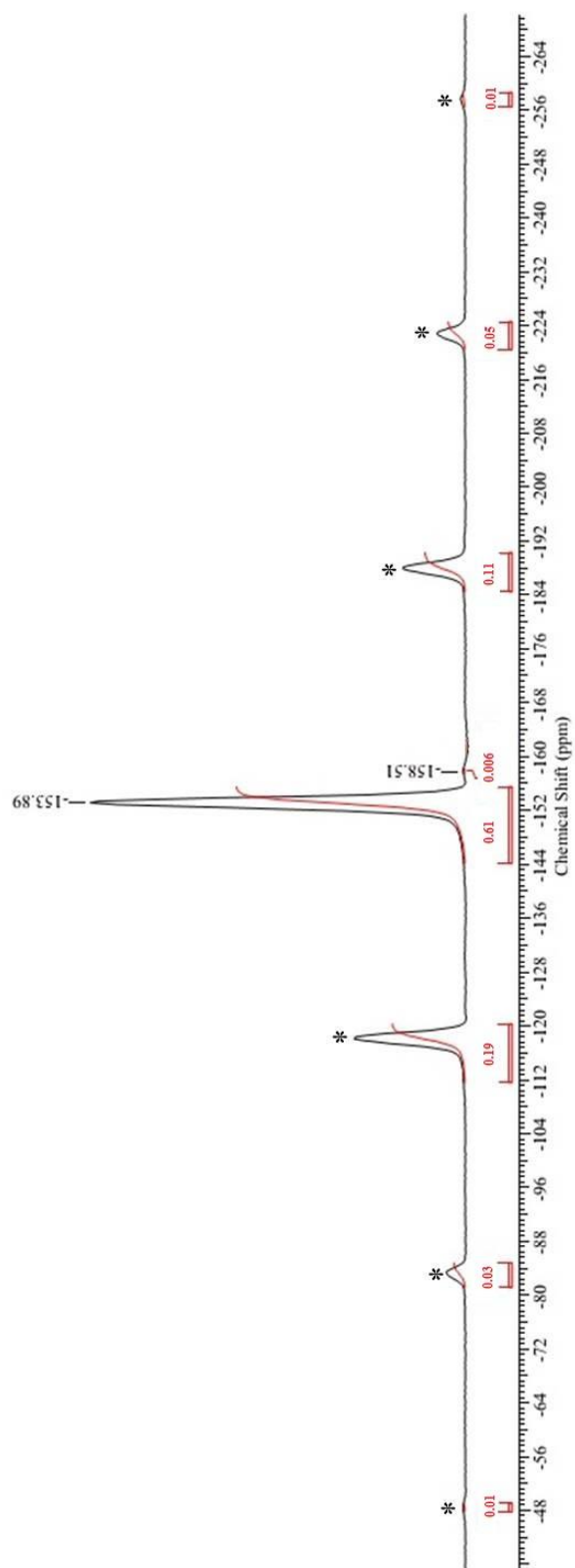


Figure 4.22 The ^{19}F SSNMR spectrum of the $[\text{AlF}(\text{bdc})]$. Spinning sidebands are marked by asterisks.

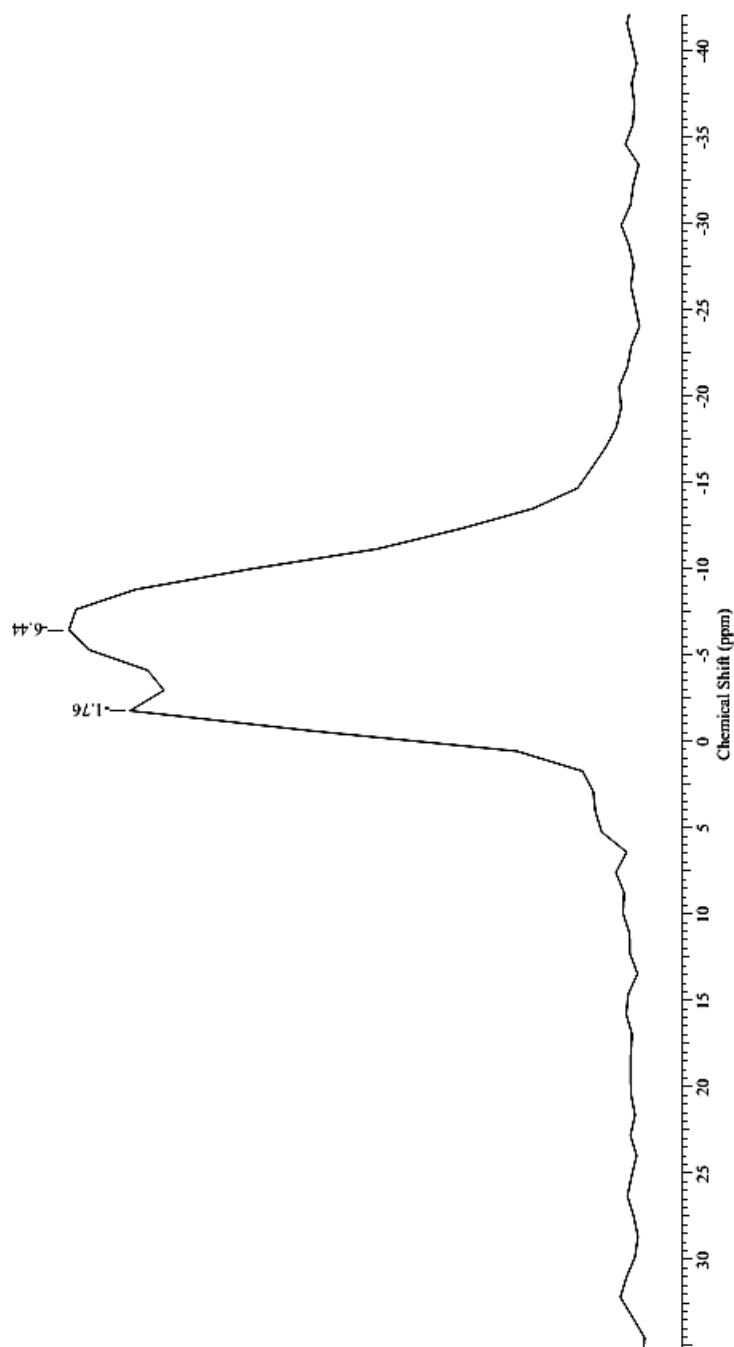


Figure 4.23 The ^{27}Al SSNMR spectrum of the calcined $[\text{AlF}(\text{bdc})]$.

4.3.4 The N_2 gas adsorption in $[\text{AlF}(\text{bdc})]$

The N_2 gas adsorption of $[\text{AlF}(\text{bdc})]$ was performed on a Micromeritics ASAP 2010. The adsorption and desorption isotherms are shown in **Figure 4.24**. No hysteresis was observed during desorption. $[\text{AlF}(\text{bdc})]$ shows a type-I N_2

adsorption isotherm as observed for many microporous solids.^[53-54] The Langmuir (if assuming the adsorption is monolayer) and the BET surface area are $1286.63 \pm 2.83 \text{ m}^2\text{g}^{-1}$ and $1020.52 \pm 17.08 \text{ m}^2\text{g}^{-1}$ respectively. These values are comparable with the surface area of other members of the MIL-53 family in the *lp* form as shown in **Table 4.5**.

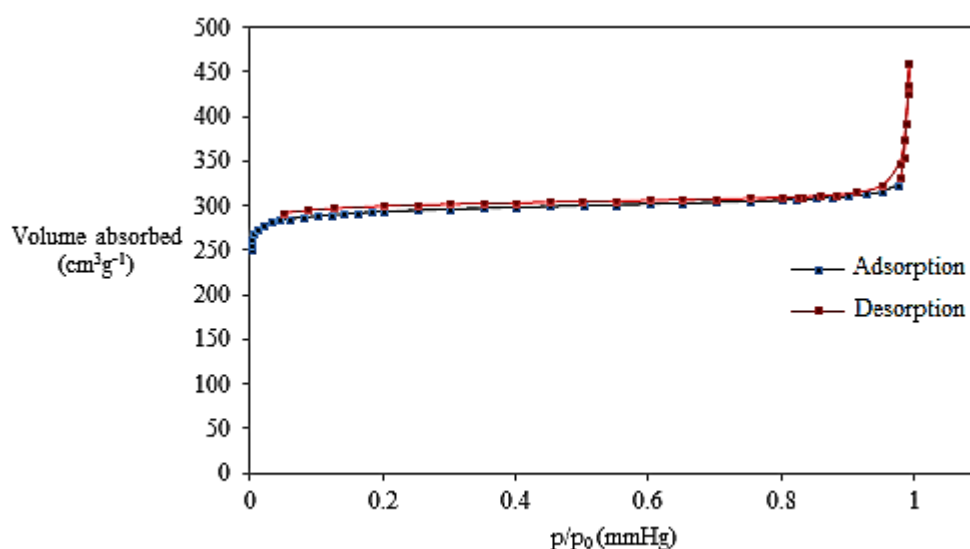


Figure 4.24 N₂ adsorption isotherm of [AlF(bdc)] measured at 77 K.

Table 4.5 Summary of the Langmuir and the BET surface areas of [Al(F)(bdc)], [Al(OH)(bdc)], [Cr(OH)(bdc)] and [VO(bdc)].

Materials	Langmuir surface area (m^2g^{-1})	BET surface area(m^2g^{-1})
[AlF(bdc)]	1286(3)	1020(17)
[Al(OH)(bdc)] ^[27]	1590(1)	1140(39)
[Cr(OH)(bdc)] ^[26]	1500	1150
[VO(bdc)] ^[23]	1320(2)	930(30)

4.3.5 Synchrotron powder thermodiffraction study

4.3.5.1 *Sample preparation prior to data collection*

The calcined sample was packed in two separate capillary tubes as the thermodiffraction study of [AlF(bdc)] was carried out in two parts over the temperature range 10 – 290 K (experimental run 1) and over the temperature range of 100 – 500 K (experimental run 2). These two experiments overlapped in the temperature range 100 – 290 K.

The thermodiffraction study in experimental run 1 required the sample to be packed in an aluminium capillary tube to allow better heat conduction during cooling. A downside of using an aluminium capillary tube is that the reflections of aluminium are present together with the reflections of the sample in the powder X-ray diffraction patterns. The thermodiffraction patterns in experimental run 2 were collected from a sample packed in a borosilicate capillary tube.

The process of packing and activation of the sample was similar in both samples. The samples were packed into 0.5 mm diameter capillary tubes to a length of 4 centimetres before being heated at 200 °C under a vacuum of 2.1×10^{-1} mbar for 24 hours. The degassed sample packed in the borosilicate capillary tube was flame-sealed under vacuum, whereas the sample packed in the aluminium capillary tube was clamped under vacuum and further sealed with super glue.

4.3.5.2 *Data collection*

Both of the thermodiffraction studies of [AlF(bdc)] were performed at the I11, Diamond Light Source (DLS), UK. In the experimental run 1, the aluminium tube was placed in a copper block which was later placed on the cold stage of the PheniX cryostat. After sample alignment in the copper block was done, the sample stage was covered by an outer cover in order to maintain the temperature at the sample stage while collecting data.

For experiment run 1, the sample was rocked during the data collection to reduce preferred orientation and sampling effects. Diffraction data were collected from 3° to 140° 2θ with a 2θ step size of 0.001° . The mean wavelength used was $0.827154(1)$ Å. The diffraction data were collected at 11 K, 40 K, 70 K, 100 K, 150 K, 200 K, 250 K and 290 K. The data collection time was 30 minutes per temperature. The powder X-ray diffraction patterns were rebinned to 0.003° and were analysed using Rietveld structure refinement.

For experimental run 2, the diffraction data were collected over the temperature range of 100 – 500 K at 25 K intervals using the same procedure as that described in section 4.2.2.1. The mean wavelength used was $0.825993(3)$ Å. The powder patterns were collected from 3° to 140° with a step size of 0.001° where the data collect time for each pattern was 30 minutes. The powder X-ray diffraction patterns were rebinned to 0.003° before the Rietveld refinements were performed.

4.3.5.3 *Data analysis*

The synchrotron powder diffraction data were fitted using the Le Bail method to obtain appropriate lattice parameters and starting peak shape profile coefficients. The crystal structure of [AlF(bdc)] reported previously (orthorhombic, *Imma*, $a = 6.550(1)$ Å, $b = 16.250(4)$ Å and $c = 13.378(2)$ Å), designated ortho-*lp* AlF(bdc)], was used as a starting model for the Le Bail fit of the powder X-ray diffraction pattern of the experiment run 2 collected from 500 K to 175 K. The profile fitting was done on the 9348 data points in the range of 3° to 40° 2θ . The first reflection of [AlF(bdc)] was excluded from the diffraction patterns. The background was fit using linear interpolation between manually designated background points. Peak shape fitting was conducted by using the fourth profile option in the GSAS program suite which is a modified pseudo-Voigt function that accounts for the effect of microstrain broadening.

The lattice parameters and the peak shape profile coefficients were further used in the Rietveld refinement. The final cycle of least squares refinement of ortho-**lp** [AlF(bdc)] consisted of 28 variables including the scale factor, detector zero point, unit cell parameters, peak shape profile parameters, atomic coordinates and isotropic atomic displacement parameter (U_{iso}) of all six atoms in the asymmetric unit. The U_{iso} of the F and O atoms were constrained to have the same value, as were those of the C atoms.

For the powder X-ray diffraction patterns from 150 K to 11 K, some extra reflections were observed as denoted by arrows as shown in **Figure 4.25**.

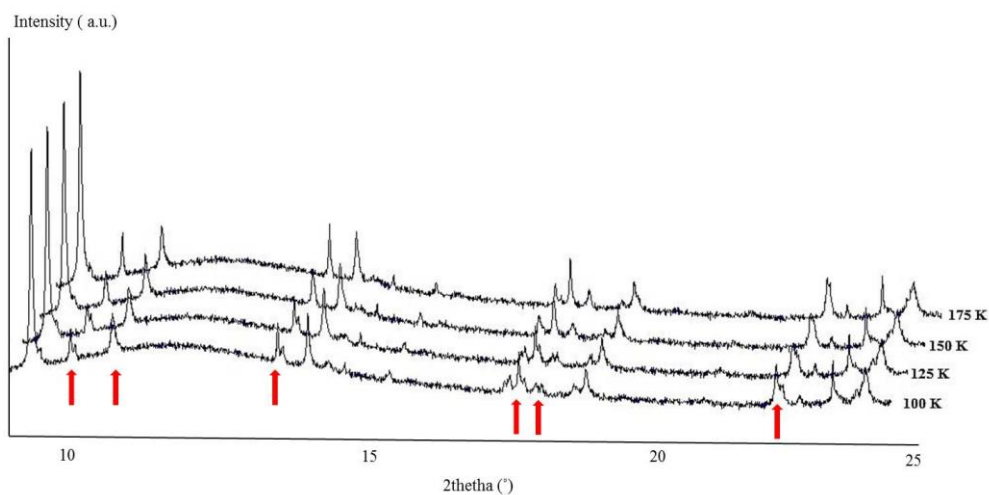


Figure 4.25 The synchrotron powder X-ray diffraction patterns of [AlF(bdc)] from 100 K to 175 K show the splitting of some peaks (designated by red arrows) upon cooling.

This peak splitting indicates that the symmetry of the crystal structure of ortho-**lp** [AlF(bdc)] has changed from the space group *Imma* to a lower symmetry space group with orthorhombic or lower crystal symmetry. Orthorhombic space groups with the lowest symmetry were considered first but were unable to account for extra reflections. Monoclinic symmetry was then considered by systematically allowing the unit cell angle α , β and γ values to be refined individually to try to generate the additional reflection positions. A variation of γ was found to yield the correct 2θ position of reflections that match with the observed extra reflections.

The new monoclinic space group of *I112/b* was chosen to index the pattern as it is a subgroup of *Imma*.

The new space group obtained was then used in the Le Bail fit of the powder X-ray diffraction data collected at the temperature below 175 K. Once the Le Bail fit was succeeded a new crystal structure adapted from the *Imma* crystallographic model which allowed for this reduction in symmetry was generated. This model was obtained by determining the atoms generated from the O1 and C1 atoms on *2/m* positions in *Imma* on reducing the symmetry to *I112/b*.

The new crystal structure designated as mono-*lp* [AlF(bdc)] was used as the starting model for the Rietveld refinement of the powder X-ray diffraction data below 175 K in the experimental run 2. For the refinements from the experimental run 1, the mono-*lp* [AlF(bdc)] model was used to refine the data sets at 11, 40, 70, 100 and 150 K and the ortho-*lp* [AlF(bdc)] was used at 200, 250 and 290 K.

In the experiment run 1 at 100 K, the profile fitting was done on the 8882 data points in the range of 3° to 40° 2 θ . The reflections of aluminium and the first reflection of [AlF(bdc)] were excluded from the powder X-ray diffraction patterns. The background was fitted in a similar way as that in the experimental run 2, as was the peak shape function.

The final cycle of least square refinement of mono-*lp* [AlF(bdc)] at 100 K consisted of 40 variables including the scale factor, detector zero point, unit cell parameters, peak profile parameters, atomic coordinates and isotropic atomic displacement parameters (U_{iso}) of all eight atoms in the asymmetric unit. The U_{iso} of the F and O atoms were constrained to have the same value, as were those of the C atoms.

The crystallographic data for the mono-*lp* [AlF(bdc)] at 100 K and the ortho-*lp* [AlF(bdc)] at 300 K are summarised in **Table 4.6** and **Table 4.7** respectively. The final atomic coordinates, occupancies and isotropic atomic displacement parameters of the mono-*lp* [AlF(bdc)] at 100 K and the ortho-*lp* [AlF(bdc)] at 300 K are given in **Table 4.8** and **Table 4.9** respectively. Selected

bond lengths and bond angles of the mono-*lp* [AlF(bdc)] at 100 K and the ortho-*lp* [AlF(bdc)] at 300 K are given in **Table 4.10** and **Table 4.11** respectively. The asymmetric unit of the mono-*lp* [AlF(bdc)] and the ortho-*lp* [AlF(bdc)] are shown in **Figure 4.26**. The final observed, calculated and difference plot for the Rietveld refinement at 100 K is shown in **Figure 4.27** and at 300 is shown in **Figure 4.28** for the plot at 300 K. These are representative final results and all the refinements of all data sets are given in the attached appendix of the CD.

Table 4.6 Crystal data and structure refinement parameters for mono-*lp* [AlF(bdc)] at 100 K

Formula	[AlFC ₈ H ₄ O ₅]
Formula weight	225
Density (gcm ⁻³)	0.967
Temperature (K)	100
Wavelength (Å)	0.827154(1)
Space group	<i>I112/b</i>
a (Å)	6.5559(1)
b (Å)	16.4362(4)
c (Å)	13.1422(4)
γ (°)	90.488(1)
V (Å ³)	1416.09(6)
Z	4
R _p	0.0747
R _{wp}	0.1008
R _F	0.1124
χ ²	6.863
Number of refined parameters	40
Scale factor	39.5(1)
Zero point (°)	-0.0055(2)
Gaussian profile coefficients	GU = 0, GV = 0. GW = 0
Lorentzian profile coefficients	LX = 0.93(8)
eta	0.720(8)
ptec	-0.1(1)
Microstrain broadening coefficients	S400 = 0.08(8), S040 = 0.070(2), S004 = 0.037(1), S220 = 0.039(4), S202 = 0.078(8), S022 = -0.105(3), S130 = -0.448(5), S310 = 0.06(1), S112 = 0.052(5)

Table 4.7 Crystal data and structure refinement parameters for ortho-*lp* [AlF(bdc)]

Formula	[AlFC ₈ H ₄ O ₅]
Formula weight	225
Density (gcm ⁻³)	0.965
Temperature (K)	300
Wavelength (Å)	0.825993(3)
Space group	<i>Imma</i>
a (Å)	6.5678(2)
b (Å)	16.4055(5)
c (Å)	13.1687(6)
V (Å ³)	1418.90(8)
Z	4
R _p	0.0331
R _{wp}	0.0424
R _F	0.0829
χ ²	2.995
Number of refined parameters	30
Scale factor	5.04(3)
Zero point (°)	-0.0097(2)
Gaussian profile coefficients	GU = 31.61±11.58, GV = -1.53±3.16, GW = 1.8(2)
Lorentzian profile coefficients	LX = 0.00, LY = 0.00
eta	0.80(1)
Microstrain broadening coefficients	S400 = 0.06(2), S040 = 0.105(4), S004 = 0.5972(1) S220 = 0.029(5), S202 = 0.051(1), S022 = -0.163(4)

Table 4.8 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for mono-*lp* [Al(F)(bdc)] at 100 K

Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Al	0.25	0.25	0.75	3.5(1)	1
F	0.0	0.25	0.6917(4)	1.4(8)	1
O1	0.1631(6)	0.1732(3)	0.8535(4)	1.4(8)	1
O2	-0.1801(7)	0.6606(3)	-0.8330(5)	1.4(8)	1
C1	-0.0028(13)	0.1371(5)	0.8660(6)	2.3(1)	1
C2	-0.0020(18)	0.0641(4)	0.9444(6)	2.3(1)	1
C3	-0.2003(13)	0.0232(6)	-0.0469(7)	2.3(1)	1
C4	0.1925(14)	0.5384(6)	-0.9720(8)	2.3(1)	1

Table 4.9 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for ortho-*lp* [AlF(bdc)] at 300 K

Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Al	0.25	0.25	0.75	2.2(2)	1
F	0.0	0.25	0.6939(6)	1.7(1)	1
O1	0.1694(6)	0.16805(25)	0.84016(35)	1.7(1)	1
C1	0.0	0.1376(7)	0.8698(9)	2.3(2)	1
C2	0.0	0.0644(6)	0.9479(9)	2.3(2)	1
C3	-0.1932(7)	0.0298(6)	0.9591(7)	2.3(2)	1

Table 4.10 Selected bond lengths (Å) and bond angles (°) for mono-*lp*-[AlF(bdc)] at 100 K

Al—F (x 2)	1.809(2)	F ¹ —Al—O2 ²	88.93(16)
Al—O1 (x 2)	1.938(5)	F ¹ —Al—O2 ³	91.07(16)
Al—O2 ² (x 2)	1.890(4)	O1—Al—O1 ¹	180.0
C1—O1	1.245(8)	O1—Al—O2 ²	91.7(2)
C1—O2 ⁵	1.302(8)	O1—Al—O2 ³	88.3(2)
C1—C2	1.582(7)	O1 ¹ —Al—O2 ²	88.3(2)
C2—C3 ⁸	1.463(10)	O1 ¹ —Al—O2 ³	91.7(2)
C3—C4 ⁷	1.413(8)	O2 ² —Al—O2 ³	180.0
C4—C2 ⁶	1.394(10)	Al—F—Al ⁴	129.9(3)
		O1—C1—O2 ¹⁰	126.4(7)
F—Al—F ⁹	180.0	O1—C1—C2	116.0(8)
F—Al—O1	92.04(15)	O2 ⁶ —C1—C2	116.8(8)
F—Al—O1 ¹	87.96(15)	C2 ¹⁴ —C3—C4 ⁷	110.2(8)
F—Al—O2 ²	91.07(16)	C3 ⁸ —C2—C1	113.0(10)
F—Al—O2 ³	88.93(16)	C3 ⁸ —C2—C4 ¹²	130.7(7)
F ¹ —Al—O1	87.96(15)	C1—C2—C4 ¹²	114.1(9)
F ¹ —Al—O1 ¹	92.04(15)	C3 ¹³ —C4—C2 ¹⁴	115.9(8)

Symmetry transformations used to generate equivalent atoms:

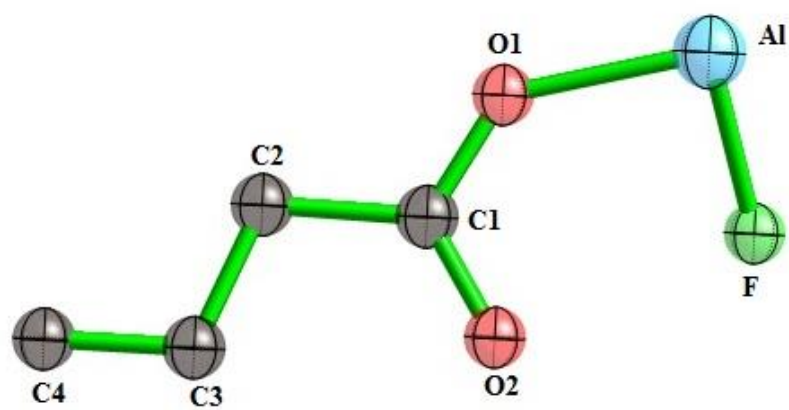
(1) $-x-1/2, -y-1/2, -z+1/2$; (2) $-x, -y+1, -z$; (3) $x+1/2, y-1/2, z+3/2$; (4) $-x, -y+1/2, z$; (5) $x, y-1/2, -z$; (6) $x, y+1/2, -z$; (7) $-x, -y+1/2, z+1$; (8) $x, y, z+1$; (9) $-x+1/2, -y+3/2, -z+3/2$; (10) $x-1, y-1/2, -z-1$; (11) $x, y, z-1$; (12) $x, y+1/2$; (13) $-x, -y+1/2, z-1$; (14) $x, y+3/2$.

Table 4.11 Selected bond lengths (Å) and bond angles (°) for ortho-*lp* [AlF(bdc)] at 300 K

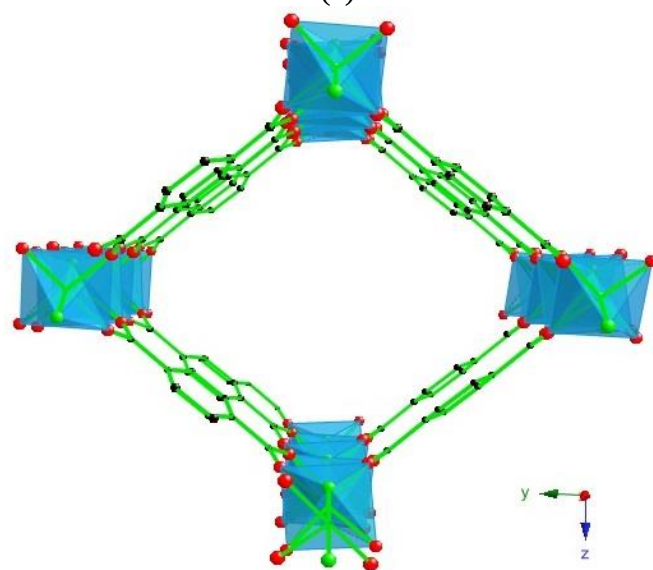
Al—O1 (x 4)	1.870(3)	F ⁵ —Al—O1 ⁶	90.14(19)
Al—F (x 2)	1.800(3)	O1—Al—O1 ¹	91.9(3)
C1—O1 (x 2)	1.281(5)	O1—Al—O1 ⁵	180.0
C1—C2	1.580(10)	O1—Al—O1 ⁶	88.1(3)
C2—C3 (x 2)	1.382(3)	O1 ¹ —Al—O1 ⁵	88.1(3)
C3—C3 ³ (x 2)	1.454(11)	O1 ¹ —Al—O1 ⁶	180.0
		O1 ⁵ —Al—O1 ⁶	91.9(3)
F—Al—F ⁴	180.0	Al—F—Al ²	131.6(4)
F—Al—O1	90.14(19)	O1—C1—O1 ²	120.6(9)
F—Al—O1 ¹	90.14(19)	O1—C1—C2	119.6(5)
F—Al—O1 ⁵	89.86(19)	C3—C2—C1	112.2(6)
F—Al—O1 ⁶	89.86(19)	C3 ³ —C3—C2	110.6(6)
F ⁵ —Al—O1	89.86(19)	C3—C2—C3 ²	130.3(11)
F ⁵ —Al—O1 ¹	89.86(19)		
F ⁵ —Al—O1 ⁵	90.14(19)		

Symmetry transformations used to generate equivalent atoms:

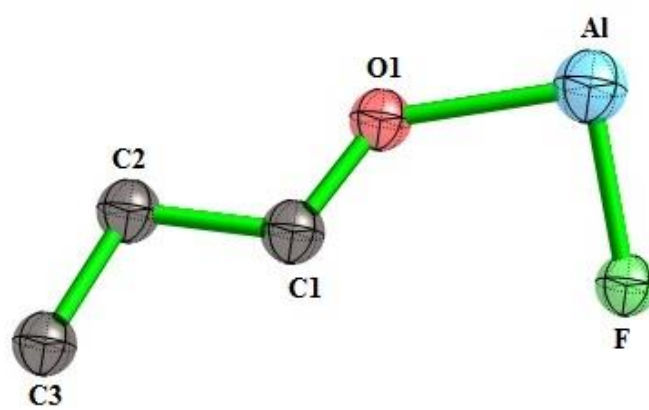
(1) $x, -y+1/2, z$; (2) $-x, y, z$; (3) $x, -y, -z+2$; (4) $-x+1/2, -y-1/2, -z+3/2$; (5) $-x+1/2, -y+3/2, -z+3/2$; (6) $-x+1/2, y+1, -z+3/2$.



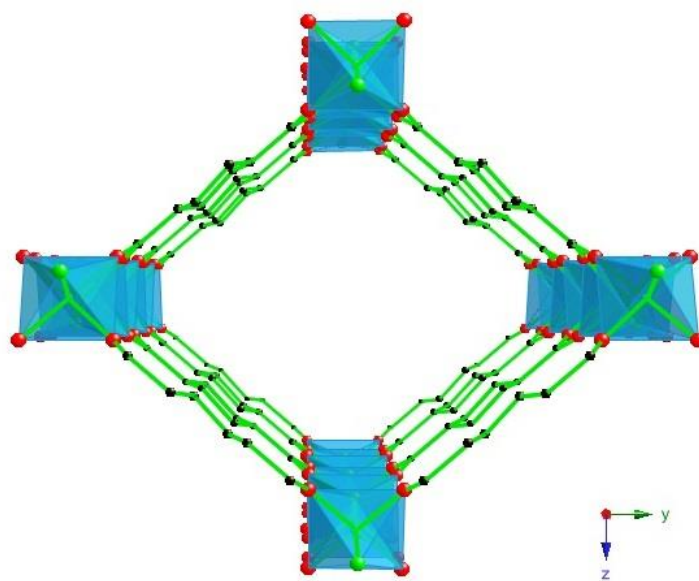
(a)



(b)



(c)



(d)

Figure 4.26 (a) The asymmetric unit of mono-*lp* [AlF(bdc)] (b) The structure of mono-*lp* [AlF(bdc)] viewed along the [100] direction. (c) The asymmetric unit of ortho-*lp* [AlF(bdc)]. (d) The structure of ortho-*lp* [AlF(bdc)] viewed along the [100] direction.

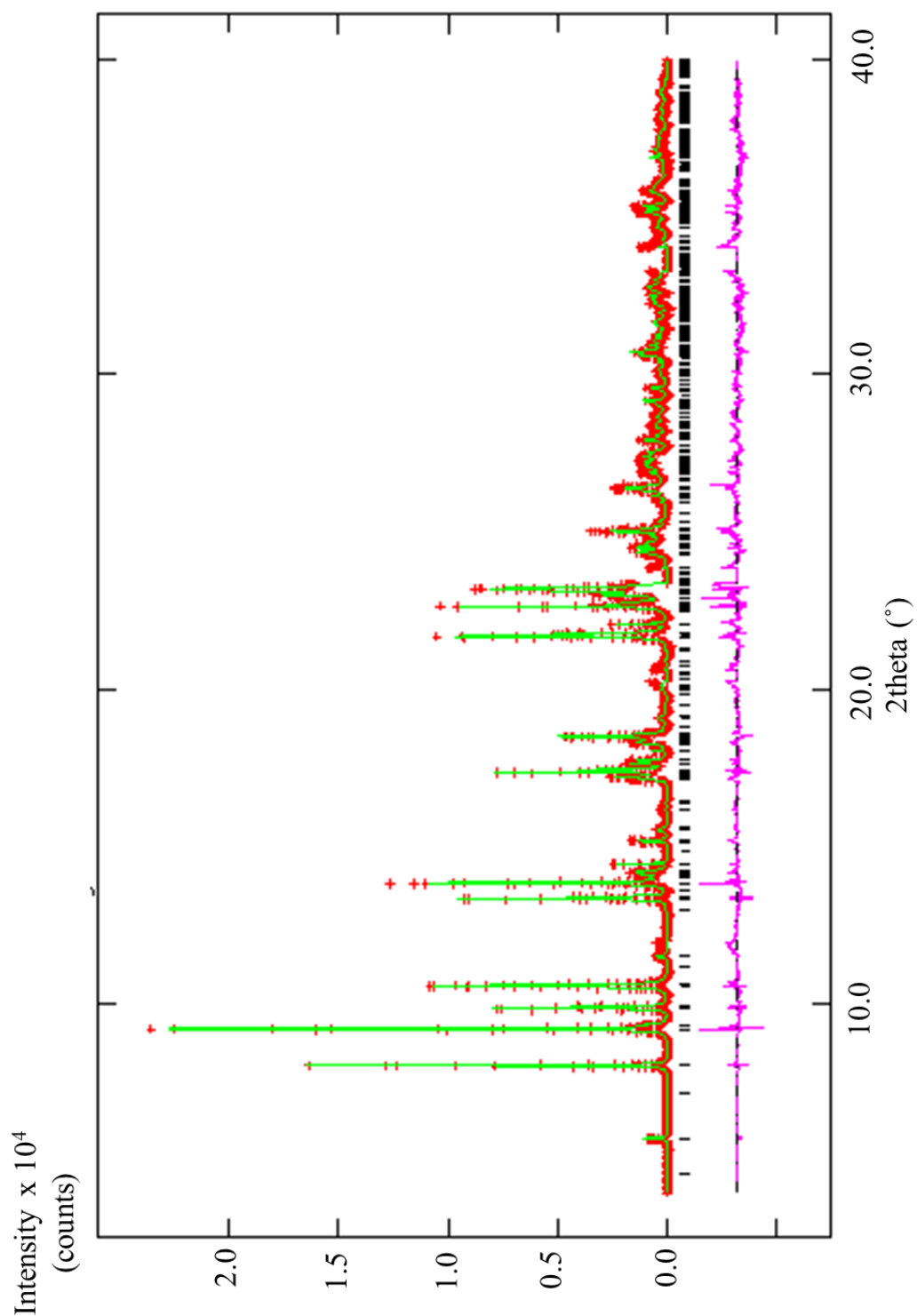


Figure 4.27 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Rietveld refinement of mono-**lp** [AlF(bdc)] at 100 K. The tick marks are the calculated 2θ angles for the Bragg peaks. The plot is scaled by 4x over the 2θ range of 9.5° - 40° .

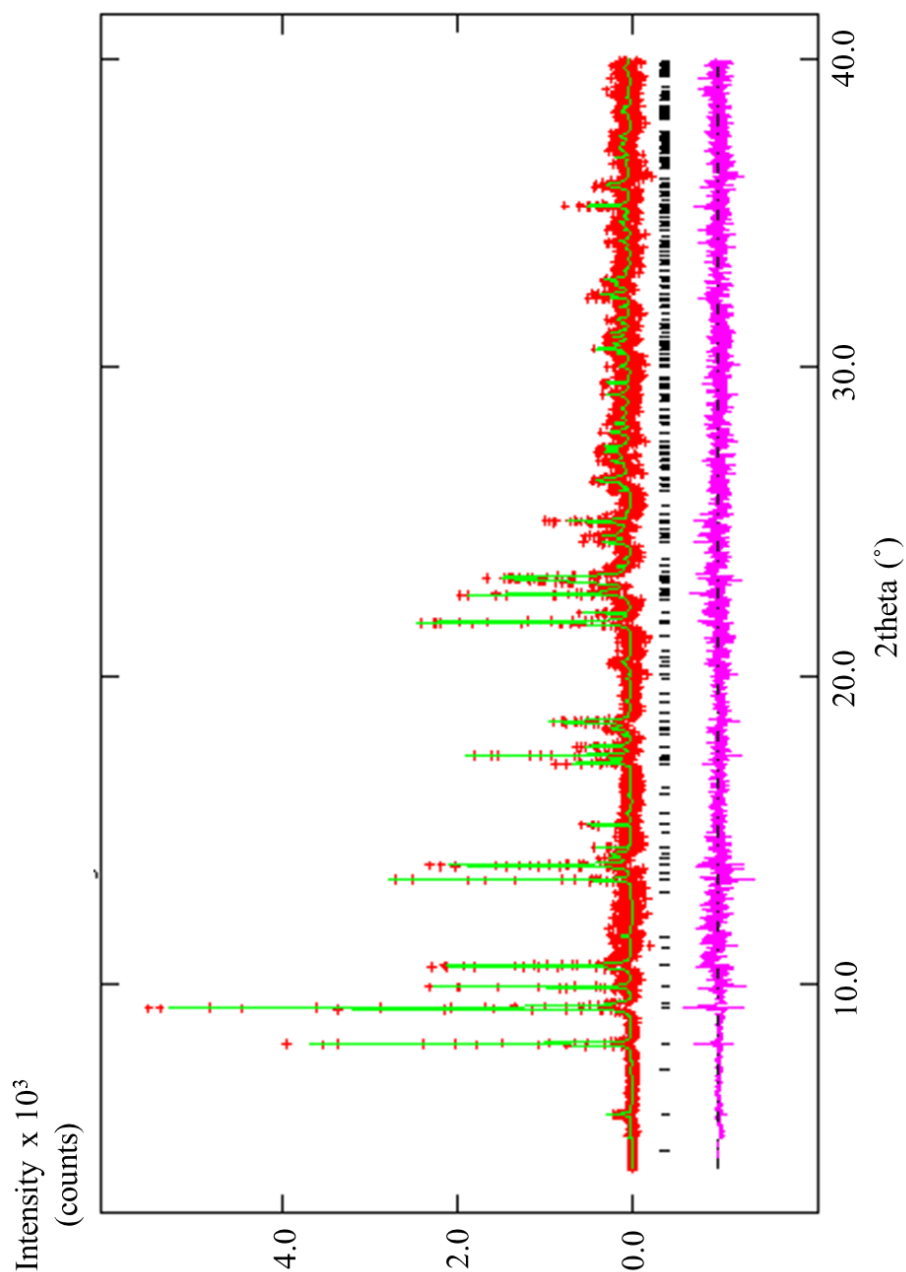


Figure 4.28 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Rietveld refinement of ortho-*lp* [AlF(bdc)] at 300 K. The tick marks are the calculated 2θ angles for the Bragg peaks. The plot is scaled by 4x and 8x over the 2θ range of 10° - 20° and by 20° - 40° respectively.

4.3.6 Results and discussion

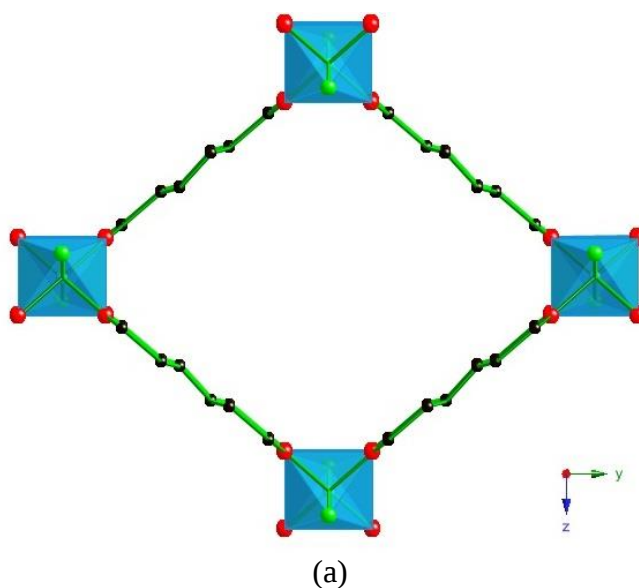
The unit cell parameters and the unit cell volume obtained from the two experiment runs are listed in **Table 4.12**.

Table 4.12 Unit cell parameters ($\text{\AA}/^\circ$), unit cell volume ($\text{\AA}^3$), goodness of fit (χ^2), R_{wp} and R_p for $[\text{AlF}(\text{bdc})]$ from 11 – 500 K

T (K)	a	b	c	γ	V	χ^2	R_{wp}	R_p
Experimental run 1								
11*	6.5528(1)	16.4367(4)	13.1422(4)	90.580(1)	1415.43(6)	9.162	0.1021	0.0732
40*	6.5528(1)	16.4391(4)	13.1381(4)	90.575(2)	1415.19(6)	7.566	0.1061	0.0742
100*	6.5559(1)	16.4362(4)	13.1423(4)	90.488(1)	1416.09(8)	6.863	0.1008	0.0747
150*	6.5622(1)	16.4151(4)	13.1768(6)	90.275(2)	1419.37(6)	5.399	0.1075	0.0815
200	6.5651(1)	16.3991(4)	13.1951(5)	90.000	1420.60(7)	5.446	0.1056	0.0800
250	6.5639(1)	16.4021(4)	13.1830(5)	90.000	1419.31(7)	4.975	0.0996	0.0754
290	6.5648(1)	16.4030(4)	13.1763(5)	90.000	1418.84(7)	4.651	0.0957	0.0726
Experimental run 2								
100*	6.5581(2)	16.4249(6)	13.1592(7)	90.503(2)	1417.41(8)	2.958	0.0406	0.0315
125*	6.5619(2)	16.4170(6)	13.1717(6)	90.398(2)	1418.93(9)	2.976	0.0412	0.0323
150*	6.5668(2)	16.3971(7)	13.2021(8)	90.139(5)	1421.5(1)	3.170	0.0429	0.0334
175	6.5685(2)	16.3904(5)	13.2097(6)	90.000	1422.16(8)	3.123	0.0442	0.0343
200	6.5681(2)	16.3927(5)	13.1996(6)	90.000	1421.19(8)	3.074	0.0440	0.0340
225	6.5680(2)	16.4018(5)	13.1830(6)	90.000	1420.16(8)	3.244	0.0439	0.0340
250	6.5685(2)	16.4032(5)	13.1796(6)	90.000	1420.04(8)	2.957	0.0434	0.0332
275	6.5677(2)	16.3037(5)	13.1740(6)	90.000	1419.29(8)	2.824	0.0425	0.0331
300	6.5678(2)	16.4055(5)	13.1687(6)	90.000	1418.90(8)	2.995	0.0424	0.0326
325	6.5677(2)	16.4042(5)	13.1657(7)	90.000	1418.43(8)	2.689	0.0417	0.0333
350	6.5675(2)	16.4026(5)	13.1643(7)	90.000	1418.11(9)	3.015	0.0428	0.0335
375	6.5676(2)	16.4019(5)	13.1631(7)	90.000	1417.96(9)	2.825	0.0430	0.0334
400	6.5677(2)	16.3984(5)	13.1640(7)	90.000	1417.76(9)	2.949	0.0426	0.0333
425	6.5680(2)	16.3948(5)	13.1676(7)	90.000	1417.91(8)	2.740	0.0426	0.0334
450	6.5681(2)	16.3927(5)	13.1667(7)	90.000	1417.64(9)	2.767	0.0428	0.0334
475	6.5680(2)	16.3885(5)	13.1682(7)	90.000	1417.43(9)	2.620	0.0417	0.0335
500	6.5688(2)	16.3828(5)	13.1723(7)	90.000	1417.54(8)	2.688	0.0423	0.0333

*refers to monoclinic phase

Unlike $[\text{Al}(\text{OH})(\text{bdc})]$, $[\text{AlF}(\text{bdc})]$ remains in a ***lp*** form over the temperature range 11 – 500 K indicating its stability in comparison to a ***np*** form. Structural refinements at each temperature data were collected and reveal that $[\text{AlF}(\text{bdc})]$ undergoes a structural distortion at ~ 175 K from an orthorhombic ***lp*** form (ortho-***lp***) to a monoclinic ***lp*** form (mono-***lp***). The structure of the ortho-***lp*** form is the same as that reported previously^[31] and is shown in **Figure 4.29** (a). The structure of the mono-***lp*** form is shown in **Figure 4.29** (b) and is very similar except for the slight tilting of adjacent corner-sharing AlO_4F_2 octahedra relative to each other about the Al-F-Al core of the chain of corner-sharing AlO_4F_2 octahedra and the accompanying rotation of the bdc groups around the central C...C axis of the bdc linker. This is the most subtle distortion of any of the ***lp*** forms of the MIL-53 family to be reported, although other subtle distortions of more narrow pore forms of members of the MIL-53 family are known.



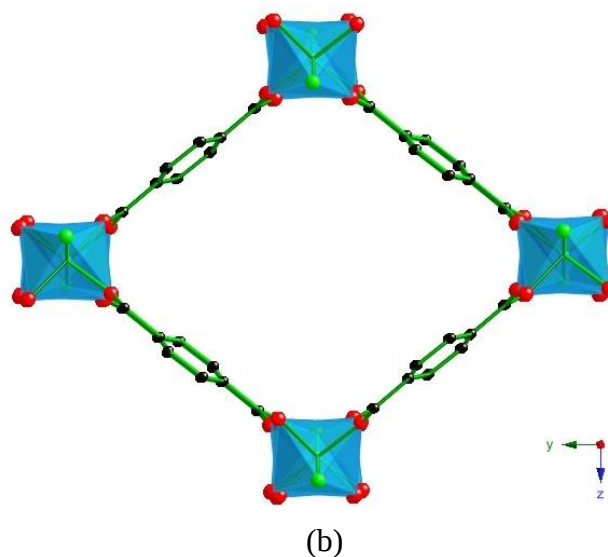


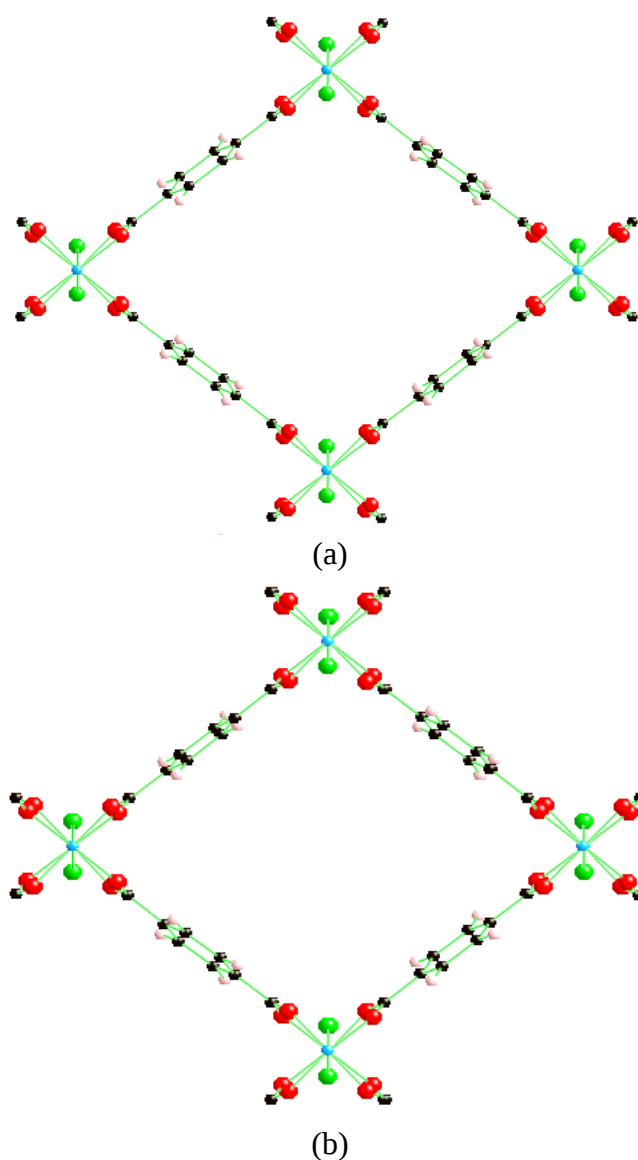
Figure 4.29 The structure of (a) ortho-*lp* [AlF(bdc)] (b) mono-*lp* [AlF(bdc)] viewed along the [100] direction.

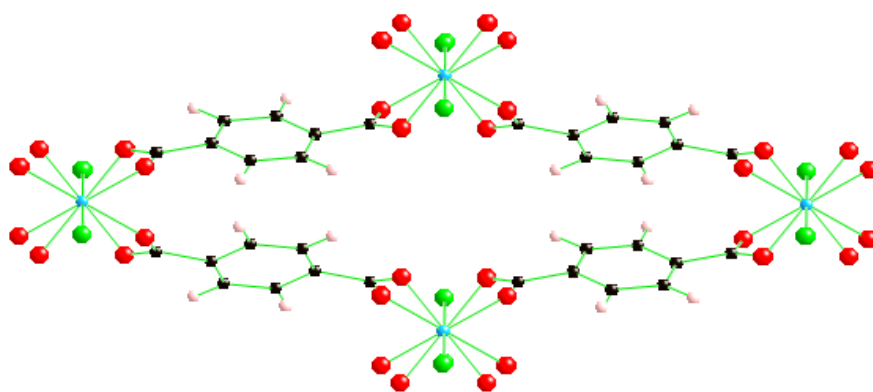
The phase transition observed in *lp*-[AlF(bdc)] is found to be significantly different from the phase transition observed in *lp*-[Al(OH)(bdc)]. In order to understand the physical origin of this difference, the relative energy of each phase i.e. of ortho-*lp* [AlF(bdc)], mono-*lp* [AlF(bdc)] and a theoretical *np*-[AlF(bdc)] was probed using computational methods. Calculations were carried out by Dr Ben Slater, Department of Chemistry, University College London and were based on the Density Function Theory (DFT)^[55] using the plane wave CASTEP code.^[56]

The total energies of each phase were calculated using the experimental structures of ortho-*lp* [AlF(bdc)] and mono-*lp* [AlF(bdc)] as models for the ortho-*lp*-[AlF(bdc)] and mono-*lp* [AlF(bdc)] while for the theoretical *np*-[AlF(bdc)] phase, the model was taken from that of the *np*-[Al(OH)(bdc)]. Structural optimisation to minimize the total energy of the structures was performed using a conjugate-gradient algorithm in the CASTEP software package with an energy cut off of 900 eV, hard pseudopotentials and k-point sampling with a maximum spacing of 0.05 reciprocal Angstroms. The structural optimisation also included the correction for the contribution of the dispersion force using a combination of the PBE function with Grimme's "D2" prescription.^[57] All the structures were completely relaxed and both cell parameters and atomic coordinates were allowed

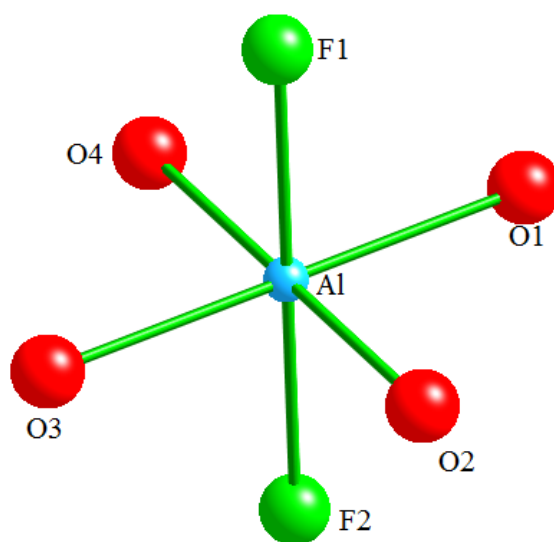
to vary freely. For the mono-***lp*** [AlF(bdc)] and the ***np***-[AlF(bdc)] structure, only the α and β crystallographic angles were constrained while in the ortho-***lp*** [AlF(bdc)], all three angles were constrained to 90° . The progress of the calculation includes a series of steps and each successive step is required to be of lower energy than the previous. Convergence criteria for the calculation is indicated by a minimum deviation in atomic cell parameters and atom positions $<0.001 \text{ \AA}$.

The final relaxed structures of all three phases are shown in **Figure 4.30** and the total energies (E) and the energy differences (ΔE) of each phase are summarised in **Table 4.13**.





(c)



(d)

Figure 4.30 The calculated structures viewed along the [100] direction of (a) *ortho-lp* [AlF(bdc)] (b) *mono-lp* [AlF(bdc)] and (c) *np*-[AlF(bdc)]. (d) The AlO₄(F)₂ octahedron with designated atoms.

Table 4.13 The total energies (E) and the energy differences (ΔE) of ortho-**lp** [AlF(bdc)], mono-**lp** [AlF(bdc)] and **np**-[AlF(bdc)]. The energies present were calculated per Al atom.

Phase	Total energy (E, kJ mol ⁻¹)	Energy difference (ΔE , kJ mol ⁻¹)
ortho- lp [AlF(bdc)]	-359283.93	-
mono- lp [AlF(bdc)]	-359284.02	0.09 ^a
np -[AlF(bdc)]	-359278.83	5.19 ^b 5.09 ^c

$$^a \Delta E = E_{\text{ortho-}lp} - E_{\text{mono-}lp}$$

$$^b \Delta E = E_{\text{ortho-}lp} - E_{np}$$

$$^c \Delta E = E_{\text{mono-}lp} - E_{np}$$

The optimised structures of ortho-**lp** [AlF(bdc)] ($a = 6.604 \text{ \AA}$, $b = 16.552 \text{ \AA}$, $c = 13.274 \text{ \AA}$ and $V = 1443.65 \text{ \AA}^3$) and mono-**lp** [AlF(bdc)] ($a = 6.603 \text{ \AA}$, $b = 16.555 \text{ \AA}$, $c = 13.265 \text{ \AA}$, $\beta = 90.15^\circ$ and $V = 1449.92 \text{ \AA}^3$) are in good agreement with the experimental structures as indicated by the $< 1\%$ difference in unit cell parameters which lies within the inherent error of the DFT approach and indicates the total energies obtained from the calculations are reliable. **Table 4.13** shows that the structure of ortho-**lp** [AlF(bdc)] and mono-**lp** [AlF(bdc)] are close in energy and the mono-**lp** [AlF(bdc)] structure is more stable than the ortho-**lp** [AlF(bdc)] by $-0.09 \text{ kJ mol}^{-1}$. This means the structure of mono-**lp** [AlF(bdc)] is enthalpically favoured and is observed at a lower temperature which agrees with experiment observations. As the temperature increases, the mono-**lp** [AlF(bdc)] transforms to the ortho-**lp** [AlF(bdc)] phase due to the entropic gain which means the structure of ortho-**lp** [AlF(bdc)] is entropically dominant.

In addition, the total energy of the structure of **np**-[AlF(bdc)] is higher in energy than the other two phases by $\sim 5 \text{ kJ mol}^{-1}$. This indicates that the **np**-[AlF(bdc)] structure is energetically unfavourable and that is why this phase is not observed. The **np**-[AlF(bdc)] phase is found to be a metastable phase. This is also implied from calculations for which the constraints on the unit cell parameters were discarded during the structural optimisation and for which there was no

further relaxation of the **np**-[AlF(bdc)] structure to the more stable ortho-**lp** [AlF(bdc)] form which implies that there is an energy barrier between these two phases.

The conversion of the ortho-**lp** [AlF(bdc)] form to the mono-**lp** [AlF(bdc)] form upon cooling instead of the **np**-[AlF(bdc)] form can be explained by the inspection of the structural geometry of the $\text{AlO}_4(\text{F})_2$ octahedra of mono-**lp** [AlF(bdc)] and **np**-[AlF(bdc)]. The maximum and minimum value of the geometric parameters of the $\text{AlO}_4(\text{F})_2$ octahedra of each form are summarised in **Table 4.14**. It is evident that the internal structural geometry of the $\text{AlO}_4(\text{F})_2$ octahedra of the **np**-[AlF(bdc)] form is highly distorted from the regular octahedral geometry especially at the O1-Al-O2 bond angle. This angle of the **np**-[AlF(bdc)] form has a smaller value than that of mono-**lp** [AlF(bdc)]. This means the two oxygen atoms are pulled closer which is unfavourable as it would increase the O1-O2 repulsion force.

Table 4.14 The geometric parameters ($\mathbf{x}$) of the $\text{AlO}_4(\text{F})_2$ octahedra of the optimised structure of mono-**lp** [AlF(bdc)] and **np**-[AlF(bdc)].

Geometric parameters ($\text{\AA}/^\circ$)	np -[AlF(bdc)]	mono- lp [AlF(bdc)]
Al-F	$\mathbf{x} = 1.850 \text{ \AA}$	$\mathbf{x} = 1.838 \text{ \AA}$
Al-O	$1.889 \text{ \AA} < \mathbf{x} < 1.927 \text{ \AA}$	$1.902 \text{ \AA} < \mathbf{x} < 1.906 \text{ \AA}$
O-Al-O	$85.9^\circ < \mathbf{x} < 94.0^\circ$	$88.176^\circ < \mathbf{x} < 92.128^\circ$
O-Al-F	$89.1^\circ < \mathbf{x} < 90.8^\circ$	$88.0^\circ < \mathbf{x} < 92.1^\circ$

The phase transition from the **lp** form to the **np** form in **lp**-[Al(OH)(bdc)] originates from the distortion of the $\text{AlO}_4(\text{OH})_2$ octahedra. The energy penalty associated with the distortion of the $\text{AlO}_4(\text{OH})_2$ octahedra is found to be offset by the energy gained from the dispersion interactions between the bdc linkers which stabilizes the low temperature **np**-[Al(OH)(bdc)] form, and hence the phase transition from the **lp** form to the **np** form is favoured in **lp**-[Al(OH)(bdc)]. In **lp**-[AlF(bdc)], the distortion of the $\text{AlO}_4(\text{F})_2$ octahedra also occurs in order to

facilitate the phase transition from the **lp** form to the **np** form. However, the energy penalty associated with the distortion of the $\text{AlO}_4(\text{F})_2$ octahedra is relative high and cannot be adequately counterbalanced by the energy gained from the presence of dispersion interactions which makes the **np**-[AlF(bdc)] phase unstable. Therefore, the phase transition from the **lp** form to the **np** form in **lp**-[Al(F)(bdc)] is unfavourable and the mono-**lp** [AlF(bdc)] form is observed instead. From this rationale, it implies that the $\text{AlO}_4(\text{F})_2$ octahedra is more rigid than the $\text{AlO}_4(\text{OH})_2$ octahedra.

The mono-**lp** form is adopted by [AlF(bdc)] from 11 K to 175 K. As the temperature is raised, the volume of the unit cell increases as shown in **Figure 4.31** and the magnitude of the γ decreases from $90.580(1)^\circ$ to 90° at 175 K. The volume of the unit cell increases over this temperature range as it converts from being a distorted structure to the higher symmetry structure of this particular framework topology. After transforming to the ortho-**lp** form at ~ 175 K then the volume of the material is seen to drop over the remaining temperature range. Such thermoresponsive behaviour has been reported for framework materials, for example, the all-silica zeolite ferrierite,^[58] but such behaviour has not been reported for MOFs.

Although there are some discrepancies between unit cell volumes obtained from the two experiments collected on the [AlF(bdc)] samples in the mono-**lp** form as shown in **Figure 4.31**, agreement is good for the unit cell volume variation for the ortho-**lp** form and the underlying thermoresponsive behaviour is identical.

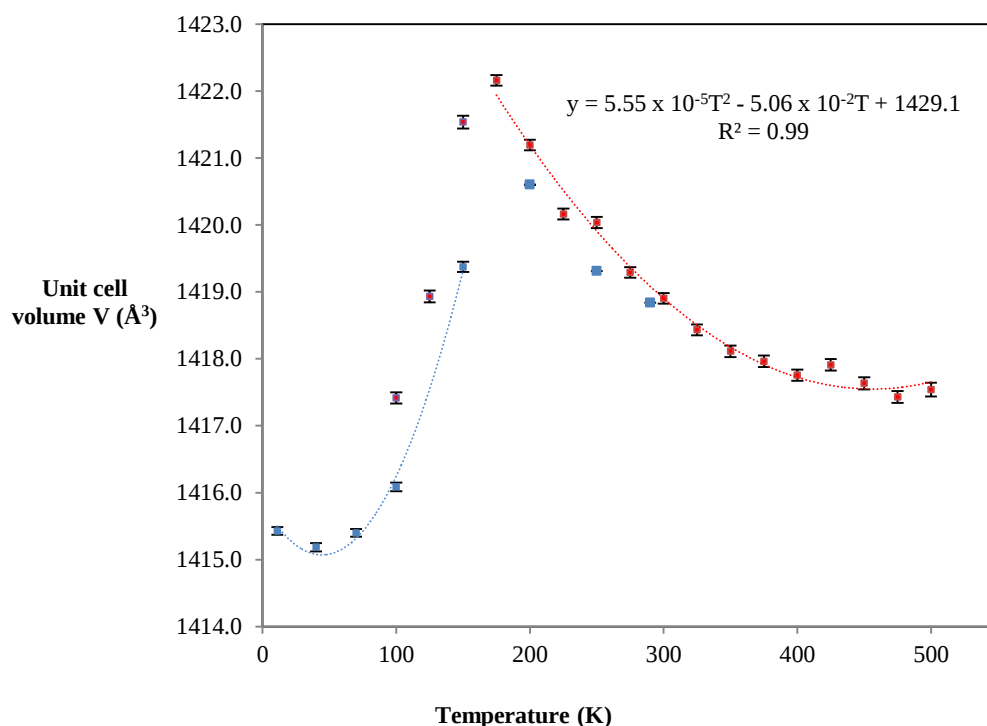
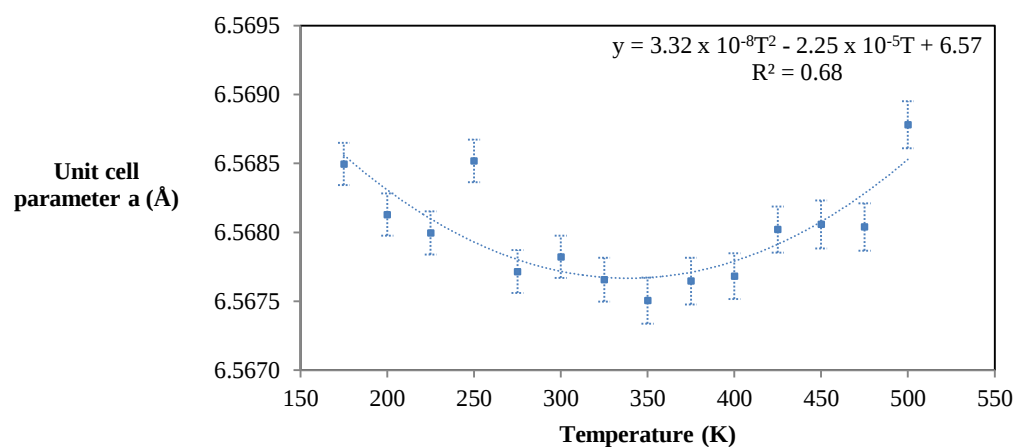
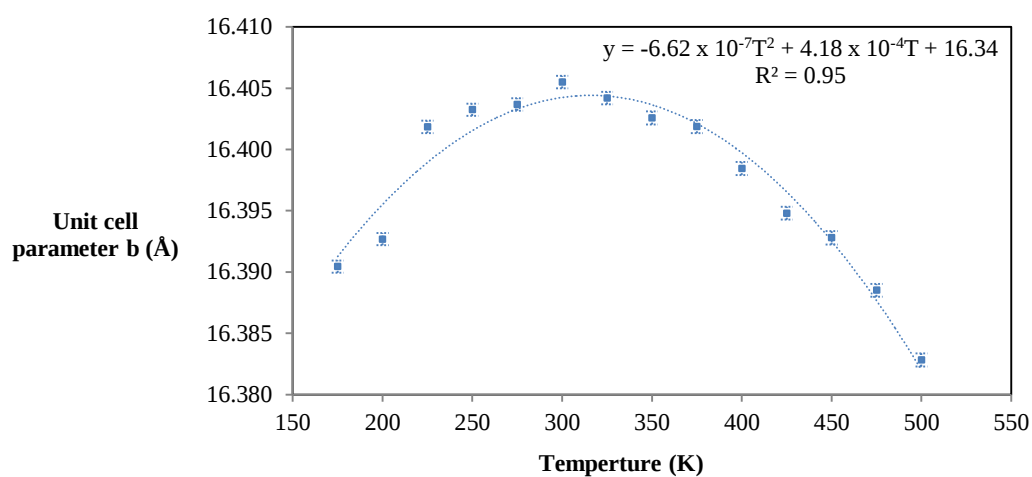


Figure 4.31 The variation of unit cell volume of $[\text{AlF}(\text{bdc})]$ obtained from the two sets of experimental data (blue and red markers represent the data from experimental run 1 and run 2 respectively).

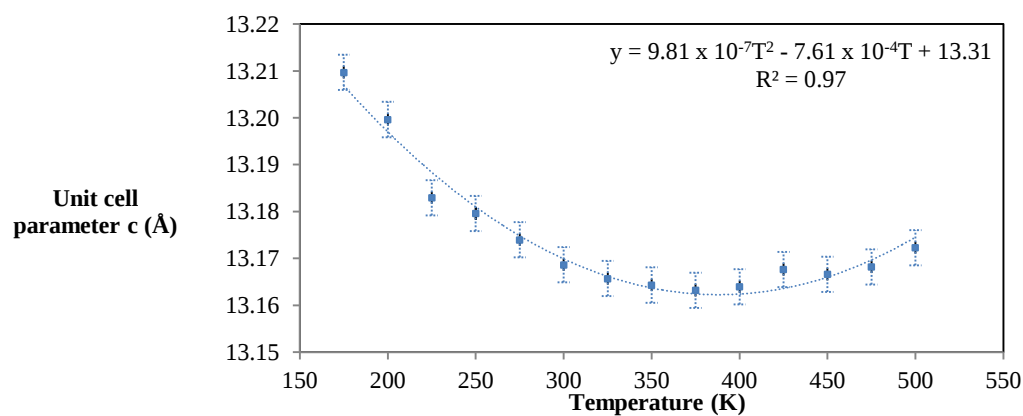
The measured variations in lattice parameters as a function of temperature of the ortho-*lp* form are shown in **Figure 4.32**. The discussion will focus on the results from experimental run 2 as this covers a wider temperature range (175 – 500 K) for the ortho-*lp* form.



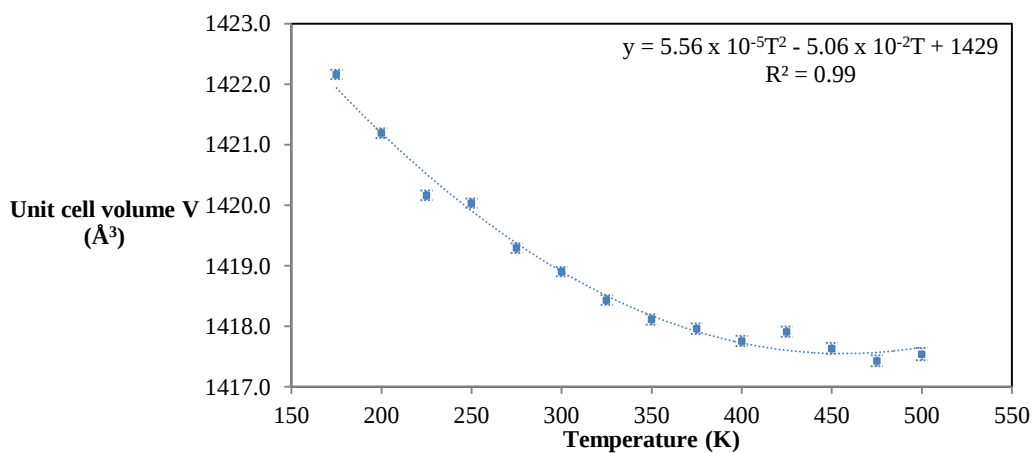
(a)



(b)



(c)



(d)

Figure 4.32 (a), (b) and (c) Plots of unit cell dimension, a, b and c as a function of temperature respectively. (d) A plot of unit cell volume V, as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

Polynomial functions are used to represent the non-linear thermoresponsive behaviour of the lattice parameters and unit cell volume. Polynomial coefficients of thermal expansion were calculated using the following expressions:

$$p = p_0 + p_1T + p_2T^2 \quad \text{Equation 4.1}$$

$$\alpha = \frac{(p_1 + 2p_2T)}{p} \quad \text{Equation 4.2}$$

and the resulting coefficients are listed in **Table 4.15**. [AlF(bdc)] exhibits overall negative volume expansion from 175 – 500 K with a minimum value of $\alpha_V = -2.19 \times 10^{-5} \text{ K}^{-1}$ at 175 K and a maximum value of $\alpha_V = 3.53 \times 10^{-6} \text{ K}^{-1}$ at 500 K.

Table 4.15 The resulting coefficients of the polynomial function of the thermoresponsive behaviours in the *a*, *b* and *c* axes and in the unit cell volume *V*.

Cell parameter	p_0	p_1	p_2
<i>a</i>	6.571	-2.25×10^{-5}	3.32×10^{-8}
<i>b</i>	16.34	4.18×10^{-4}	-6.62×10^{-7}
<i>c</i>	13.31	-7.61×10^{-4}	9.81×10^{-7}
<i>V</i>	1429	-5.06×10^{-2}	5.56×10^{-5}

The expansion behaviour in the [001] and the [010] directions are rather anomalous as from 175 - ~325 K expansion along the *b*-axis and contraction along the *c*-axis occurs followed by a reversal of behaviour from ~325 – 500 K. If one of the rhombus-shaped channels in the (100) plane is again considered, as shown in **Figure 4.33** (a) and similarly defined as that in [Al(OH)(bdc)], that is bounded by four bdc ligands with Al atoms at the vertices of the rhombus, then the internal rhombus angle α , initially decreases from 175 - ~325 K before increasing from ~325 – 500 K as shown in **Figure 4.33** (b). The change of the internal O1-Al-O1 angle is show in **Figure 4.33** (c).

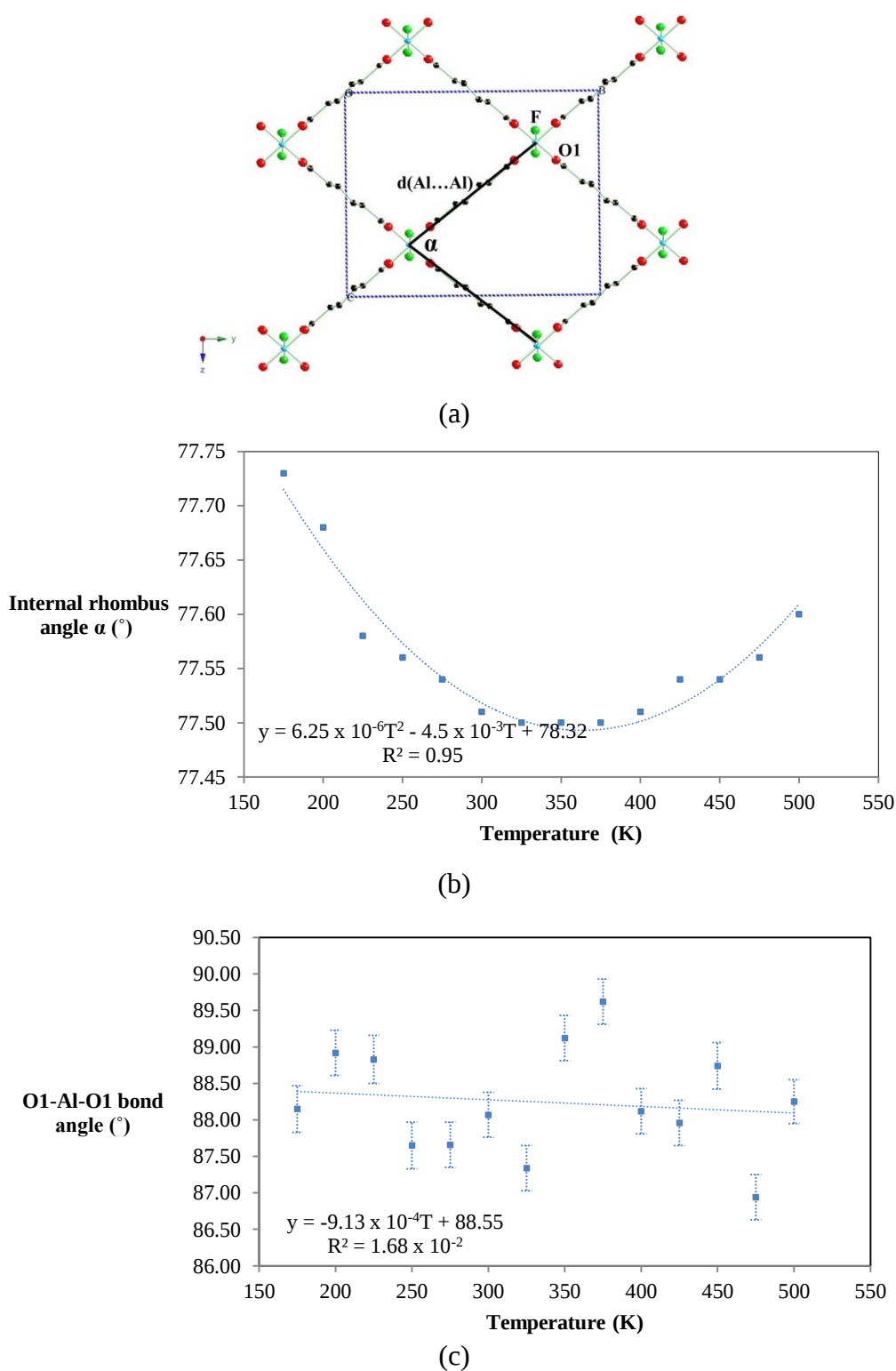
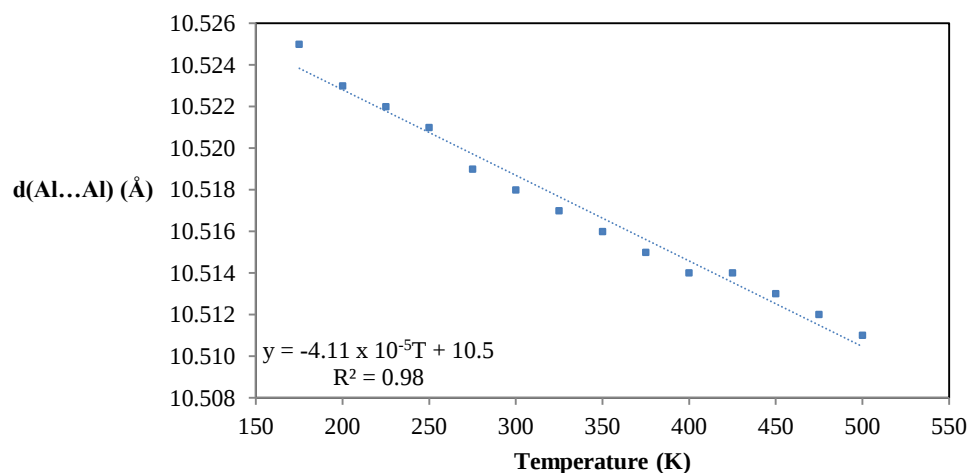
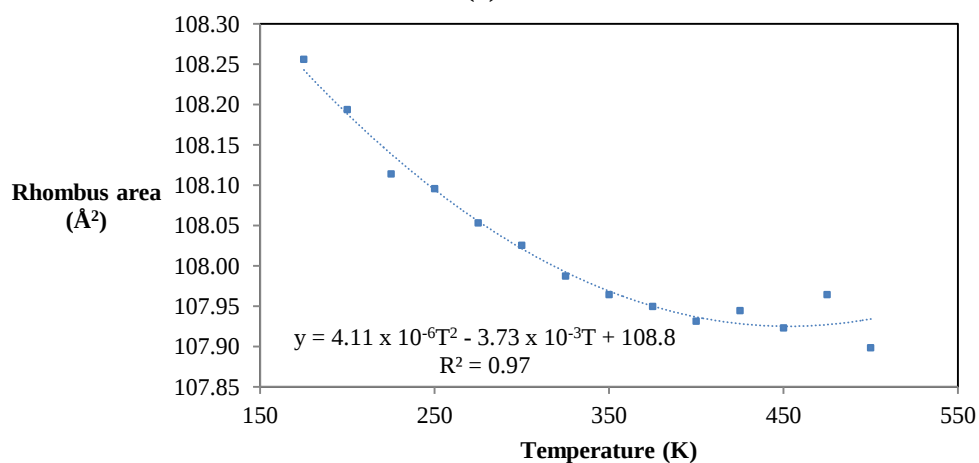


Figure 4.33 (a) The framework of $[AlF(bdc)]$ viewed along the $[100]$ direction showing the rhombus-shaped channel that is made of four bdc ligands bound four infinite chains of AlO_4F_2 together. (b) The variation of the internal rhombus angle α as a function temperature. (c) The variation of the O1-Al-O1 angle as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

However, interestingly the $d(\text{Al}\dots\text{Al})$ distance on the sides of the rhombus decrease in a linear fashion over the entire temperature range as shown in **Figure 4.34 (a)**. The combination of the variation of the internal rhombus angle α and the $d(\text{Al}\dots\text{Al})$ distance yields a smooth decrease of the area of the rhombus over the entire temperature range, as shown in **Figure 4.34 (b)**, which forms the major component of the smooth volume contraction as temperature increases.



(a)



(b)

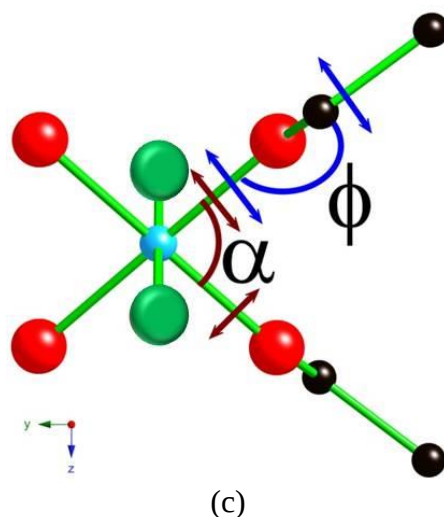


Figure 4.34 (a) The temperature dependence of the $d(\text{Al}\dots\text{Al})$ distance. (b) The temperature dependence of the rhombus area. (c) A schematic showing the internal rhombus angle α and the bending angle about the $\text{O}\dots\text{O}$ vector, ϕ . The blue, green, red and black balls are represented aluminium, fluorine, oxygen and carbon atoms respectively.

The contraction of the $d(\text{Al}\dots\text{Al})$ distances of the rhombus edges could arise from contributions from a variety of dynamic lattice vibrations or static framework distortions. If the chains of corner-sharing AlO_4F_2 octahedra are considered to be completely rigid, then vibrations in which the chains librate around an axis passing through the Al atoms along the $(\text{AlO}_4\text{F})_\infty$ chains would cause the $d(\text{Al}\dots\text{Al})$ distances to decrease as the vibrations increase in magnitude with temperature. These vibrations will occur by a concerted “knee cap”^[46] bending mode around ϕ as represented in **Figure 4.34** (c) and some bending within the $\text{C}-\text{C}_6\text{H}_6-\text{C}$ core of the bdc linker itself. The latter may involve vibrations such as shown schematically in **Figure 4.35** and reported in the study of the negative thermal expansion behaviour of the dicarboxylate MOF-5.^[43]

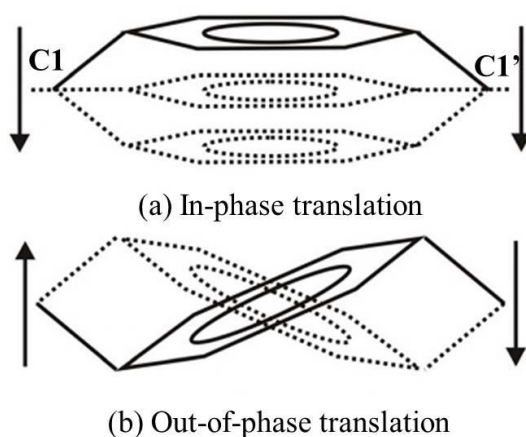


Figure 4.35 The possible vibrational modes of the bdc linker that may lead to the contraction of the $d(\text{Al}\dots\text{Al})$ distance (a) illustrates the in-phase transverse vibration and (b) shows the out-of-phase transverse vibration. These vibrations have been suggested to be the crucial factor driving the NTE in MOF-5.^[43]

In MOF-5, it has been suggested that the transverse vibrational modes of the bdc linker as shown in **Figure 4.35** are the main contributor to the NTE in MOF-5. The evidence supporting this propose is the contraction of the bdc linker, measured from C1 to C1' as defined in **Figure 4.35**. The rate of contraction is found to be $2.0 \times 10^{-4} \text{ \AA K}^{-1}$ which is 5 times greater than the rate of contraction of the $d(\text{Al}\dots\text{Al})$ distance in $[\text{AlF}(\text{bdc})]$. This may indicate that the dynamic lattice vibrations are not the major cause of the decrease in $d(\text{Al}\dots\text{Al})$ distances.

A decrease in the $d(\text{Al}\dots\text{Al})$ distance could also result from a static deformation of the framework as the temperature is increased involving the same “knee cap”^[46] bending mode in the manner depicted in **Figure 4.34** (c) and possibly additional bending within the core of the bdc linker. Such static framework distortions have been reported for the MIL-53-type material $[\text{VO}(\text{bdc})]$ that were induced by loading the framework with various non-framework organic molecules^[4]. Unfortunately, the structure refinements we present are not of high enough quality to determine which of these dynamic or static processes contribute or is dominant. The possible modes of the static distortion of the framework of $[\text{AlF}(\text{bdc})]$ are illustrated as shown in **Figure 4.36**.

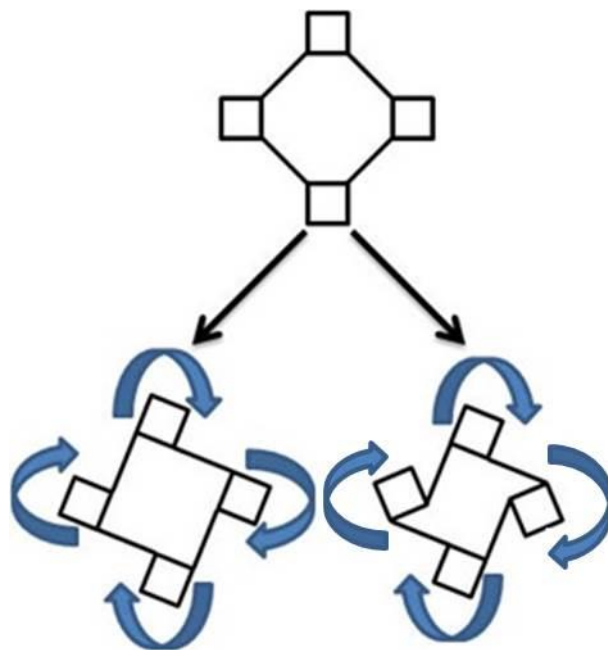


Figure 4.36 The possibilities of the static framework distortion that involves “knee cap”^[46] bending mode of the carboxylate group and the bending within the core of the bdc linker.

The variation of the internal rhombus angle α , implies that the AlO_4F_2 octahedra are not completely rigid with respect to angular deformation. However, the total angular variation of α is $\pm\sim 0.23^\circ$ for ortho-**lp** [$\text{AlF}(\text{bdc})$] while it is 0.69° for **lp** [$\text{Al}(\text{OH})(\text{bdc})$] over equal temperature ranges. This indicates that the AlO_4F_2 octahedra are more rigid than the $\text{AlO}_4(\text{OH})_2$ octahedra with respect to angular deformation and is supported by the calculations. The fact that the rhombus edge distance, the $d(\text{Al}\dots\text{Al})$ distance, decreases in ortho-**lp** [$\text{AlF}(\text{bdc})$] indicates that the “knee cap”^[46] bending mode is closer in energy to that of the rotation of the bdc linkers around the $-\text{Al}-\text{F}-\text{Al}-$ chain running through the core of the corner-sharing AlO_4F_2 octahedra.

These results suggest that the difference in thermoresponsive behaviour of ortho-**lp** [$\text{AlF}(\text{bdc})$] and **lp** [$\text{Al}(\text{OH})(\text{bdc})$] is dependent on the rigidity of the chain of corner-sharing AlO_4X_2 octahedra with the AlO_4F_2 octahedra being more rigid than the $\text{AlO}_4(\text{OH})_2$ octahedra. This means the former has a greater contribution of the “knee cap” bending mode in its framework thermoresponsive behaviour compared to the rotation of the bdc linkers about the $-\text{Al}-\text{X}-\text{Al}-$ chain running

through the core of the $(\text{AlO}_4\text{X})_\infty$ chain whilst the latter has the opposite degree of contribution of two motions.

The near constant value of the a lattice parameter also suggests a greater rigidity in the chain of AlO_4F_2 octahedra, when compared with the chain of $\text{AlO}_4(\text{OH})_2$ octahedra, that prevents the type of correlated rocking of the carboxylate groups about the axis of the bdc linker that introduces a twisting motion about the Al-X-Al linkage that causes a contraction of the a lattice parameter in **lp** $[\text{Al}(\text{OH})(\text{bdc})]$.

The anomalous behaviour of the variation in the b and c unit cell parameters may reflect very subtle changes in interaction energies and entropy as temperature is varied and the structure of $[\text{AlF}(\text{bdc})]$ flexes in response. Such subtle changes are reflected by the relatively small energy differences in these systems, for example a difference of 3 kJ mol^{-1} between the **np** and **lp** form of $[\text{Al}(\text{OH})(\text{bdc})]$.^[39] These changes have such a noticeable effect as the variation in unit cell parameters we are observing is relatively small as reflected by the small total unit cell volume of $4.62 \text{ \AA}^3$ observed over the 175 – 500 K temperature range. The anomalous behaviour could also be due to the presence of non-framework species in the material. However, we discount this possibility as the thermogravimetric data as shown in **Figure 4.19** of the material prior to loading in the capillary tubes displays no mass loss before framework decomposition at 500 °C, the ^{19}F SSNMR spectrum indicates the presence of one crystallographic F atom with only 0.6% of an additional minor source of F atoms as shown in **Figure 4.22**, no non-framework species were located in the difference Fourier maps derived at the end of the structure refinements and repetition of the experiments within the 200 – 300 K temperature range produced similar volume contraction behaviour.

The results show that the thermoresponsive behaviour of $[\text{Al}(\text{OH})(\text{bdc})]$ and $[\text{AlF}(\text{bdc})]$ are highly dependent on the atom X with the influence of X on the rigidity of the AlO_4X_2 octahedra appearing to dominate the thermoresponsive behaviour.

4.4 Thermoresponsive behaviour of [Cr(OH)(bdc)]

4.4.1 Synthesis and activation

The synthesis of [Cr(OH)(bdc)] was based on the procedure previously reported.^[26] All starting materials involved in the synthesis were used without further purification. [Cr(OH)(bdc)]·0.75(H₂bdc) was synthesised by dissolving Cr(NO₃)₃·9H₂O (Sigma-Aldrich, 99 %, 0.7935 g) and H₂bdc (Sigma-Aldrich, 0.3296 g) in deionized water (10 ml) followed by addition of HF (Aristar, 48 % wt in water, 0.08 g) into the mixture. The mixture was then placed into a 23 ml Teflon-lined stainless steel autoclave and heated for 3 days at 220 °C. The product was recovered by suction filtration and washed with deionized water. The powder X-ray diffraction pattern shown in **Figure 4.37** confirms that phase pure [Cr(OH)(bdc)]·0.75(H₂bdc) was synthesised.

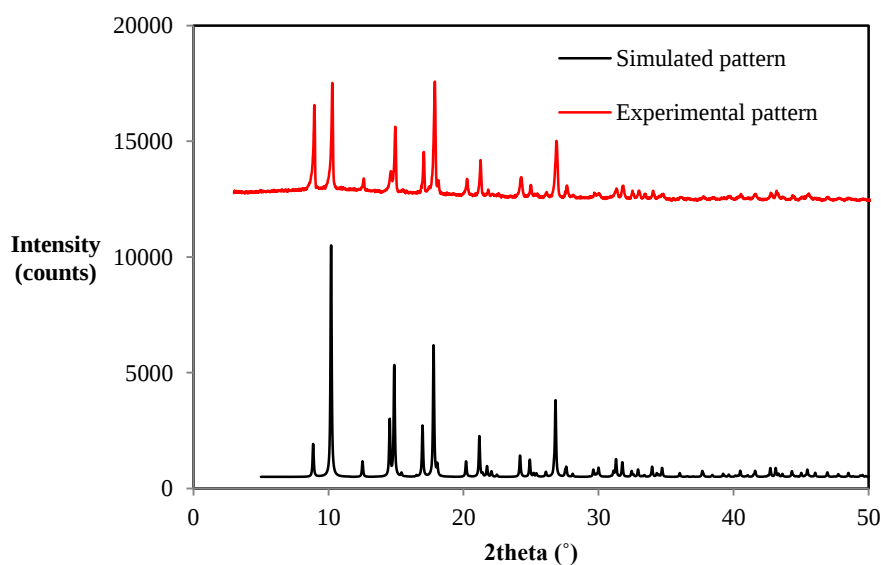
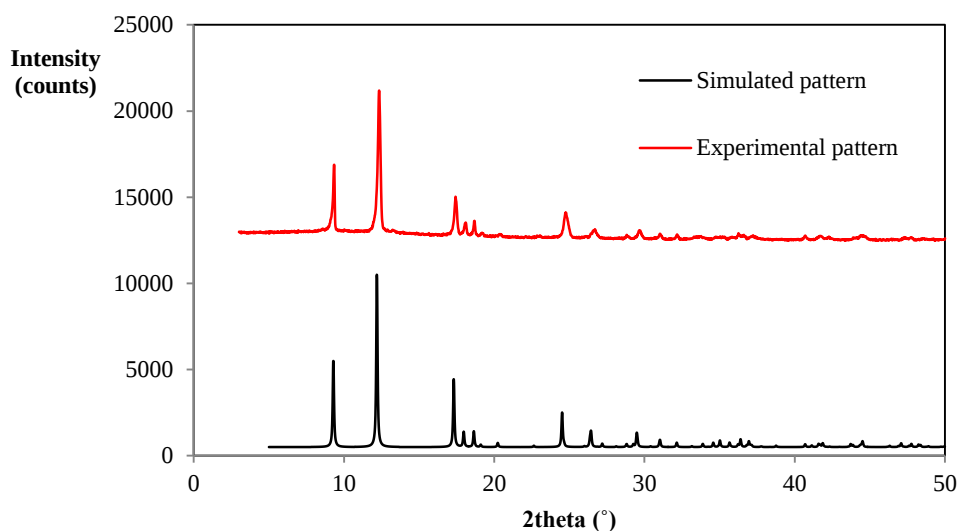


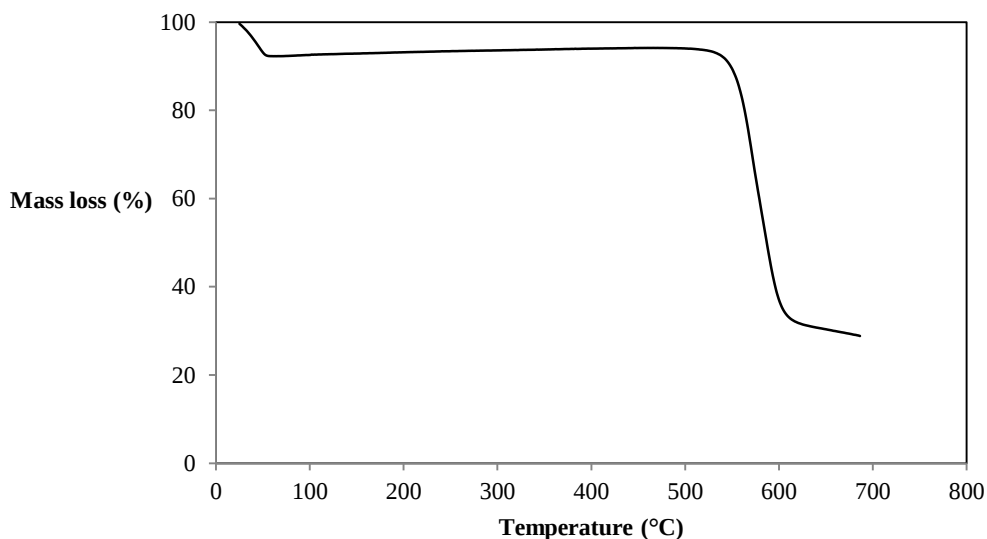
Figure 4.37 The experimental (red) and simulated (black) powder X-ray diffraction patterns of [Cr(OH)(bdc)]·0.75(H₂bdc).

300 mg of [Cr(OH)(bdc)]·0.75(H₂bdc) was soaked with 5 ml of DMF (Sigma-Aldrich, 99.8 %) in a Teflon-lined stainless steel autoclave and heated at 150 °C for 24 hours. This treatment allows the excess of H₂bdc located in the

framework pores to be exchanged by DMF. After filtration and washing with DMF, the dried product was calcined under air at 300 °C for 3 days resulting in the fully activated framework. The success of calcination was confirmed by the powder X-ray diffraction as shown in **Figure 4.38** (a) and the thermogravimetric data as shown in **Figure 4.38** (b).



(a)



(b)

Figure 4.38 The experimental (red) and simulated (black) powder X-ray diffraction patterns of $[\text{Cr}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$. (b) Thermogravimetric analysis data of $[\text{Cr}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$.

The thermogravimetric data for $[\text{Cr}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$ was collected by heating the sample under nitrogen from 25 to 700 °C at a heating rate of 5 °Cmin⁻¹. The TGA plot is shown in **Figure 4.38** (b). The first mass loss of 5.5 %, between 25 and ~65 °C, is due to the loss of one equivalent of water molecule absorbed inside the pores (calculated to be 7.2 %). The second mass loss of 64 % between 500 and 700 °C corresponds to the framework collapse due to the departure of the bdc molecules, calculated to be 65.3 %. The discrepancy between the experimental and the calculated values arise from incomplete decomposition of the bdc molecules.

A sample of $[\text{Cr}(\text{OH})(\text{bdc})]\cdot(\text{H}_2\text{O})$ was packed in a 0.5 mm borosilicate capillary tube to a length of about 4 centimetres and evacuated at 2.3×10^{-1} mbarr at 200 °C for 48 hours to obtain the **lp**- $[\text{Cr}(\text{OH})(\text{bdc})]$. The degassed sample was sealed under vacuum ready for data collection at the synchrotron.

4.4.2 Synchrotron powder thermodiffraction study

4.4.2.1 Data collection

The diffraction data were collected at 25 K intervals in the temperature range of 100 - 500 K. The diffractometer was operated to collect the data from 3° to 140° 2θ and the mean wavelength used was 0.825993(3) Å. The data collection time was 30 minutes per temperature with a 2θ step size of 0.001°. The powder patterns were rebinned with the 2θ step size of 0.003° and were analysed using the Rietveld structural refinement in the GSAS software package.

4.4.2.2 Data analysis

Inspection of synchrotron X-ray powder diffraction patterns indicated an unidentified phase present together with the **lp** form of $[\text{Cr}(\text{OH})(\text{bdc})]$ over the entire temperature range studied. Representative powder X-ray diffraction patterns

at 100 K, 125 K, 150 K, 175 K, 200 K and 300 K are shown in **Figure 4.39**. The reflections of the unknown phase were marked by red asterisks and may arise from an impurity phase formed during the synthesis as the intensity of this phase is constant in all powder diffraction patterns.

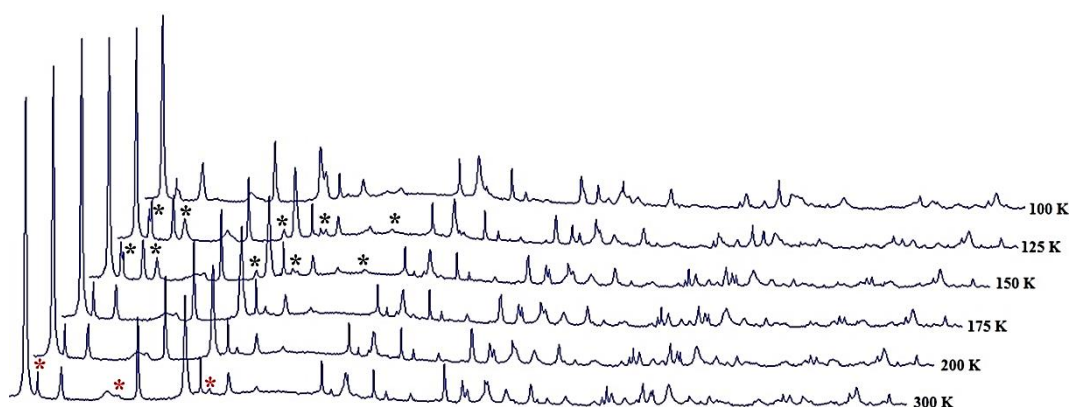


Figure 4.39 A comparison of powder X-ray diffraction patterns of *lp*-[Cr(OH)(bdc)]. The reflections marked by red asterisks in the powder pattern at 300 K correspond to the unknown phase. Black asterisks indicate another unidentified phase which appears to present only in the powder patterns at 125 K and 150 K.

The powder X-ray diffraction patterns at 125 K and 150 K were further complicated as there were other extra reflections present (marked by black asterisks in **Figure 4.39**). At first, they were assumed to correspond to an empty *np*-[Cr(OH)(bdc)]. However, as such phase has never been reported before, an empty *np*-[Al(OH)(bdc)] was considered instead. It was found that those extra reflections did not correspond to the reflections of the *np*-[Al(OH)(bdc)]. The indexing of those extra peaks was unsuccessful and therefore was designated as an unidentified phase.

Apart from the two unidentified phases, there was also present a Cr₂O₃ phase. The Le Bail fits of all the powder diffraction patterns therefore were performed on 11357 data points by excluding reflections from the two unidentified phases and the first reflection of the *lp*-[Cr(OH)(bdc)]. Two phase fitting was performed including the *lp*-[Cr(OH)(bdc)] and Cr₂O₃ phase. The starting models of both phases were taken from that reported previously.^[26] The

background was fit using linear interpolation between manually designated background points. Peak shape fitting was conducted by using the fourth profile option in the GSAS program suite which is a modified pseudo-Voigt function that accounts for the effect of microstrain broadening.

The crystal structure of ***lp***-[Cr(OH)(bdc)] was solved in the same space group as ***lp***-[Al(OH)(bdc)]. However, the extended Hermann-Mauguin symbol is different, *Imcm* for the case of ***lp***-[Cr(OH)(bdc)] and *Imma* for the case of ***lp***-[Al(OH)(bdc)]. The difference between these two symbols is the cell setting symbol assignment. The space group *Imma* is under a standard cell setting, *abc*, whereas the space group *Imcm* results from the cell setting *bca*.

The lattice parameters and peak shape profile coefficients obtained from the Le Bail fitting were subsequently used in the Rietveld refinement. The Rietveld refinements were performed only on the ***lp***-[Cr(OH)(bdc)] phase while the Cr₂O₃ phase was modelled using Le Bail option. The final cycle of least squares refinement comprised of 36 refined parameters including the scale factor, detector zero point, unit cell parameters of both phases, peak shape profile parameters of both phases, preferred orientation from the (110) plane for ***lp***-[Cr(OH)(bdc)] and atomic coordinates and isotropic atomic displacement parameters of all six atoms in the asymmetric unit of the ***lp***-[Cr(OH)(bdc)]. The isotropic atomic displacement parameters (*U*_{iso}) of the O atoms were constrained to have the same value, as were those of the carbon atoms.

The crystallographic data for a representative refinement (300 K) are summarized in **Table 4.16**. The final atomic coordinates, occupancies and isotropic atomic displacement parameters of ***lp***-[Cr(OH)(bdc)] are given in **Table 4.17**. Selected bond lengths and bond angles of ***lp***-[Cr(OH)(bdc)] are given in **Table 4.18**. The asymmetric unit and the full structure of ***lp***-[Cr(OH)(bdc)] are shown in **Figure 4.40**. The final observed, calculated and difference plot for the Rietveld refinement at 300 K is shown in **Figure 4.41**. This is a representative final result and all the refinements of all data sets are given in the attached appendix of the CD.

Table 4.16 Crystal data and structure refinement parameters for ***lp***-[Cr(OH)(bdc)]* at 300 K

Formula	[Cr(C ₈ H ₅ O ₅)]
Formula weight	228.079
Density (gcm ³)	1.014
Temperature (K)	300
Wavelength (Å)	0.825993(3)
Space group	<i>Imcm</i>
a (Å)	16.8444(3)
b (Å)	12.9985(4)
c (Å)	6.82599(8)
V (Å ³)	1494.56(5)
Z	4
R _p	0.0497
R _{wp}	0.0647
R _F	0.0769
χ ²	8.811
Number of refined parameters	36
Scale factor	10.68(3)
Zero point (°)	-0.0098(1)
Gaussian profile coefficients	GU= 0.000, GV= 0.000, GW= 0.035(4)
Lorentzian profile coefficients	LX= 0.73(8)
eta	0.46(1)
Microstrain broadening coefficients	S400= 0.045(1), S040= 0.42(1), S004= 0.029(2) S220= -0.092(3), S202=- 0.0033(8), S022= 0.030(3)

*The crystallographic data of Cr₂O₃: Trigonal, $R\bar{3}cH$, a = 4.95793(9) Å, c = 13.5924(8) Å and V = 289.35(2) Å³.

Table 4.17 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for *lp*-[Cr(OH)(bdc)] at 300 K

Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
Cr	0.25	-0.25	0.25	1.97(5)	1
O1	0.1666(2)	0.8421(3)	0.1635(3)	1.97(9)	1
O2	0.25	0.6753(5)	0.0	1.97(9)	1
C1	0.1366(4)	0.8681(7)	0.0	3.3(2)	1
C2	0.0649(5)	0.9462(7)	0.0	3.3(2)	1
C3	0.0374(3)	0.9694(5)	-0.1835(5)	3.3(2)	1

Table 4.18 Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) for *lp*-[Cr(OH)(bdc)] at 300 K

Cr1—O1	1.937(2)	O2 ² —Cr1—O1 ⁴	92.22(14)
Cr1—O2	1.937(2)	O2 ² —Cr1—O1 ⁵	92.22(14)
C1—O1	1.277(4)	O1 ¹ —Cr1—O1 ³	92.9(2)
C1—C2	1.568(8)	O1 ¹ —Cr1—O1 ⁴	180.0
C2—C3	1.368(4)	O1 ¹ —Cr1—O1 ⁵	87.1(2)
C3—C3 ⁹	1.487(8)	O1 ³ —Cr1—O1 ⁴	87.1(2)
		O1 ³ —Cr1—O1 ⁵	180.0
O2 ¹ —Cr1—O2 ²	180.0	O1 ⁴ —Cr1—O1 ⁵	92.9(2)
O2 ¹ —Cr1—O1 ¹	92.22(14)	Cr1 ⁶ —O2—Cr1 ⁷	121.2(3)
O2 ¹ —Cr1—O1 ³	92.22(14)	O1—C1—O1 ⁸	122.1(7)
O2 ¹ —Cr1—O1 ⁴	87.78(14)	O1—C1—C2	118.7(4)
O2 ¹ —Cr1—O1 ⁵	87.78(14)	C3 ¹⁰ —C3—C2	113.9(4)
O2 ² —Cr1—O1 ¹	87.78(14)	C3—C2—C3 ¹¹	132.1(8)
O2 ² —Cr1—O1 ³	87.78(14)	C3—C2—C1	113.8(4)

Symmetry transformations used to generate equivalent atoms:

(1) x, y-1, z; (2) x, -y+1/2, z+1/2; (3) -x+1/2, y-1, z; (4) -x-1/2, -y-1/2, -z-1/2; (5) x-1, -y-1/2, -z-1/2; (6) x, y+1, z; (7) x, -y+1/2, z-1/2; (8) x-1, y-1, -z-1; (9) -x, -y+2, z; (10) -x-1, -y+2, z; (11) x+1, y, -z.

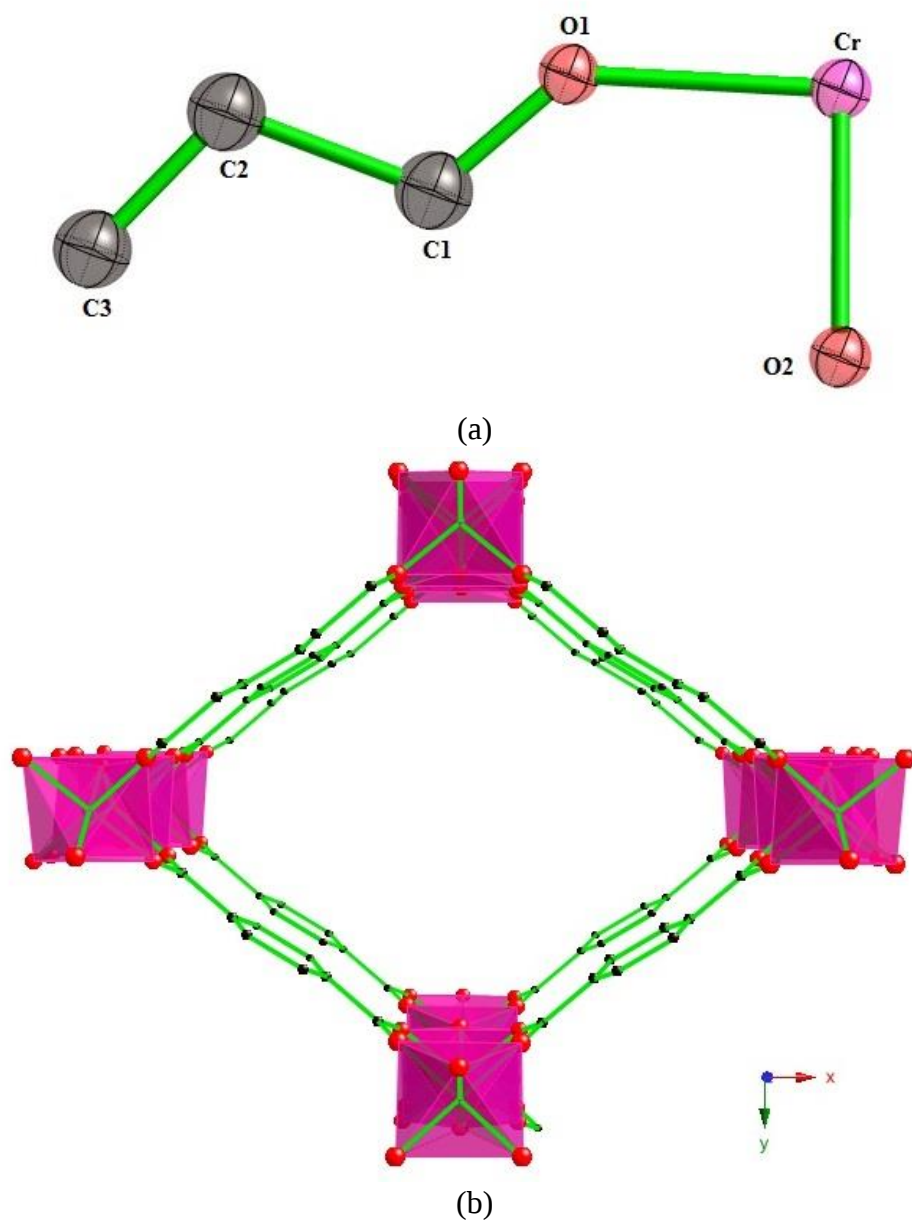


Figure 4.40 (a) The asymmetric unit of lp -[Cr(OH)(bdc)]. (b) The structure of lp -[Cr(OH)(bdc)] viewed along the [001] direction.

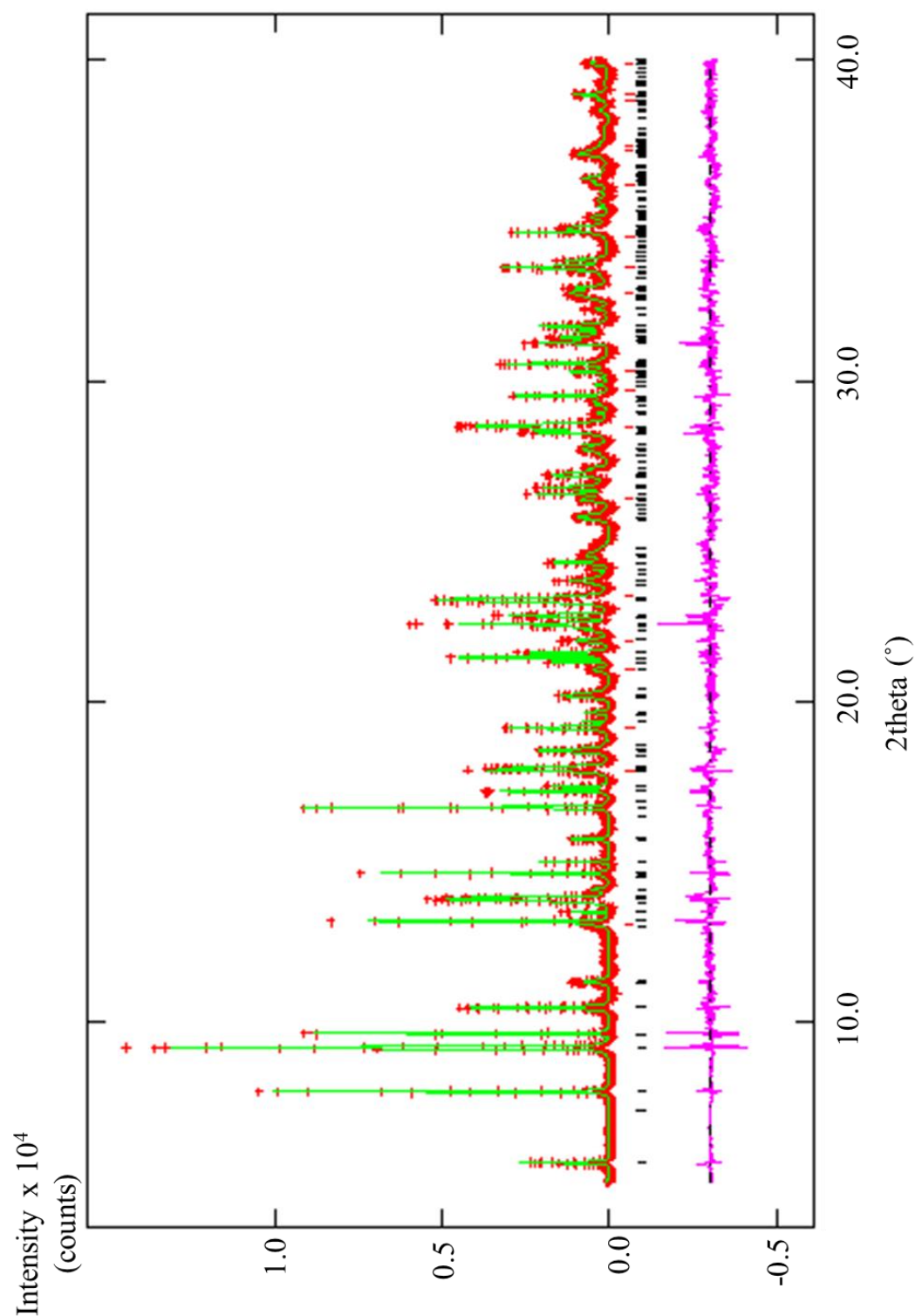


Figure 4.41 The final observed (red crosses), calculated (green line) and difference (purple line) plot for two phases Rietveld refinement of *lp*-[Cr(OH)(bdc)] and Cr₂O₃ at 300 K. The black and the red tick marks are calculated 2θ angles for the Bragg peaks of *lp*-[Cr(OH)(bdc)] phase and Cr₂O₃ phases respectively. The plot is scaled by 4x and 8x over the 2θ range of 9.5° - 20° and 20° - 40° respectively.

4.4.3 Results and discussion

The unit cell dimensions and unit cell volume of the ***lp***-[Cr(OH)(bdc)] from 100 - 500 K are listed in **Table 4.19**.

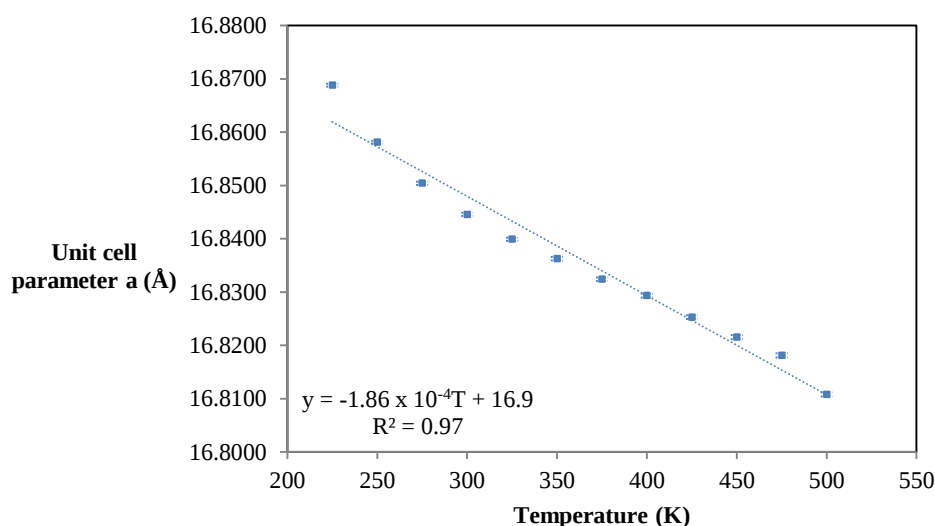
Table 4.19 Unit cell dimensions (Å) and unit cell volume (Å³), goodness of fit (χ^2), R_{wp} and R_p for ***lp***-[Cr(OH)(bdc)] from 100 - 500 K

Temperature (K)	a	b	c	V	χ^2	R_{wp}	R_p
100	16.6304(8)	13.329(1)	6.8274(3)	1513.4(1)	49.78	0.1462	0.1038
125	16.7596(5)	13.1400(5)	6.82261(1)	1502.45(7)	20.39	0.953	0.713
150	16.9199(2)	12.9676(3)	6.82261(9)	1496.95(5)	9.470	0.0660	0.0497
175	16.9137(2)	12.9139(3)	6.82441(7)	1490.60(4)	7.515	0.0588	0.0450
200	16.8872(2)	12.9491(3)	6.82511(7)	1492.48(4)	7.512	0.0592	0.0453
225	16.8688(3)	12.9719(3)	6.82529(7)	1493.51(4)	8.554	0.0634	0.0495
250	16.8581(3)	12.9844(3)	6.82564(7)	1494.08(4)	8.258	0.0624	0.0484
275	16.8504(3)	12.9923(3)	6.82578(7)	1494.34(4)	8.148	0.0621	0.0475
300	16.8446(3)	12.9978(4)	6.82586(7)	1494.46(5)	8.811	0.0647	0.0497
325	16.8399(3)	13.0016(4)	6.82567(8)	1494.45(5)	8.635	0.0641	0.0492
350	16.8362(3)	13.0047(4)	6.82554(8)	1494.45(5)	8.981	0.0654	0.0500
375	16.8324(3)	13.0077(4)	6.82559(8)	1494.47(5)	9.021	0.0656	0.0501
400	16.8293(4)	13.0105(4)	6.82576(8)	1494.55(5)	9.551	0.0674	0.0514
425	16.8253(4)	13.0136(5)	6.82585(9)	1494.57(5)	9.643	0.0678	0.0519
450	16.8215(4)	13.0171(5)	6.82617(9)	1494.71(6)	10.21	0.0697	0.0534
475	16.8181(4)	13.0209(5)	6.82654(9)	1494.93(6)	10.71	0.0696	0.0531
500	16.8108(4)	13.0300(5)	6.82742(9)	1495.51(6)	9.962	0.0689	0.0524

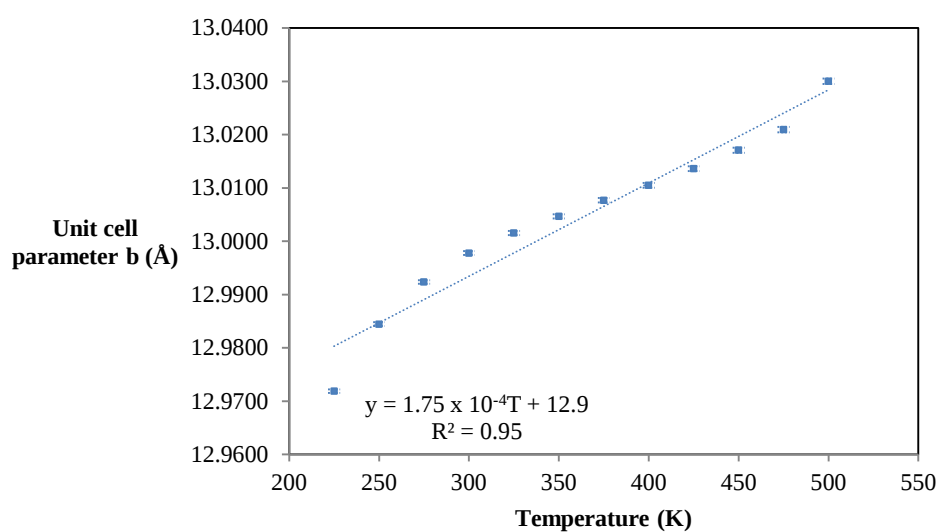
The diffraction data results indicate that ***lp***-[Cr(OH)(bdc)] stays in the ***lp*** form from 500 K to 175 K while a small amount of an unidentified phase appears at 150 K and 125 K. The reflections from the unidentified phase are found to disappear when cooling to 100 K. The diffraction data at 100 K reveals the presence of the ***lp***-[Cr(OH)(bdc)] together with a small fraction of the ***np***-[Cr(OH)(bdc)]. The latter phase was confirmed by indexing the emerging extra

low intensity reflections using the crystallographic detail of the empty *np*-[Al(OH)(bdc)]. The extra reflections observed at 125 K and 150 K did not correspond to any of the *np*-[Al(OH)(bdc)] and it was also not possible to index them to any other phase. The intensities of the reflections from the *lp*-[Cr(OH)(bdc)] phase decrease as the temperature is decreased. From above results, it is believed that a small fraction of *lp*-[Cr(OH)(bdc)] may undergo phase transition from the *lp* form to the *np* form through an intermediate phase at 125 K and 150 K. However, a precise determination of the occurrence of the phase transition cannot be elucidated due to the complicated overlapping of the reflections for each of the present phases and the relatively low intensity and number of the extra reflections which prevent the process of indexing for both the two unidentified phases.

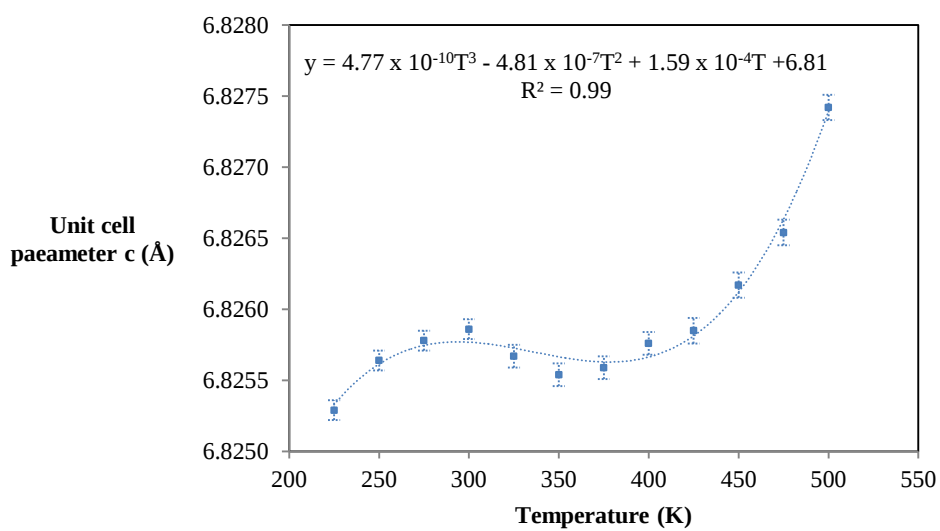
The unit cell parameters and the unit cell volume vary in an erratic manner from 100 – 200 K that is not in alignment with the behaviour expected or observed for the [Al(OH)(bdc)] and [AlF(bdc)] samples. This may be connected with the unidentified phases. For this reason, the thermoresponsive behaviour of [Cr(OH)(bdc)] will be elucidated from the data at 225 – 500 K. The temperature dependence of the unit cell parameters *a*, *b* and *c* and the unit cell volume *V* from 225 K to 500 K are shown in **Figure 4.42**.



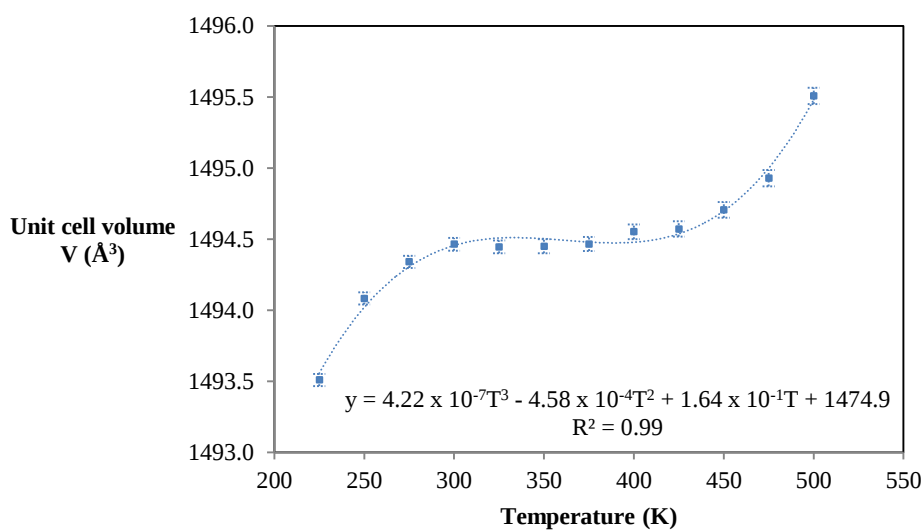
(a)



(b)



(c)



(d)

Figure 4.42 The variation of unit cell parameter (a) a , (b) b and (c) c and (d) unit cell volume V as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

Overall, thermal expansion is observed in the ***lp***-[Cr(OH)(bdc)] as the temperature is increased. The non-linear thermal expansion of the unit cell parameter c , and the unit cell volume V , are represented by polynomial functions defined in the following expressions:

$$p = p_0 + p_1T + p_2T^2 + p_3T^3 \quad \text{Equation 4.3}$$

$$\alpha = \frac{(p_1 + 2p_2T + 3p_3T^2)}{p} \quad \text{Equation 4.4}$$

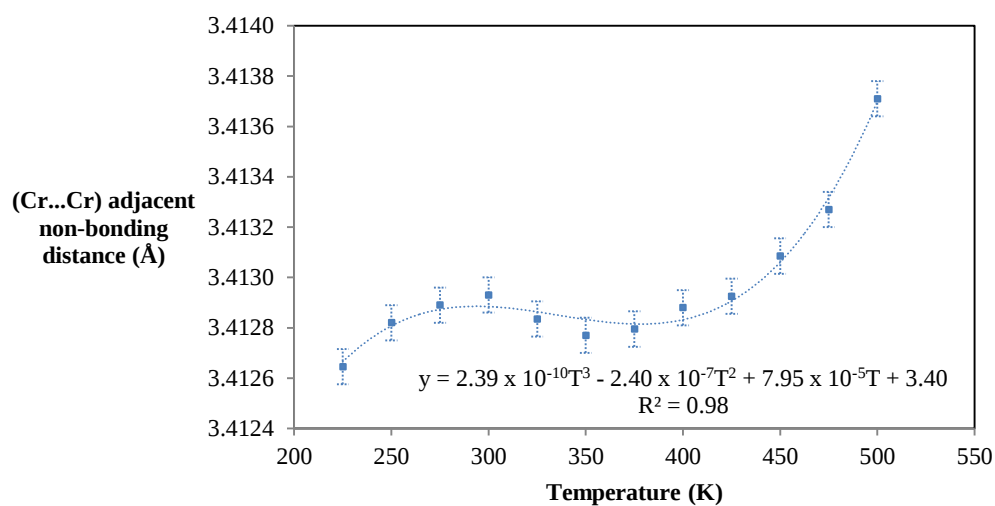
and the resulting coefficients of the polynomial function and the coefficients of thermal expansion at 250 K are listed in **Table 4.20**.

Table 4.20 The resulting coefficients of the polynomial function and the thermal expansion coefficients of the unit cell parameters a , b and c and the volume V at 250 K.

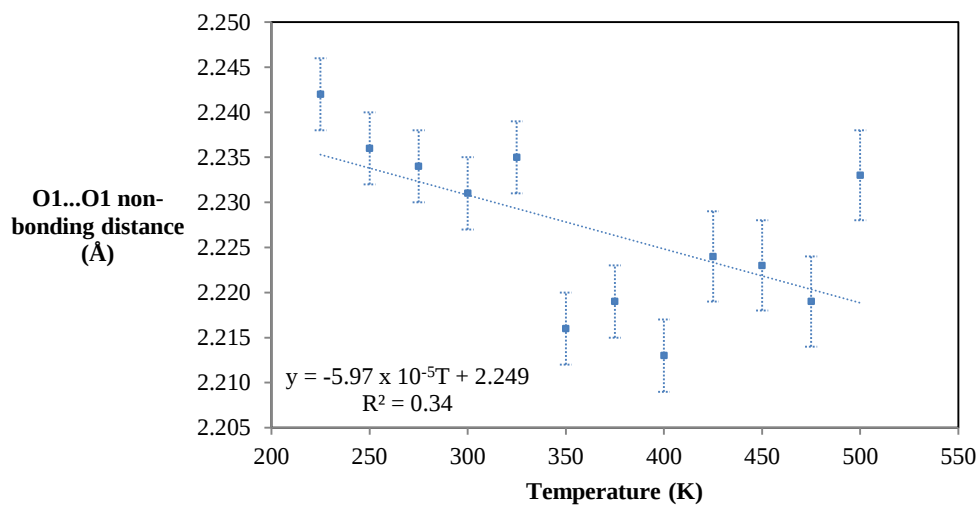
Cell parameter	p_0	p_1	p_2	p_3	α (K^{-1})
a	16.9	-1.86×10^{-4}	0	0	-1.10×10^{-5}
b	12.9	1.75×10^{-4}	0	0	1.35×10^{-5}
c	6.81	1.59×10^{-4}	-4.81×10^{-7}	4.77×10^{-10}	1.08×10^{-6}
V	1474.9	1.64×10^{-1}	-4.58×10^{-4}	4.22×10^{-7}	9.44×10^{-6}

A smooth linear thermal contraction is observed in the [100] direction which is outweighed by a linear thermal expansion in the [010] direction and a non-linear expansion in the [001] direction. This yields a non-linear volume expansion that involves a $\sim 2 \text{ \AA}^3$ of volume change. The maximum value of the volumetric coefficient of thermal expansion is $\sim 15 \times 10^{-6} K^{-1}$ at 225 and 500 K and the minimum value is $-0.98 \times 10^{-6} K^{-1}$ at 375 K.

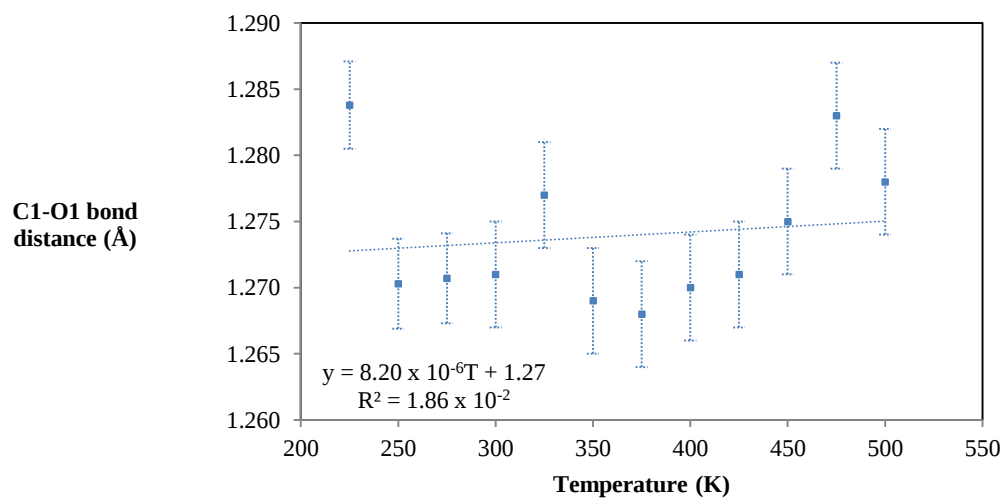
The possible mechanism responsible for the temperature dependence of the variation of the geometric parameters can be elucidated from the structure refinements at each temperature. Thermal expansion in the [001] direction which is equivalent to the a axis of ***lp***-[Al(OH)(bdc)] is considered normal behaviour and the transverse vibrational modes as elucidated in [Al(OH)(bdc)] may still be present in ***lp***-[Cr(OH)(bdc)] but are less dominant and are outweighed by the change in angular deformation which is dominant. Evidence that confirms the domination by angular deformation is that the Cr-O2 and Cr-O1 distances show near no expansion as shown in **Figure 4.43** (d) and (e) but the Cr-O2-Cr angle increases considerably more than the corresponding Al-O2-Al angle as shown in **Figure 4.43** (f). However, the precision of these results is too low to completely describe the mechanism of expansion in this case. The variations of the relevant geometric parameters that support the transverse vibrational modes responsible for the thermal behaviours observed along this direction are given in **Figure 4.43** (a) – (g).



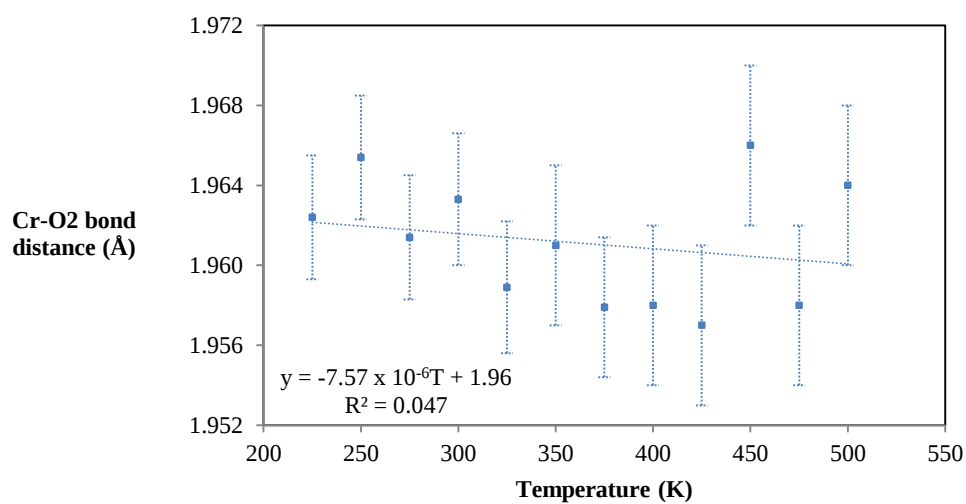
(a)



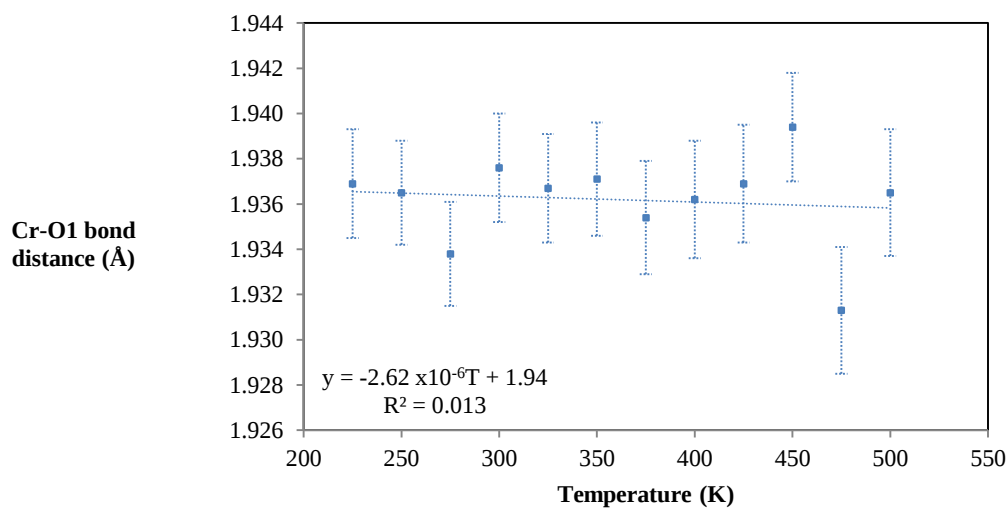
(b)



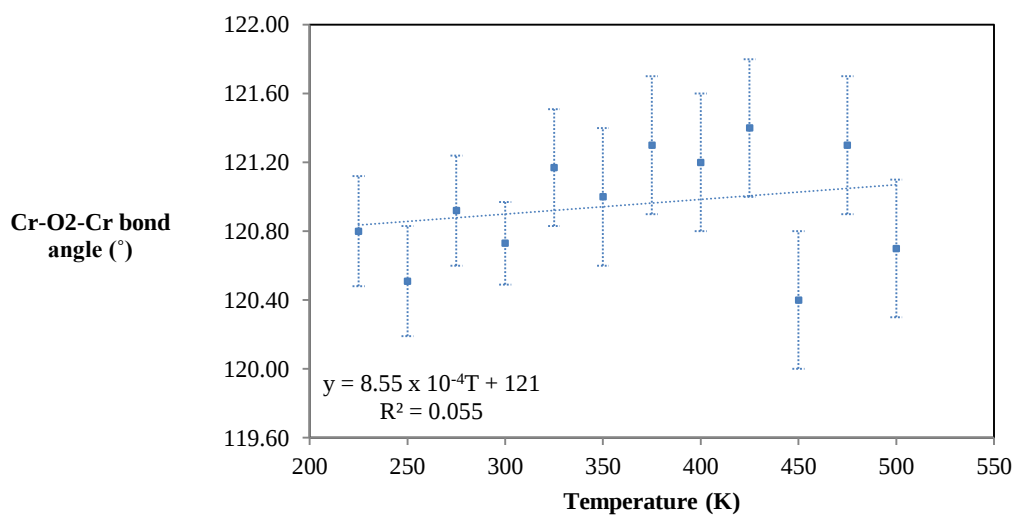
(c)



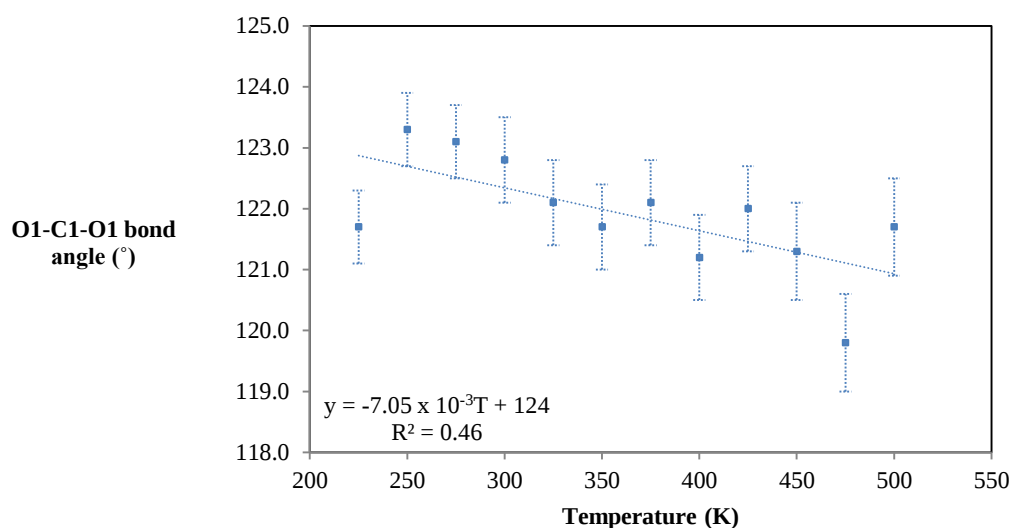
(d)



(e)



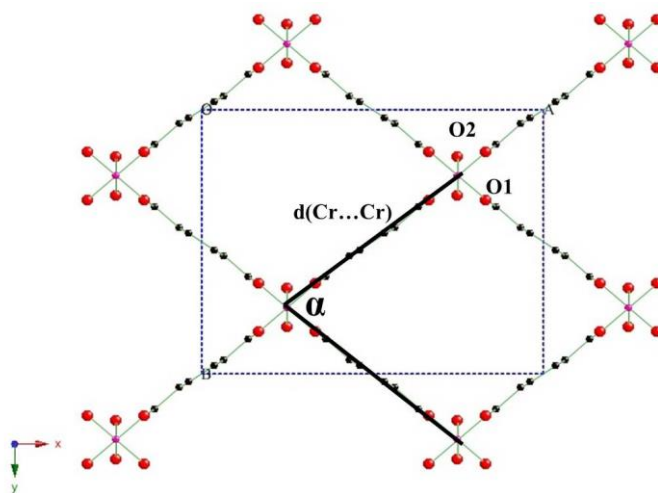
(f)



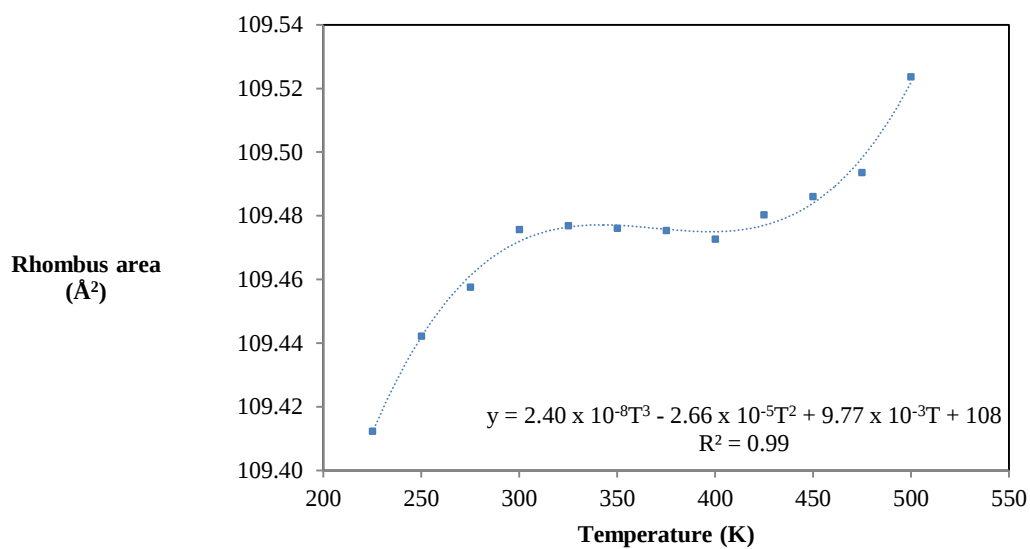
(g)

Figure 4.43 The variation of the observed geometric parameters as a function of temperature (a) the Cr...Cr adjacent non-bonding distance (b) the O1...O1 non-bonding distance (c) the C1-O1 distance (d) Cr-O2 distance (e) Cr-O1 distance (f) Cr-O2-Cr bond angle (g) O1-C1-O1 bond angle. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

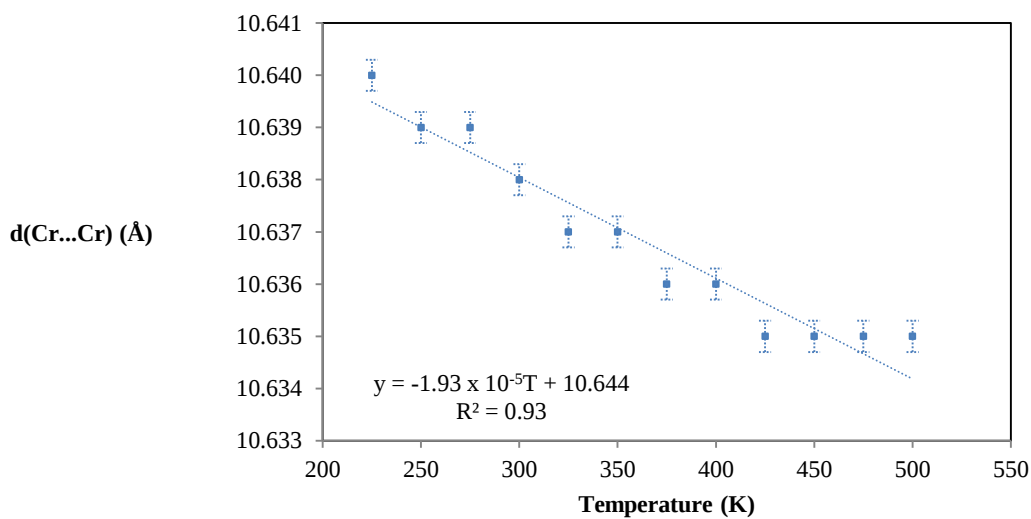
Thermal contraction in the [100] direction and expansion in the [010] direction can be explained in a similar way as in the previous two materials that is by considering one of the rhombus-shaped channels along the (001) plane which is equivalent to the (100) plans in *lp*-[Al(OH)(bdc)] and *lp*-[Al(F)(bdc)] defined as shown in **Figure 4.44** (a).



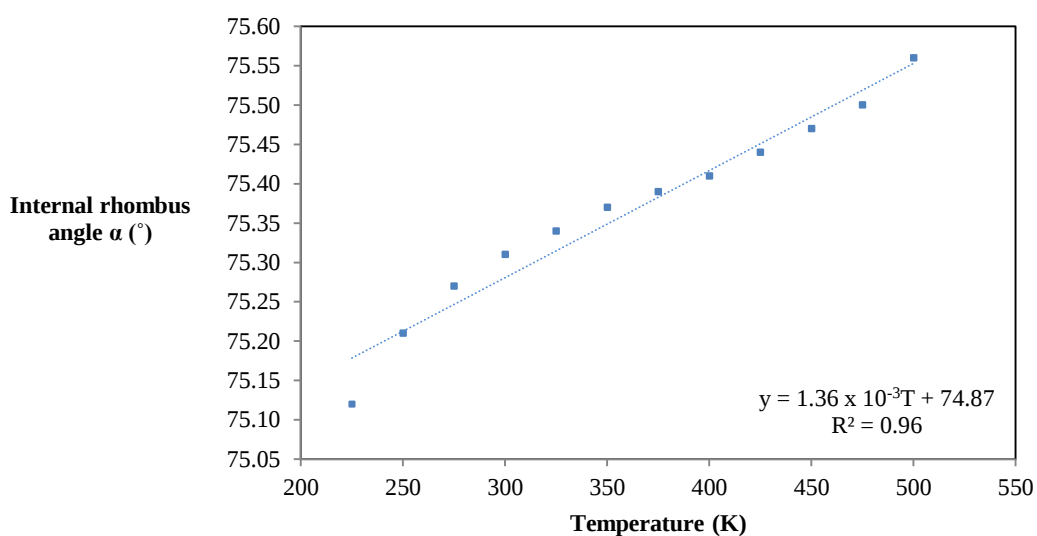
(a)



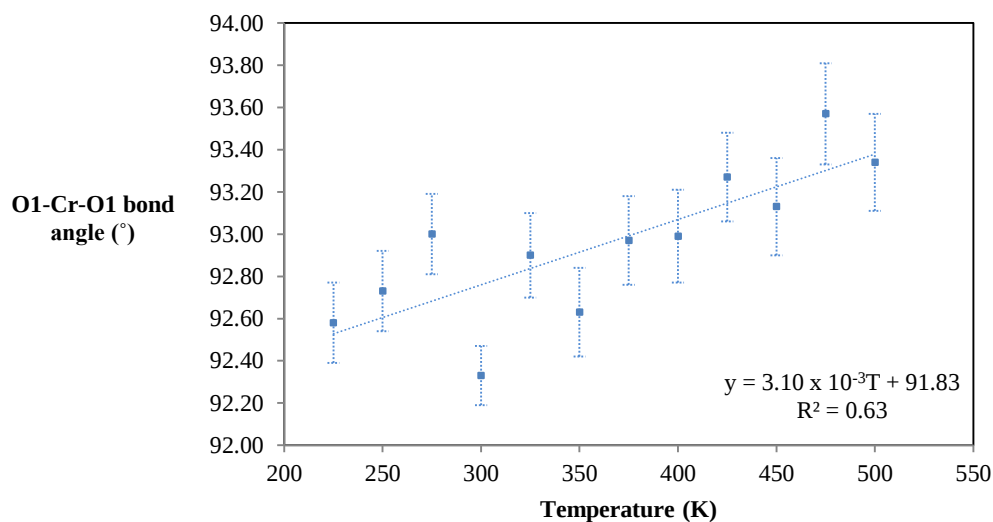
(b)



(c)



(d)



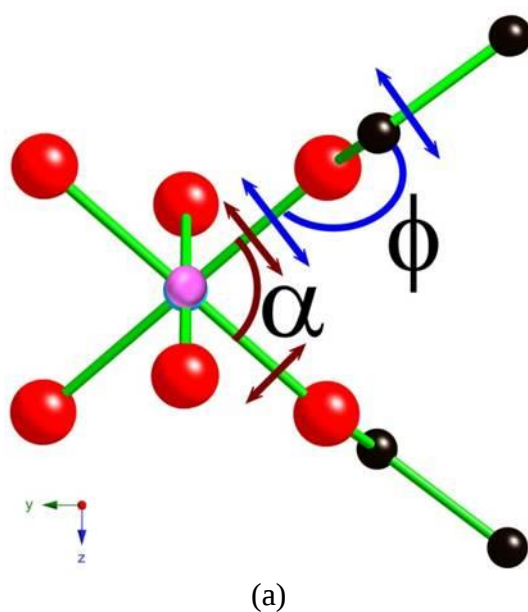
(e)

Figure 4.44 a) The framework of *lp*-[Cr(OH)(bdc)] viewed on the (001) plane showing the rhombus-shaped channel. b) The variation of the rhombus area as a function of the temperature. (c) The variation of $d(\text{Cr}\dots\text{Cr})$ as a function of the temperature. d) The temperature dependence of the internal rhombus angle α . e) The temperature dependence of the O1-Cr-O1 bond angle. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

The rhombus area is found to increase as the temperature is raised, as shown in **Figure 4.44** (b), which is a result from a combination of the variation of the $d(\text{Cr}\dots\text{Cr})$ distance and the internal rhombus angle α as shown in **Figure 4.44** (c) and (d). The internal rhombus angle α shows a smooth linear increase similar

to that in *lp*-[Al(OH)(bdc)]. The increase of the internal rhombus angle is driven by a distortion of the internal O1-Cr-O1 bond angle of the CrO₄(OH)₂ octahedra that increase in a smooth linear fashion as shown in **Figure 4.44** (e).

The d(Cr...Cr) distance of the rhombus edges is observed to contract with temperature. The variation of d(Cr...Cr) distance is shown in **Figure 4.44** (c) and is represented by the expression $-1.93 \times 10^{-5}T + 10.644$ with a coefficient of thermal expansion of this distance of $-1.80 \times 10^{-6} \text{ K}^{-1}$. The origin of the contraction of the d(Cr...Cr) distance may be explained through the rationale proposed for that in [AlF(bdc)] and shown schematically in **Figure 4.45** (a) (b) and (c). This means the contraction of the d(Cr...Cr) distance may arise from contributions from a variety of dynamic lattice vibrations or static framework distortions. If the chains of corner-sharing CrO₄OH₂ octahedra are considered to be completely rigid, then vibrations in which the chains librate around an axis passing through the Cr atoms along the (CrO₄(OH))_∞ chains would cause the d(Cr...Cr) distances to decrease as the vibrations increase in magnitude with temperature. These vibrations will occur by a concerted “knee cap”^[46] bending mode as represented in **Figure 4.45** (a) and possibly some bending within the C-C₆H₆-C core of the bdc linker itself as shown schematically in **Figure 4.45** (b).



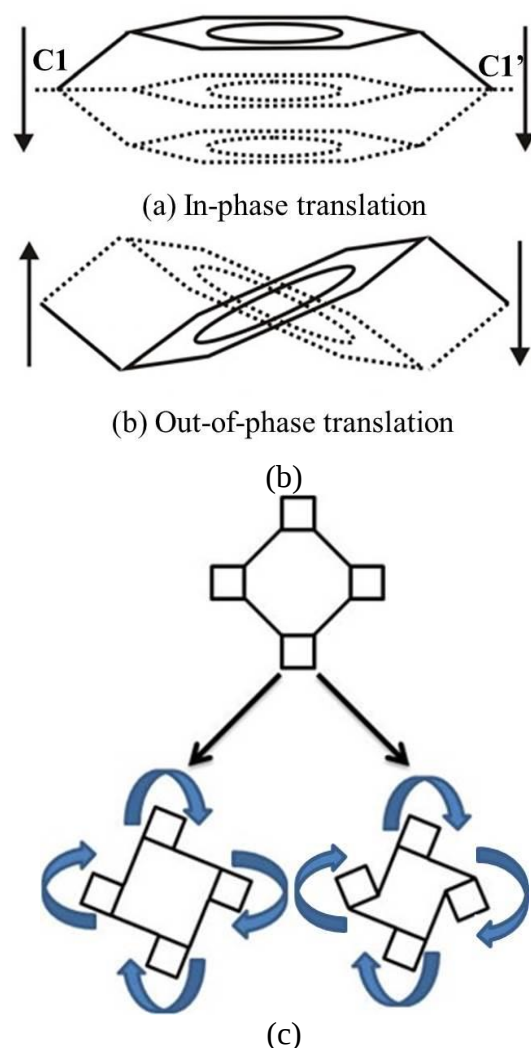


Figure 4.45 a) A schematic showing the internal rhombus angle, α and the “knee cap” bending mode about the O...O vector, ϕ . The pink, red and black balls represent chromium, oxygen and carbon atoms. (b) The possible transverse vibrational modes of the benzene ring that may cause the reduction in the $d(\text{Cr}\dots\text{Cr})$ distance. (c) The possibilities of the static framework distortion that involves “knee cap” bending mode of the carboxylate group and the bending within the core of the bdc linker.

A decrease in the $d(\text{Cr}\dots\text{Cr})$ distance could also result from a static deformation of the framework as the temperature is increased involving the same “knee cap”^[46] bending mode in the manner depicted in **Figure 4.45** (a) and possibly additional bending within the core of the bdc linker. The possible modes of the static distortion of the framework of ***lp***-[Cr(OH)(bdc)] are illustrated as shown in **Figure 4.45** (c).

In conclusion, the study of the thermoresponsive behaviour of *lp*-[Cr(OH)(bdc)] over the temperature range of 100 – 500 K shows that a small fraction of *lp*-[Cr(OH)(bdc)] undergoes a phase transition at ~150 K to an unidentified phase that is present only at 125 K and 150 K before transforming to *np*-[Cr(OH)(bdc)] at 100 K. Over the temperature range of 225 – 500 K, non-linear volume expansion is observed in *lp*-[Cr(OH)(bdc)] and results from a combination of the contraction along the [100] direction and the expansion along the [010] and the [001] direction.

The magnitude of the coefficient of volumetric thermal expansion in *lp*-[Cr(OH)(bdc)] is found to be greater than *lp*-[Al(OH)(bdc)]. The coefficients of thermal expansion of the unit cell parameters of *lp*-[Cr(OH)(bdc)] and *lp*-[Al(OH)(bdc)] are compared and are listed in **Table 4.21**. The comparison is made between the equivalent axes in each structure. Therefore, thermal behaviour along the *c*, *a* and *b* axes of *lp*-[Cr(OH)(bdc)] are compared to that along the *a*, *b* and *c* axes of *lp*-[Al(OH)(bdc)] respectively. The thermoresponsive behaviour of the unit cell edges *a*, *b* and *c* of ortho-*lp* [AlF(bdc)] are not included in this comparison as their trends show both expansion and contraction over the entire temperature range studied.

Table 4.21 The coefficients of thermal expansion at 250 K of the unit cell parameters of *lp*-[Al(OH)(bdc)] and *lp*-[Cr(OH)(bdc)].

α (K ⁻¹)	<i>lp</i> -[Al(OH)(bdc)]	<i>lp</i> -[Cr(OH)(bdc)]
α_a	-9.44×10^{-7}	1.08×10^{-6}
α_b	-1.48×10^{-5}	-1.10×10^{-5}
α_c	2.43×10^{-5}	1.35×10^{-5}
α_v	8.55×10^{-6}	9.44×10^{-6}

The thermoresponsive behaviour found in the *b* and *c* axes of both materials, [Al(OH)(bdc)] and [Cr(OH)(bdc)] are similar except that the magnitude of the coefficients of thermal expansion in [Al(OH)(bdc)] are greater than those of [Cr(OH)(bdc)], for instance, the magnitude of the coefficient of thermal expansion

in the b axis of $[\text{Al}(\text{OH})(\text{bdc})]$ is 34.5 % greater than that of $[\text{Cr}(\text{OH})(\text{bdc})]$. The greater magnitude of expansion in these two axes of $[\text{Al}(\text{OH})(\text{bdc})]$ arises from the greater degree of angular deformation of the internal geometry of the corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra as the coefficient of thermal expansion of the internal rhombus angle α is larger than that of the O1-Cr-O1 by $\sim 59.5\%$. This indicates that rotation of the bdc linkers around the -M-OH-M- chain running through the core of the corner-sharing $\text{MO}_4(\text{OH})_2$ octahedra is easier in $[\text{Al}(\text{OH})(\text{bdc})]$ than in $[\text{Cr}(\text{OH})(\text{bdc})]$.

The reduction of the rhombus edge distance in $[\text{Cr}(\text{OH})(\text{bdc})]$ contrasts to the constant value of this parameter in $[\text{Al}(\text{OH})(\text{bdc})]$. This indicates that the “knee cap” bending mode and vibrations of the bdc core contribute via dynamic lattice vibrations or static framework distortions to the thermoresponsive behaviour in $[\text{Cr}(\text{OH})(\text{bdc})]$ more than in $[\text{Al}(\text{OH})(\text{bdc})]$. The above two arguments suggest the $\text{CrO}_4(\text{OH})_2$ octahedra are more rigid than the $\text{AlO}_4(\text{OH})_2$ octahedra.

It can be concluded that the $\text{AlO}_4(\text{OH})_2$ octahedra are more flexible than the $\text{CrO}_4(\text{OH})_2$ octahedra. The energy applied to $[\text{Al}(\text{OH})(\text{bdc})]$ therefore promotes the distortion at the internal geometry of $\text{AlO}_4(\text{OH})_2$ octahedra. In contrast, as the $\text{CrO}_4(\text{OH})_2$ octahedra are more rigid, the internal geometry of the octahedra is varied to a smaller degree as the temperature is increased and the energy therefore is dissipated through other motions or distortion in the framework which involve bending at the “knee cap” and vibration in the bdc linkers and this causes the reduction of the rhombus edge $d(\text{Cr}\dots\text{Cr})$ distance.

These profound variations in thermal behaviour between $[\text{Cr}(\text{OH})(\text{bdc})]$ and $[\text{Al}(\text{OH})(\text{bdc})]$ arise from only the difference in the cations, Cr^{3+} and Al^{3+} . Alteration of cation affects the balance between ionic and covalent bonding in such materials. In this case, Al^{3+} which has a slightly smaller ionic radius than Cr^{3+} ($r_{\text{Al}^{3+}} = 54 \text{ pm}$, $r_{\text{Cr}^{3+}} = 63 \text{ pm}$)^[59] forms a more M-O bond covalent character. The more covalent bonding character means that less negative charge occurs at the oxygen atoms of the carboxylate group of the bdc linker in $[\text{Al}(\text{OH})(\text{bdc})]$ and hence there is less oxygen – oxygen repulsion between such

atoms. The less oxygen – oxygen repulsion force of the oxygen atoms in the O1-Al-O1 bond angle in [Al(OH)(bdc)] assists changes in the O1-Al-O1 bond angle resulting in a higher degree of distortion and flexibility.

4.5 Thermoresponsive behaviour of [VO(bdc)]

4.5.1 Synthesis, activation and thermal analysis

The synthesis of [VO(bdc)] was based on the procedure previously reported.^[23] All chemicals in this synthesis were used without further purification. VCl₃ (Sigma-Aldrich, 97 %, 0.8450 g) and H₂bdc (Sigma-Aldrich, 98%, 0.231 g) were dissolved in deionized water (10 ml). The mixture was then placed into 23 ml Teflon-lined stainless steel autoclave. The mixture was heated to 200 °C for 4 days and cooled down naturally at room temperature. After that the mother liquor was filtered off leaving a dark yellow fine powder product. The product was washed with deionized water. The dried product of 300 mg was treated solvothermally with 5 ml of DMF (Sigma-Aldrich, 99.8 %) at 150 °C overnight to get rid of the bdc residual inside the pore. The powder product was recovered by filtration and washed with 20 ml of DMF. The sample was then calcined under air atmosphere at 325 °C for 24 hours in order to completely empty the pores of the [VO(bdc)] framework. The powder diffraction pattern of the calcined *lp*-[VO(bdc)] compared with the reference pattern is shown in **Figure 4.46**.

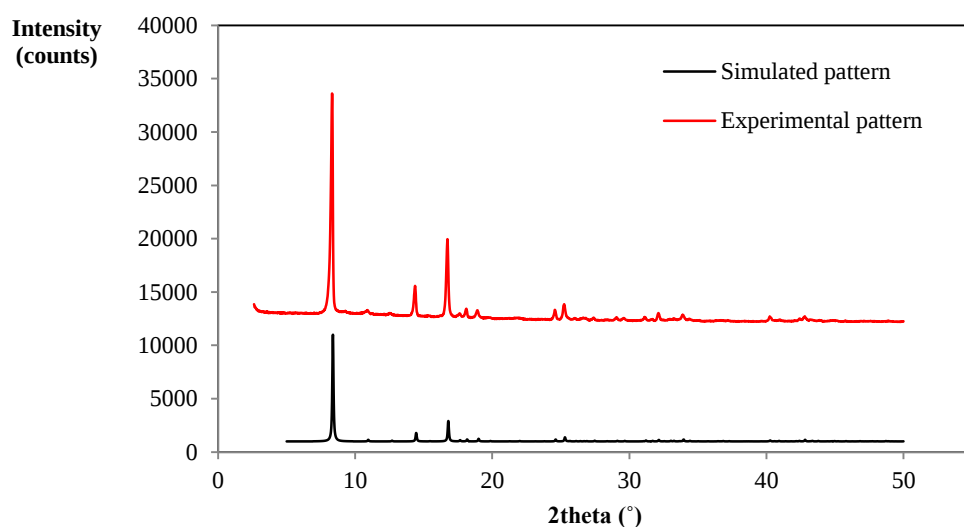


Figure 4.46 The experimental (red) and simulated (black) powder X-ray diffraction patterns of [VO(bdc)].

To confirm that framework activation was successful, thermogravimetric analysis data were collected on [VO(bdc)] and is shown in **Figure 4.47**.

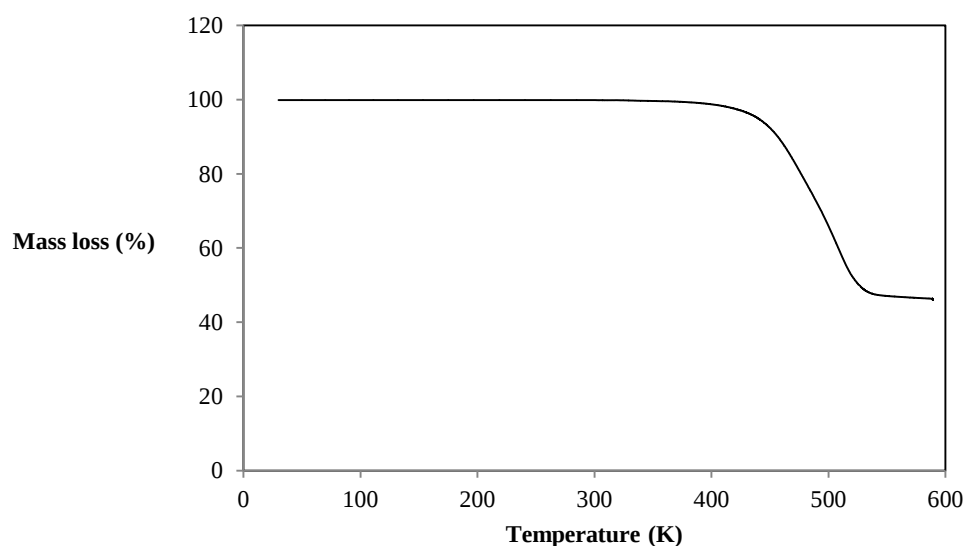


Figure 4.47 The TGA plot of [VO(bdc)] collected under N₂ and a heating rate of 2 °Cmin⁻¹.

The TGA curve of the [VO(bdc)] shows one significant mass loss at ~400 °C. The mass loss observed is 52.19 %. This corresponds to the partial loss of the

of bdc molecules which subsequently causes the framework to collapse. The calculated mass loss of the bdc molecules if completely decomposed is 62.4 %. The discrepancy between the observed and the calculated mass loss is due to an incomplete loss of the bdc molecules.

The sample of [VO(bdc)] was packed in a 0.5 mm diameter aluminium capillary tube to a length of 4 centimetres and evacuated at 2.1×10^{-1} mbar at 150 °C for 48 hours to obtain a fully degassed sample. The degassed sample was sealed under vacuum, ready for the data collection at the synchrotron.

4.5.2 Synchrotron powder thermodiffraction study

4.5.2.1 *Data collection*

The thermodiffraction study of [VO(bdc)] was performed at the I11, Diamond Light Source (DLS), UK by using the same experimental set up as described in section 4.3.5.2, the experimental run 1 of [AlF(bdc)]. Seven synchrotron powder patterns were collected over the temperature range of 11 – 290 K (data collected at 12 K, 50 K, 100 K, 150 K, 200 K, 250 K and 290 K respectively). The mean wavelength used was 0.827154(1) Å. Each diffraction pattern was collected from 3° to 140° 2 θ with a 2 θ step size of 0.001° for 30 minutes. In addition, the sample was rocked during the data collection to reduce preferred orientation and to improve sampling effects. The powder patterns were rebinned to a step size of 0.003° before data analysis.

4.5.2.2 *Data analysis*

It was noticeable from the synchrotron powder diffraction pattern that all the reflections were asymmetric on the right hand side, as shown in **Figure 4.48**. This was assumed to be due to two slightly different phases of [VO(bdc)], with one phase being present in much larger quantities than the other. The minor [VO(bdc)] phase may have formed due to partial framework collapse during calcination.

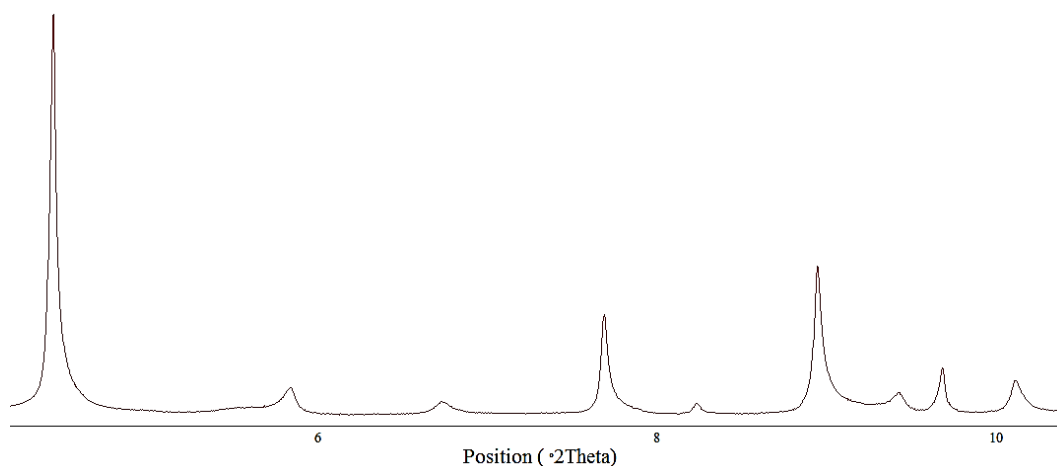


Figure 4.48 The synchrotron powder X-ray diffraction pattern of [VO(bdc)] over the 2θ range of 0° - 10° .

The data therefore was fitted with two phases as the reflections of the minor phase were overlapped with the major phase. The Le Bail fitting was initially used to fit the diffraction data with the starting model obtained from the literature for *lp*-[VO(bdc)] (orthorhombic, *Pnma*, $a = 6.818 \text{ \AA}$, $b = 16.143 \text{ \AA}$, $c = 13.939 \text{ \AA}$). The refinement was performed on 9139 observations where the first reflection at $2\theta = 4.45^\circ$ and the reflections of Al were excluded from the powder X-ray diffraction patterns. The background was fit using linear interpolation between manually designated background points. The peak shape profile of [VO(bdc)] was fitted by using a modified pseudo-Voigt function. The selected profile function considers the effect of microstrain broadening which is commonly observed in powder diffraction. As in the other orthorhombic MIL-53 members, S_{400} , S_{040} , S_{004} , S_{220} , S_{202} and S_{002} were the refined parameters modelling the microstrain broadening in [VO(bdc)].

The lattice parameters and peak profile coefficients obtained from the Le Bail fitting were then used in the Rietveld refinement. The Rietveld refinements were performed only on the major phase while the second phase was modelled using the Le Bail option. The final cycle of the least squares refinement involved 34 variables including the scale factor, detector zero point, unit cell parameters, peak profile coefficients, atomic coordinates and isotropic atomic displacement parameters (U_{iso}) of all eight atoms in the asymmetric unit. The U_{iso} of the O

atoms were constrained to have the same value during the refinement, as were those of the four C atoms.

The crystallographic data at 290 K were summarised in **Table 4.22**. The final atomic coordinates, occupancies and isotropic atomic displacement parameters are given in **Table 4.23**. Selected bond lengths and bond angles are given in **Table 4.24**. The asymmetric unit and the structure of [VO(bdc)] are shown in **Figure 4.49** (a) and (b). And the final observed, calculated and difference plot for the Rietveld refinement at 290 K is shown in **Figure 4.50**. This is a representative final result and all the refinements of all data sets are given in the attached appendix of the CD.

Table 4.22 Crystal data and structure refinement parameters for [VO(bdc)]* at 290 K

Formula	[VC ₈ O ₅ H ₄]
Formula weight	227.025
Density (gcm ⁻³)	0.985
Temperature (K)	290
Wavelength (Å)	0.827154(1)
Space group	<i>Pnma</i>
a (Å)	6.8176(1)
b (Å)	16.0881(5)
c (Å)	13.9580(6)
V (Å ³)	1530.93(7)
Z	4
R _p	0.0737
R _{wp}	0.1091
R _F	0.1061
χ ²	8.323
Number of refined parameters	41
Scale factor	21.405
Zero point (°)	-0.00540(2)
Gaussian profile coefficients	GU = 0.000, GV = 0.000, GW = 0.000
Lorentzian profile coefficients	LX = 0.000
eta	0.398(8)
Microstrain broadening coefficients	S400 = 0.031(2), S040 = 0.084(2), S004 = 0.282(4) S220 = 0.009(1), S202 = 0.051(2), S022 = -0.102(2)

*The unit cell parameters of the minor phase: a = 6.8093(6) Å, b = 16.211(1) Å, c = 13.779(1) Å and V = 1521.0(2) Å³.

Table 4.23 Final atomic coordinates, isotropic atomic displacement parameters ($\text{\AA}^2$) and occupancies for [VO(bdc)] at 290 K

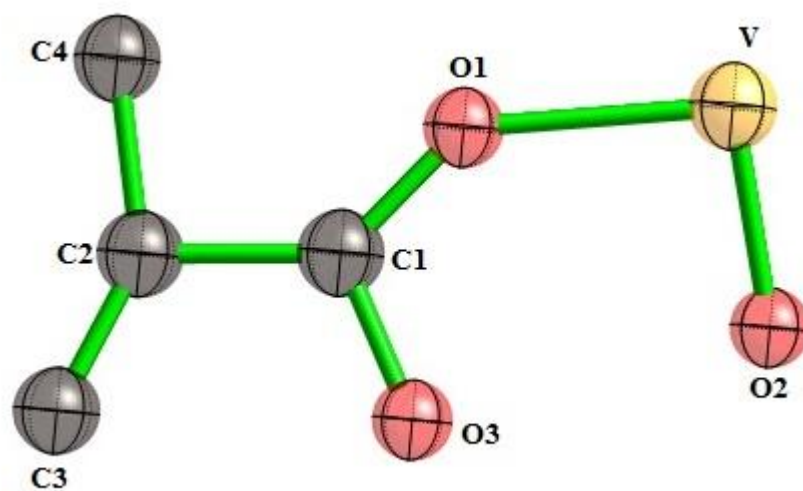
Atom	x	y	z	$U_{\text{iso}} \times 10^2$	Occupancy
V	0.1904(7)	0.25	0.7355(4)	4.5(1)	1
O1	0.319(1)	0.1567(6)	0.6542(6)	3.7(2)	1
O2	0.457(2)	0.2500	0.8068(7)	3.7(2)	1
O3	0.642(1)	0.1594(6)	0.6682(6)	3.7(2)	1
C1	0.473(3)	0.0539(9)	0.554(1)	4.4(3)	1
C2	0.493(2)	0.1213(8)	0.628(1)	4.4(3)	1
C3	0.684(2)	0.038(1)	0.540(1)	4.4(3)	1
C4	0.293(2)	0.031(1)	0.529(1)	4.4(3)	1

Table 4.24 Selected bond lengths (Å) and bond angles (°) for [VO(bdc)] at 290 K

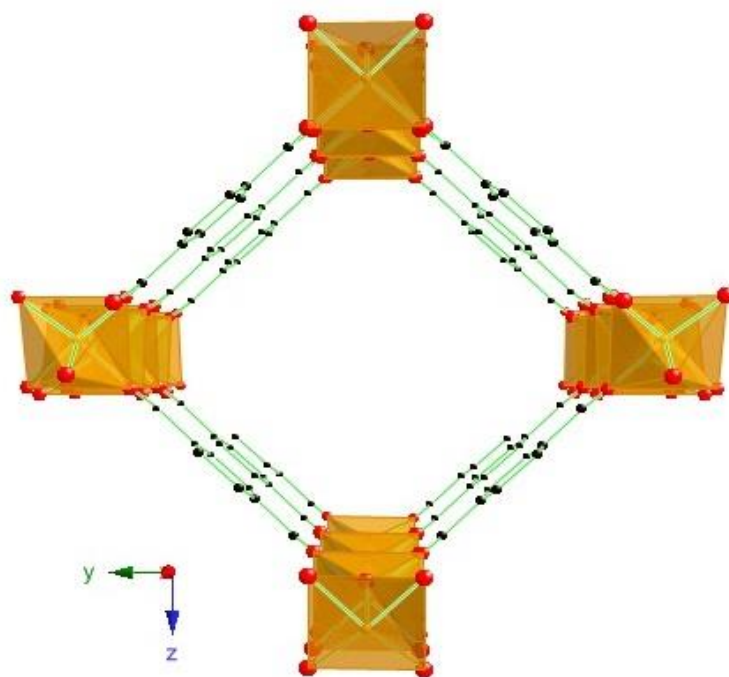
V—O2	2.07(1)	O2 ⁴ —V—O3 ⁴	94.4(4)
V1—O2 ⁷	1.700(11)	O1—V—O1 ¹	92.7(6)
V—O1	2.075(9)	O1—V—O3 ⁴	163.7(5)
V1—O3 ⁷	2.010(9)	O1—V—O3 ⁵	84.9(3)
C1—O3	1.307(12)	O1 ¹ —V—O3 ⁴	84.9(3)
C2—C1	1.504(15)	O1 ¹ —V—O3 ⁵	163.7(5)
C3—C2	1.478(14)	O3 ⁴ —V—O3 ⁵	92.9(6)
C4—C2	1.327(15)	V—O2—V ²	130.9(5)
		O1—C1—O3	111.5(10)
O2—V—O2 ³	171.5(5)	O1—C1—C2	113.5(15)
O2—V—O1	83.9(4)	O3—C1—C2	134.7(15)
O2—V—O1 ¹	83.9(4)	C3—C2—C1	97.1(17)
O2—V—O3 ⁴	79.8(4)	C4—C2—C1	118.2(18)
O2—V—O3 ⁵	79.8(4)	C4—C2—C3	144.7(15)
O2 ⁶ —V—O1	101.9 (4)	C4 ⁸ —C3—C2	108.6(15)
O2 ⁶ —V—O1 ¹	101.9(4)	C3 ⁸ —C4—C2	106.7(15)
O2—V—O2 ³	171.5(5)		
O2 ⁴ —V—O3 ⁵	94.4(4)		

Symmetry transformations used to generate equivalent atoms:

(1) $x, -y+1/2, z$; (2) $x+1/2, -y+1/2, -z+3/2$; (3) $x+1/2, -y+1/2, -z+5/2$; (4) $x+1/2, -y+3/2, -z+5/2$;
(5) $x+1/2, y, -z+5/2$; (6) $x-1/2, -y+3/2, -z+3/2$; (7) $x-1/2, -y+1/2, -z+3/2$; (8) $-x+1, -y, -z+1$;



(a)



(b)

Figure 4.49 (a) The asymmetric unit of [VO(bdc)]. (b) The structure of [VO(bdc)] viewed along the [100] direction.

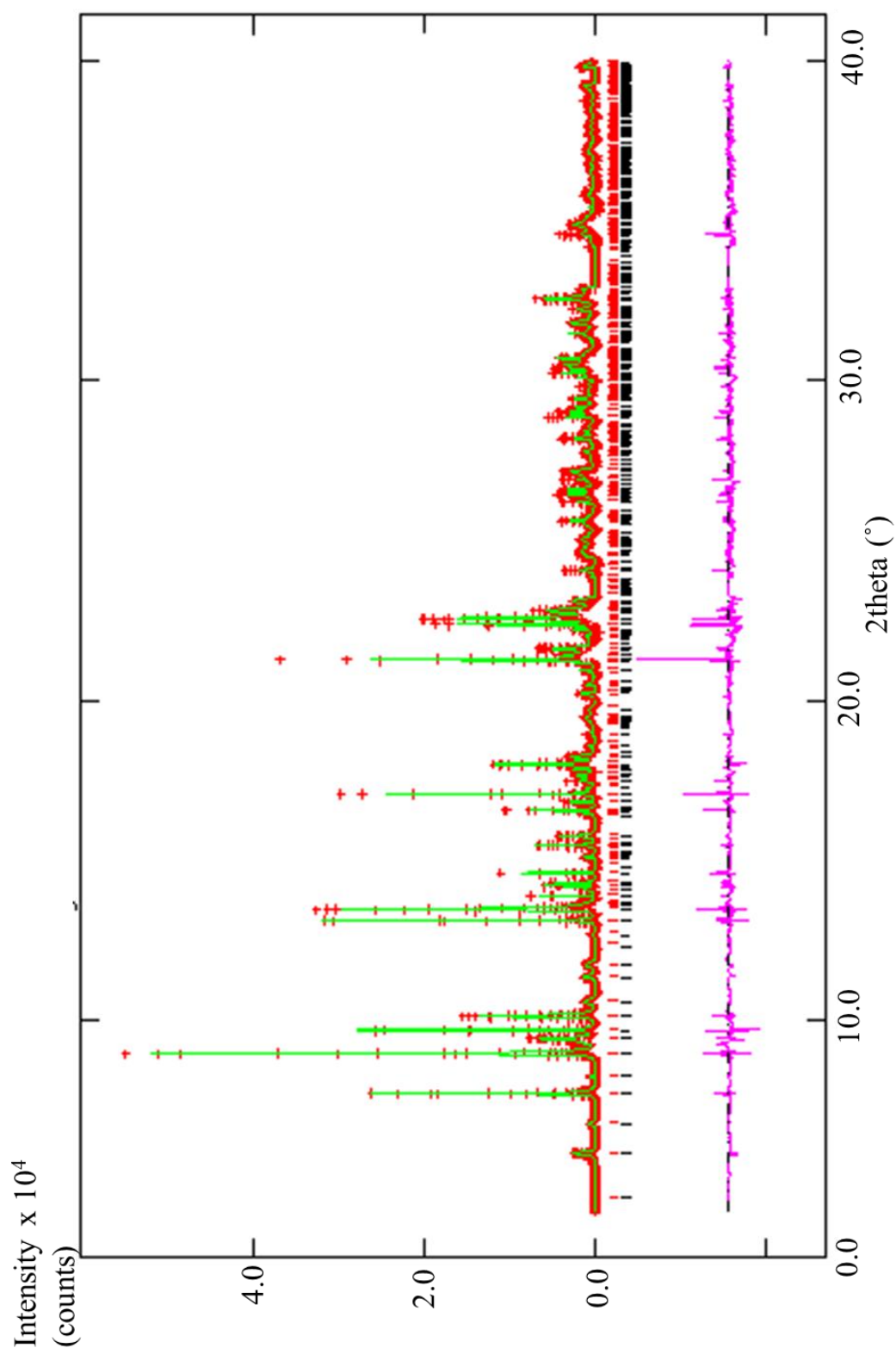


Figure 4.50 The final observed (red crosses), calculated (green line) and difference (purple line) plot for Rietveld refinement of [VO(bdc)] at 290 K. The tick marks are the calculated 2θ angles for the Bragg peaks where the black and red tick marks represent the major and minor phase respectively. The plot is scaled by 4x and 8x over the 2θ range of 9.2° - 20° and 20° - 40° respectively.

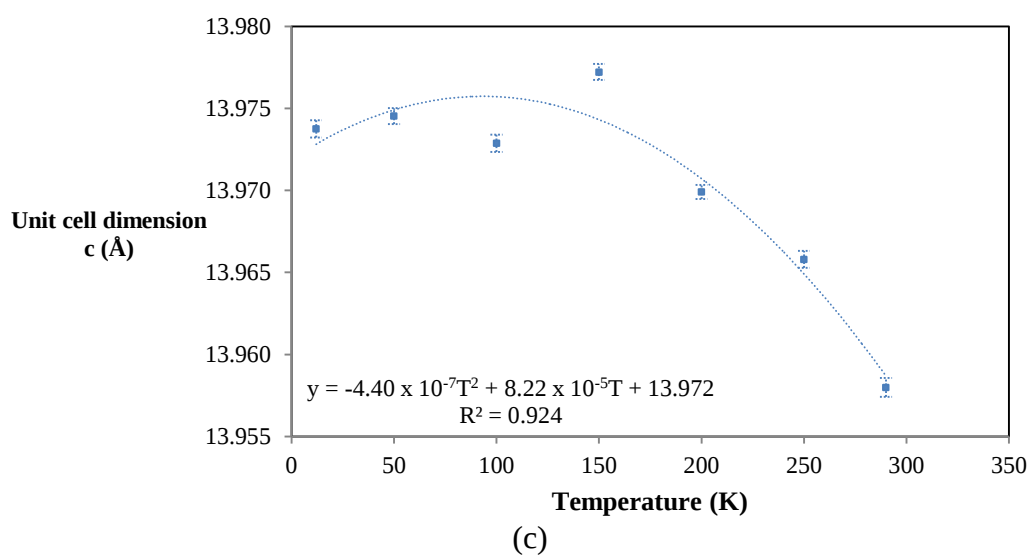
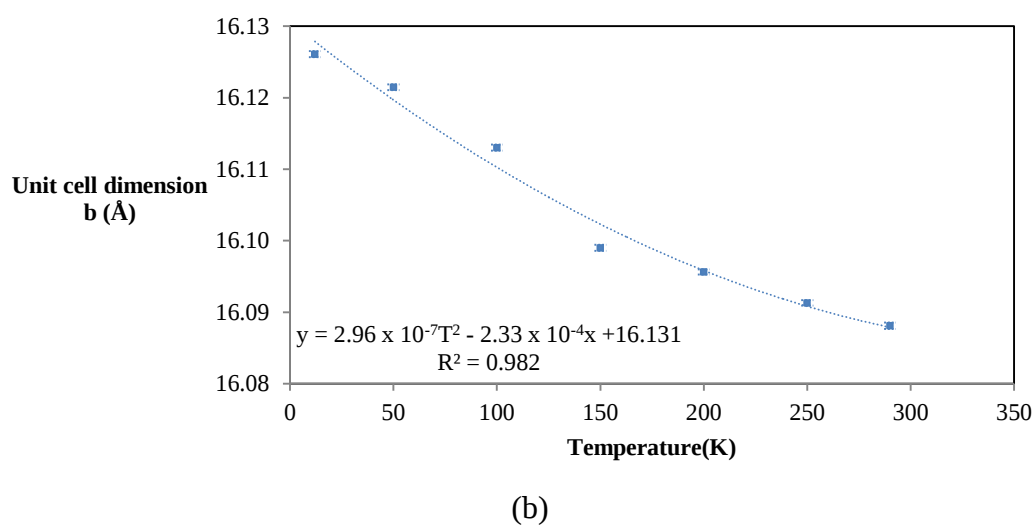
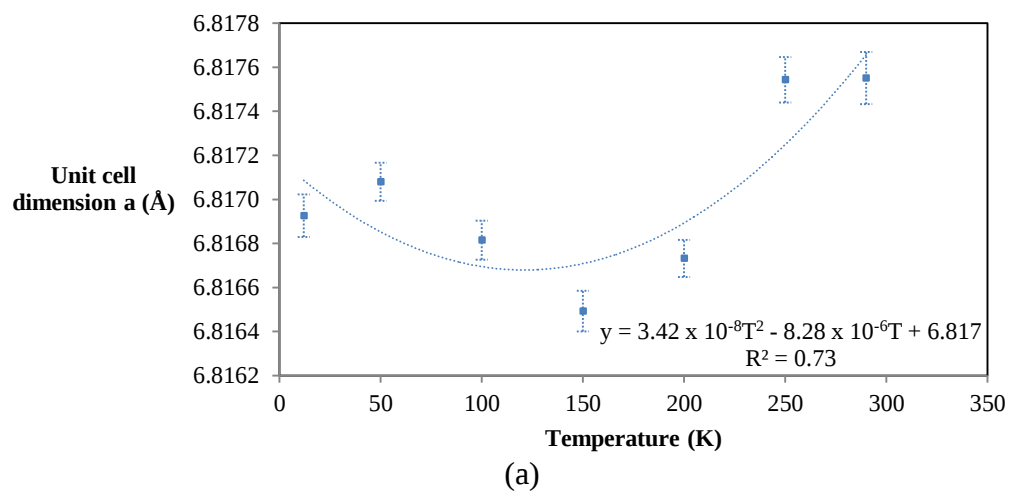
4.5.3 Results and discussion

The unit cell dimensions and unit cell volume of [VO(bdc)] are listed in **Table 4.25**.

Table 4.25 Unit cell dimensions (Å), unit cell volume (Å³), goodness of fit (χ^2), R_{wp} and R_p for [VO(bdc)] from 12 - 290 K

Temperature (K)	a	b	c	V	χ^2	R_{wp}	R_p
12	6.8169(1)	16.1261(4)	13.9738(5)	1536.14(6)	9.03	0.1128	0.0825
50	6.81708(9)	16.1215(4)	13.9745(5)	1535.82(6)	7.93	0.1057	0.0791
100	6.81682(9)	16.1130(4)	13.9729(5)	1534.72(6)	8.94	0.0119	0.0807
150	6.81649(9)	16.0991(4)	13.9772(5)	1533.84(5)	7.65	0.1033	0.0763
200	6.81673(8)	16.0956(4)	13.9699(4)	1532.77(5)	6.40	0.0947	0.0690
250	6.8175(1)	16.0913(4)	13.9658(5)	1532.09(5)	8.39	0.1089	0.0748
290	6.8176(1)	16.0881(5)	13.9580(6)	1530.93(7)	8.33	0.1091	0.0737

[VO(bdc)] is found to remain in the **lp** form over the temperature range studied. The thermodiffraction study shows linear volume contraction, $V = -1.88 \times 10^{-2}T + 1536.6$ with a coefficient of thermal expansion, $\alpha_v = -1.23 \times 10^{-5} \text{ K}^{-1}$. The variation of the unit cell parameters *a*, *b* and *c* and the unit cell volume *V* as a function of temperature are shown in **Figure 4.51**.



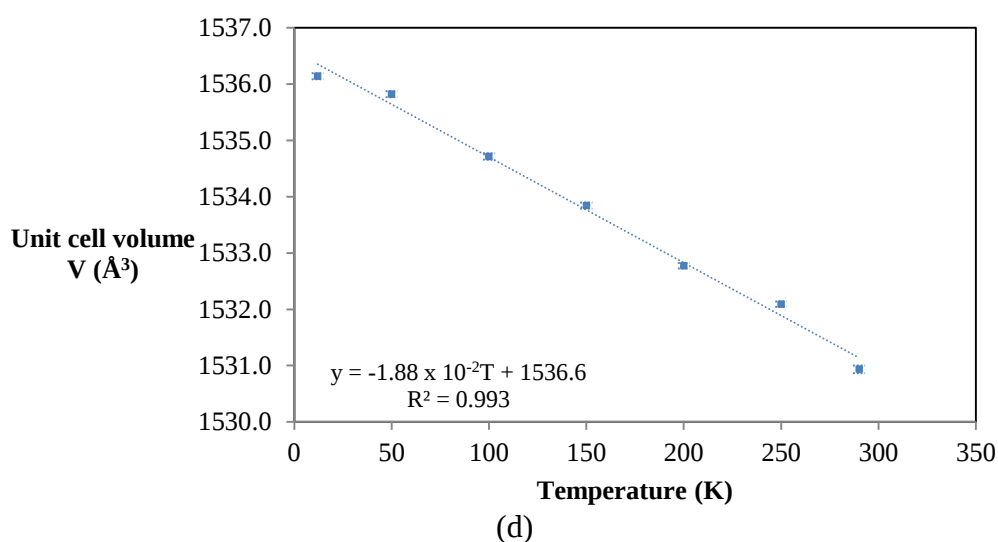


Figure 4.51 The measured variation of the unit cell parameters (a) a , (b) b and (c) c and (d) the unit cell volume V as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

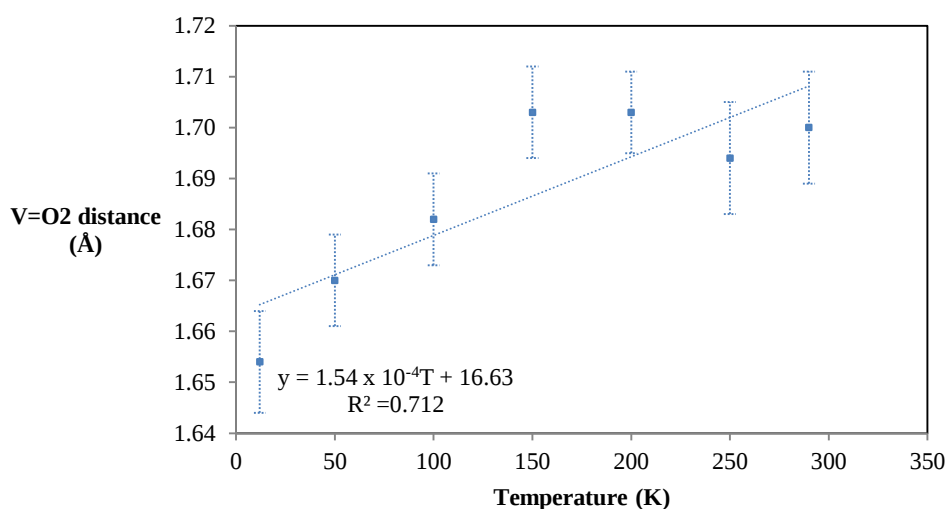
As in [AlF(bdc)], the variation of unit cell parameters, a , b and c can be represented by a polynomial function. Polynomial coefficients were calculated using Equation 4.1 and Equation 4.2. The resulting coefficients are listed in **Table 4.26**.

Table 4.26 The resulting coefficients of the polynomial function of thermal behaviour in the a , b and c axes and the volume of [VO(bdc)].

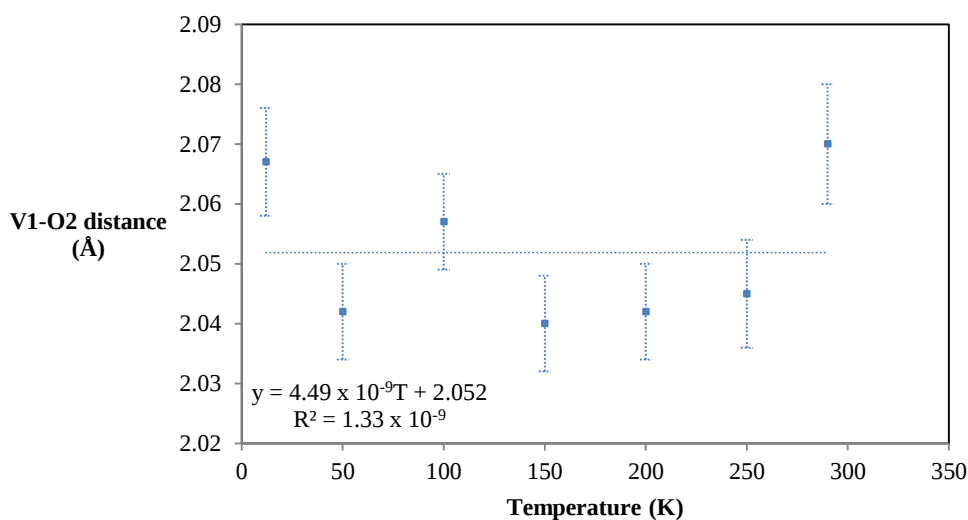
Cell parameter	p_0	p_1	p_2
a	6.817	-8.28×10^{-6}	3.42×10^{-8}
b	16.131	-2.33×10^{-4}	2.96×10^{-7}
c	13.972	8.22×10^{-5}	-4.40×10^{-7}
V	1536.6	-1.88×10^{-2}	0

A slight overall increase in the [100] direction was observed together with decreases in the [010] and [001] directions. The overall change in the a unit cell parameter is extremely small. Contractions in both the [010] and [001] directions over the studied range are the main factor that causes NTE in this material.

The Rietveld refinement of the structure at each temperature allows us to elucidate the mechanism driving the NTE behaviour. The slight thermal expansion in the [100] direction follows a usual phenomenon, thermal expansion. The variation of the geometric axial V-O parameters varies in an unusual manner as shown in **Figure 4.52**. This may result from the low precision of these refinements and the greater structural complexity of the materials



(a)



(b)

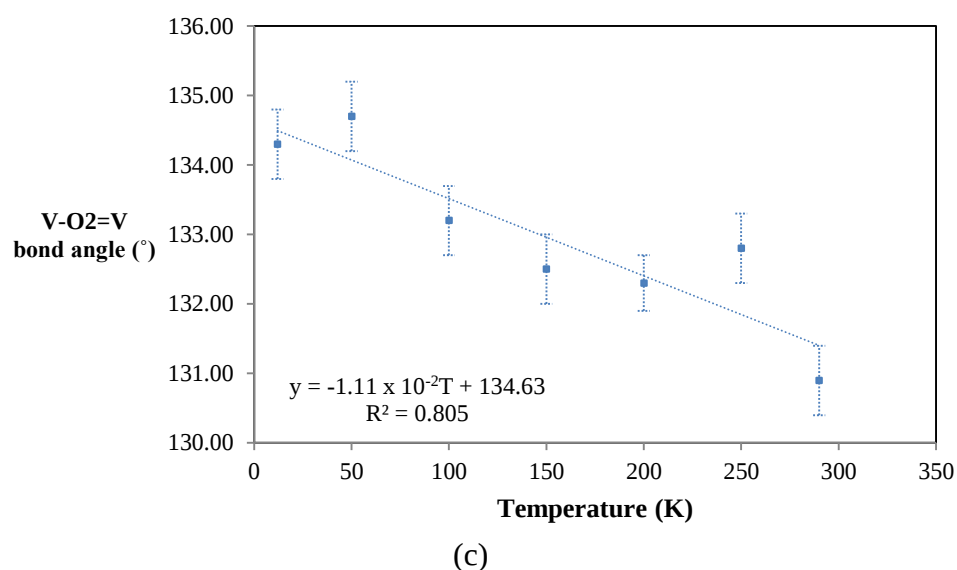
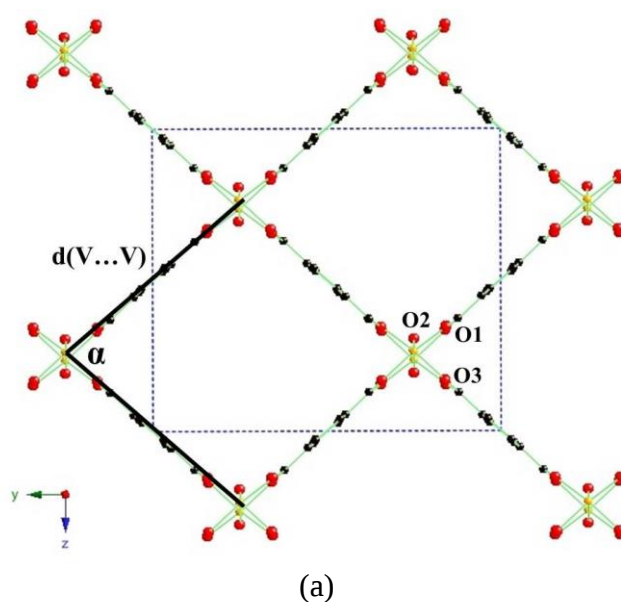
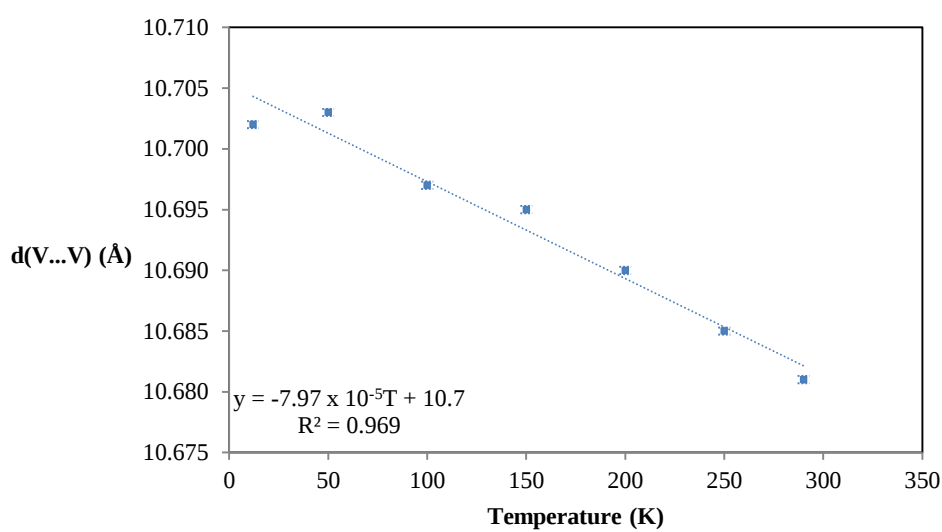


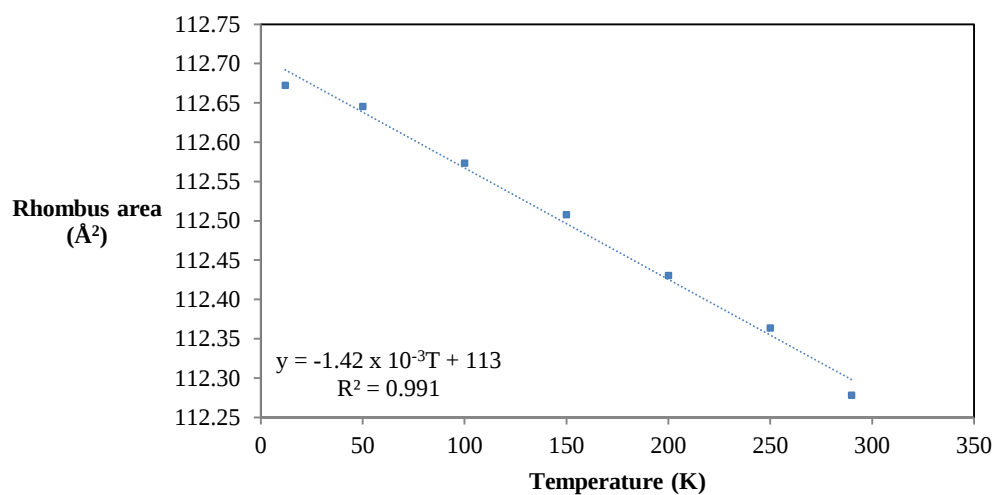
Figure 4.52 The temperature dependence of (a) V=O2 bond distance (b) V-O2 bond distance and (c) V-O2=V bond angle. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

Thermal contraction in the [010] direction varies in a rather smooth fashion whilst in the [001] direction, a slight increase observed up to 100 K before a decrease is observed over the remaining temperature range. The mechanism responsible for the contraction in the [010] and [001] direction is elucidated by considering one of the rhombus-shaped channels in the (100) plane as defined in **Figure 4.53** (a).

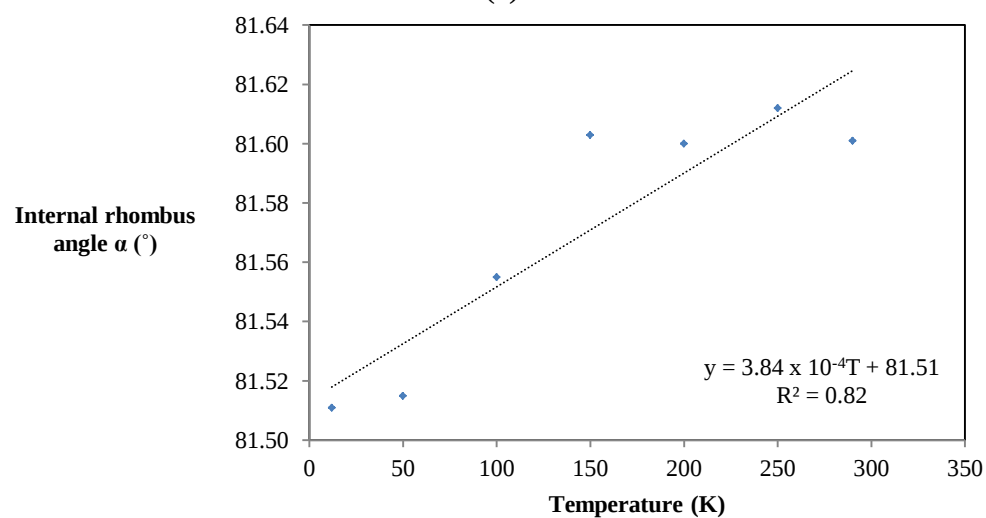




(b)



(c)



(d)

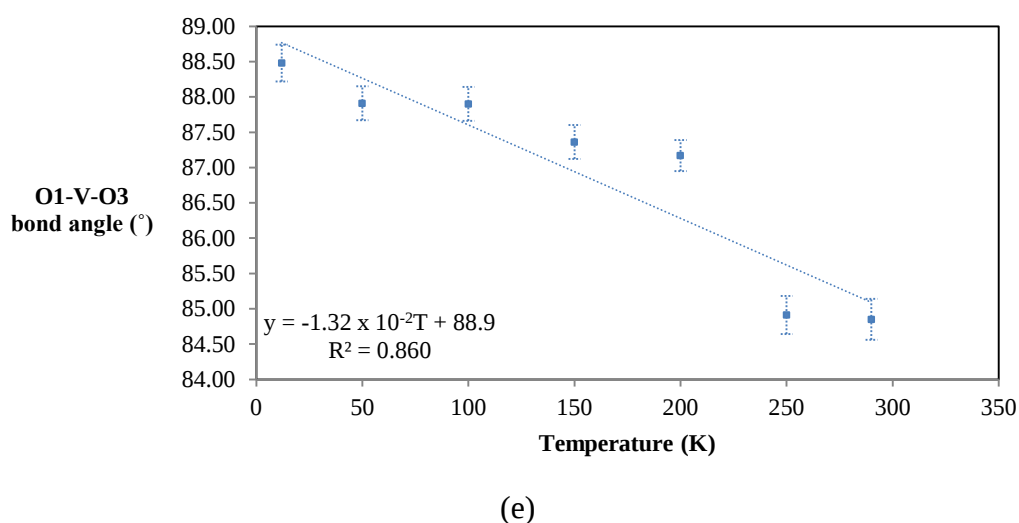


Figure 4.53 (a) A schematic illustrating rhombus-shaped channel viewed in the (100) plane. A rhombus is made by four bdc ligands linked by the vanadium atoms at each vertex. The non-bonding distance $V...V$, $d(V...V)$ corresponds to the distance from the vanadium atom at a vertex to the adjacent one. (b) The temperature dependence of the rhombus edge distance $d(V...V)$. (c) The temperature dependence of the rhombus area. (d) The temperature dependence of the internal rhombus angle α . (e) The variation of the O1-V-O3 bond angle as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

Similar to $[AlF(bdc)]$ and $[Cr(OH)(bdc)]$, the $d(V...V)$ distance on the sides of the rhombus decreases in a linear fashion over the entire temperature range as shown in **Figure 4.53** (b). A smooth decrease of the rhombus area as shown in **Figure 4.53** (c) is observed. The contraction of the rhombus area is driven by a combination of the variation of the internal rhombus angle α as shown in **Figure 4.53** (d) and the contraction of the $d(V...V)$ distance. Interestingly, the mechanism behind the contraction for $[VO(bdc)]$ in the (100) plan is not a “wine rack” thermo-mechanical mechanism like in cases of the other three materials, although all the four materials adopt an identical framework connectivity, as the decrease is observed in both the b and c directions.

The variation of the internal rhombus angle suggests that the VO_6 octahedra are not completely rigid with respect to angular deformation. The increase of thermal energy will promote the distortion of the octahedra which in this case causes a reduction of the internal O1-V-O3 bond angle as shown in **Figure 4.53** (e). The internal rhombus angle α increases by a degree of 0.09°

while the internal O1-V-O3 bond angle is found to decrease by a degree of $\sim 4.5^\circ$. Regardless of the limitation of the full structure determination, this implies that, in **lp**-[VO(bdc)], the “knee cap” bending mode is more dominant than the rotation of the bdc linkers about the $(\text{VO}_4(\text{O}))_\infty$ core of the chain of the VO_6 octahedra. The domination of the “knee cap” bending mode in this material is supported by the greatest magnitude of the contraction of the $d(\text{V}\dots\text{V})$ distance when compared to those in [AF(bdc)] and [Cr(OH)(bdc)].

The contraction of the $d(\text{V}\dots\text{V})$ distance can be explained by using the same rationale as proposed in cases of [AlF(bdc)] and [Cr(OH)(bdc)] and shown schematically in **Figure 4.45** (a), (b) and (c). This means the contraction of the $d(\text{V}\dots\text{V})$ distance originates from contributions from a variety of dynamic lattice vibrations or static framework distortions. However, from the arguments above, it is more likely that the static framework distortion is the main cause of the contraction of the $d(\text{V}\dots\text{V})$ distance and hence thermoresponsive behaviour of **lp**-[VO(bdc)].

The static deformation of the **lp**-[VO(bdc)] framework upon the insertion of various guest molecules has been reported before by Jacobson *et al.*^[4] The change of the structure upon guest molecule insertion was evident by means of single-crystal X-ray diffraction and was found to be driven by a concerted rotation of the chain of VO_6 octahedra involving the “knee cap” bending mode and the static bending of the bdc linker in the direction toward/away from the channel axis. The static distortion of [VO(bdc)] is shown graphically in **Figure 4.54**. This result is found to support the mechanism of NTE behaviour of **lp**-[VO(bdc)] observed in this work.

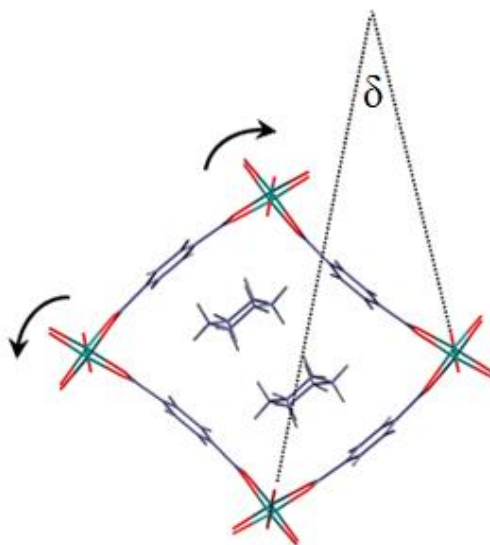


Figure 4.54 An illustration of the static framework distortion of [VO(bdc)] upon the insertion of guest molecules. δ indicates the angle of twisting between the zigzag-V=O-V=O-backbone planes of two neighbouring octahedral chains. The black arrows indicate the twisting motion of the VO_6 octahedra.^[4]

Overall comparison of thermoresponsive behaviour of [VO(bdc)] with the other materials is difficult as it contains a different metal ion, a higher oxidation state and a different connecting atom O. However, it can be seen that the composition plays a systematic role in the thermoresponsive behaviour.

4.6 Conclusion

The thermoresponsive behaviour of the four isostructural materials is found to vary considerably. [Al(OH)(bdc)] exhibits positive thermal expansion as does [Cr(OH)(bdc)] while [AlF(bdc)] and [VO(bdc)] show negative thermal expansion. Within the four candidate materials and at some particular temperatures, [AlF(bdc)] has the greatest magnitude of volume contraction while [Cr(OH)(bdc)] is found to have the greatest magnitude of volume expansion. The coefficients of thermal expansion in [Al(OH)(bdc)] and [VO(bdc)] are constant over the entire temperature range studied. [VO(bdc)] shows no phase transition as it stays in the **lp** form over the temperature range studied. [AlF(bdc)] stays in the **lp** form with only a subtle distortion. [Cr(OH)(bdc)] stays in the **lp** form where a minority transforms into the **np** form at 100 K. This result conflicts with a previous study as the transition temperature is lower than that previously reported. [Al(OH)(bdc)] stays in the **lp** form before transforming to the **np** form at 125 K. This behaviour is consistent with that reported previously. It can be noticed that the presence of the –OH group assists the phase transition. Also, the inherent nature of the metal octahedra has a profound effect upon the phase transition as the presence of the ligand with higher electronegativity ($F^- > O^{2-} > OH^-$) may decrease the flexibility of the octahedra which possibly eliminates or suppresses the phase transition like in the case of [AlF(bdc)]. On the other hand, the presence of higher oxidation state transition metals may decrease the flexibility of the octahedra which may also possibly prevent the phase transition like in the case of [VO(bdc)].

The thermoresponsive behaviour of the four materials is driven by the changes occurring on the plane across the direction of the pore. The mechanism behind the changes on this plane is a “wine rack” thermo-mechanical mechanism which is defined by the connectivity of the framework. However, this mechanism is applicable to only the thermal behaviour of [Al(OH)(bdc)], [AlF(bdc)] and [Cr(OH)(bdc)], while in [VO(bdc)] this feature is not observed. The changes on the plane across the pore direction are determined by the variation of the internal

rhombus angle α and the d (M... M) distance, all of which are summarized in **Table 4.27**.

Table 4.27 The summary of total angular variation of the internal rhombus angle α , d and the coefficients of thermal expansion of the d (M...M) distance, $\alpha_{d(M...M)}$.

Materials	d (°) (temperature range K)	$\alpha_{d(M...M)}$ (K ⁻¹)
[Al(OH)(bdc)]	0.69 (150 – 500)	0
[Cr(OH)(bdc)]	0.44 (225 – 500)	-1.80 x 10 ⁻⁶
[AlF(bdc)]	$ d = 0.23$ (175 – 350) $ d = 0.10$ (350 – 500)	-3.91 x 10 ⁻⁶
[VO(bdc)]	0.09 (12 – 290)	-7.46 x 10 ⁻⁶

The variation of the internal rhombus angle α results from the contributions of the two distinct types of vibration which are the rotation of the bdc linkers around the $(MO_4(X))_\infty$ core of the chain of $MO_4(X)_2$ octahedra and the “knee cap” bending mode at the carboxylate group of the bdc linkers. The relative contributions of these two modes of vibration are determined by the flexibility of the $MO_4(X)_2$ octahedra as evident in **Table 4.27**. The flexibility of the $MO_4(X)_2$ octahedra is found to be determined by the anion types and the oxidation state of the metal ions. The higher electronegativity and the higher oxidation state of the metal ions increase the rigidity of the $MO_4(X)_2$ octahedra.

The contraction of the d (M...M) distance originates from either the lattice dynamic vibrations or the static distortion of the bdc linkers. The dynamic lattice vibrations involve the concerted libration of the chains of metal octahedra around an axis passing through the M atoms along the $(MO_4X)_\infty$ chains, a “knee cap” bending mode and possibly some bending within the C-C₆H₆-C core of the bdc linker itself. The static deformation occurs as a result of the “knee cap” bending mode and possibly additional bending within the core of the bdc linker. However, it is more likely that the decrease of the d (M...M) distance is due to the static distortion. In addition, the magnitude of the coefficient of thermal contraction of the d (M...M) distance seems to determine the coefficient of volumetric thermal

contraction. This means the greater the magnitude of the thermal contraction of the d(M...M) distance, the greater the magnitude of the volumetric thermal contraction.

The architecture of the framework is also found to determine the thermal behaviour of the materials and also the magnitude of the coefficient of thermal expansion. In the case of the materials studied in this chapter, the presence of one-dimensional inorganic chain parallel to the channel axis limits the possibilities of dynamic motion since it has a lesser degree of freedom. A less constrained framework if one considers the dimensionality of the inorganic component is a framework consisting of zero-dimensional inorganic cluster such as MOF-5 and HKUST-1. It can be seen that the negative thermal expansion coefficient of both materials is greater than any member in the MIL-53 family. The way in which the chains of octahedra are connected together defines the pore shape which, in case of the MIL-53, is rhombus shaped. This particular shape of the framework is found to be more restricted and thus prevents or limits the transverse vibrations of the bdc linker. This shape also implies a reverse relationship between the two component directions lying on the rhombus plane that can be depicted as a “wine rack” feature.

In conclusion, [VO(bdc)] is found to be the best wise candidate for a use in controlling the expansivity of a composite as it exhibits NTE behaviour over a broad temperature range without the presence of a phase transition and has a thermal stability up to 400 °C.

4.7 References

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5. Thermoresponsive behaviour of $[\text{Sc}_2(\text{bdc})_3]$

5.1 Introduction

In the previous chapter, the thermal behaviour of the bdc containing MIL-53 family has been revealed. Possible variations of the constituent atoms such as cation type, anion type and oxidation state of the metal ion have been tested to determine if they have a significant effect on the thermal behaviour observed. However, it is noticeable that the framework construction highly dominates the thermal behaviour of such materials. In this chapter, thermal behaviour of a bdc containing MOF that is scandium terephthalate $[\text{Sc}_2(\text{bdc})_3]$ will be studied. This material has similar framework connectivity to that of the MIL-53 family as well as the dimensionality of the inorganic component. The investigation of the thermal behaviour in this material, therefore, provides better understanding in the factors influencing the thermoresponsive behaviour of materials.

$[\text{Sc}_2(\text{bdc})_3]$ can be synthesised by solvothermal reaction between a scandium salt and the bdc linker.^[1-3] Its three dimensional structure is made from ScO_6 octahedra that are connected through the bdc linkers to form channel system with pores running along the $[100]$ direction as shown in **Figure 5.1**. The inset in **Figure 5.1** shows the chain of isolated ScO_6 octahedra that is made of ScO_6 octahedra linked by three carboxylate groups of the bdc ligands running parallel to the a axis direction. A chain of isolated ScO_6 octahedra is linked with six adjacent chains of ScO_6 octahedra. There are two sets of bdc linkers which are chemically equivalent but crystallographically independent. The first set is the bdc linkers that link the two chains of ScO_6 octahedra at the same fractional coordinate which causes an extension of the framework in the b axis direction and this set of the bdc linkers is coloured in white as shown in **Figure 5.1**. The second set is the bdc linkers lying in the direction parallel to the $\{011\}$ plane. They connect alternatively to the chains of ScO_6 octahedra at higher and lower coordinates in x and are coloured in green in as shown in **Figure 5.1**.

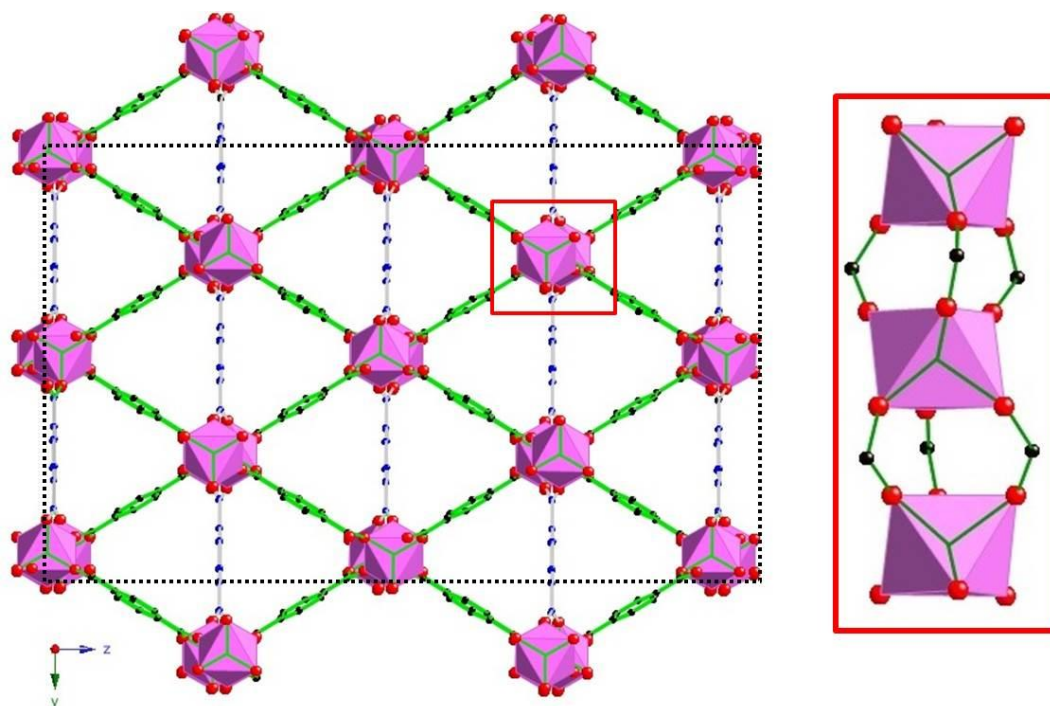


Figure 5.1 (a) The structural framework of $[\text{Sc}_2(\text{bdc})_3]$ viewed in the $[100]$ direction. The black-dotted line represents the unit cell axis. Two independent sets of the bdc linkers are coloured in green and white. The inset shows the magnified view of the connectivity of the inorganic chain. The pink octahedra represent the ScO_6 octahedra while the red and black balls represent the oxygen and carbon atoms respectively.

$[\text{Sc}_2(\text{bdc})_3]$ has a smaller pore (BET surface area = $721 \text{ m}^2\text{g}^{-1}$) than the members of the MIL-53 family as it has a higher bdc content. The two materials are similar in term of the inorganic component since they both have the one dimensional extended inorganic components. The chain of octahedra of MIL-53, however, is made by the corner-sharing $\text{MO}_4(\text{X})_2$ octahedra while in $[\text{Sc}_2(\text{bdc})_3]$, it is made from isolated ScO_6 octahedra linked together by the carboxylate groups of the bdc linker only. The pore shape of $[\text{Sc}_2(\text{bdc})_3]$ is triangular and can also be considered as a rhombus that cut in the middle by the bdc linker. The comparison of the structural frameworks of $[\text{Sc}_2(\text{bdc})_3]$ and the MIL-53 materials is shown in **Figure 5.2**.

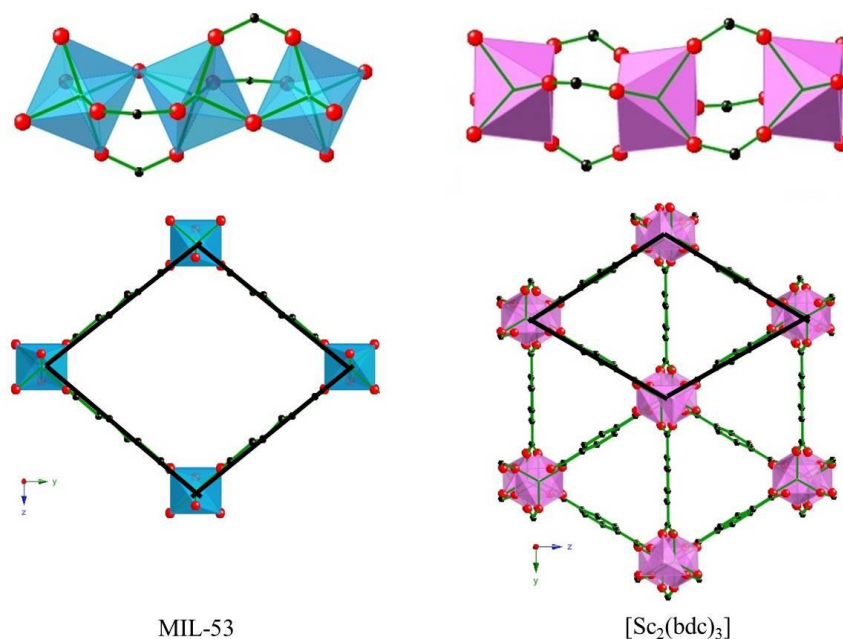


Figure 5.2 The differences between the framework topology of the MIL-53 family and $[\text{Sc}_2(\text{bdc})_3]$ which are the fashion of how the metal octahedra are linked and the connectivity in the plane of the pore opening.

$[\text{Sc}_2(\text{bdc})_3]$ was first reported in 2005 and has been tested for the adsorption of a variety of fuel-gases such as H_2 , CH_4 and C_2H_6 . Unlike the MIL-53 materials, the $[\text{Sc}_2(\text{bdc})_3]$ framework shows no evidence of the “breathing effect”. Recently, the thermoresponsive behaviour of $[\text{Sc}_2(\text{bdc})_3]$ has been investigated and reveals the existence of a phase transition at 225 K from monoclinic ($C2/c$, $a = 8.75468(15) \text{ \AA}$, $b = 34.37449(16) \text{ \AA}$, $c = 11.16967(1) \text{ \AA}$, $\beta = 111.7476(1)^\circ$, $V = 3122.13(6) \text{ \AA}^3$) to orthorhombic system ($Fddd$, $a = 8.75292(4) \text{ \AA}$, $b = 20.7551(5) \text{ \AA}$, $c = 34.35779(8) \text{ \AA}$, $V = 6241.70(4) \text{ \AA}^3$). Above the transition temperature and until 623 K, the orthorhombic phase shows negative thermal expansion (NTE) with $\alpha_v = -2.4 \times 10^{-5} \text{ K}^{-1}$. The mechanism behind the NTE behaviour was proposed to be due to the twisting vibrational mode of the carboxylate groups of the bdc linkers that causes a significant decrease of the $\text{Sc} \dots \text{Sc}$ distance along the inorganic chain.

However, this explanation was provided with limited supporting evidence that included the temperature dependence of the unit cell parameters and some

highly constraint structural models observed from Rietveld refinement of synchrotron powder X-ray diffraction data which offers relatively low structural precision. Therefore, in this work, the NTE behaviour of the orthorhombic $[\text{Sc}_2(\text{bdc})_3]$ will be observed and determined in greater detail of the origin of this unusual thermal behaviour, using single crystal X ray diffraction that enables a more accurate determination of the NTE mechanism. In addition, the effect of structural framework in comparison with the thermoresponsive behaviour of the MIL-53 family framework as presented in the previous chapter will be made.

5.2 Experimental

5.2.1 Synthesis, data collection and data analysis

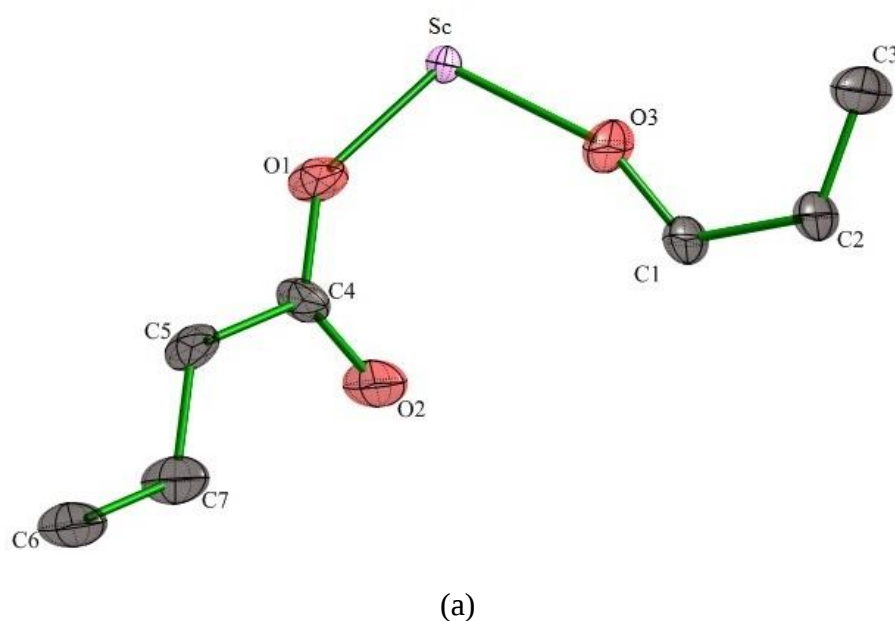
The [Sc₂(bdc)₃] crystals were provided by Prof Paul A. Wright, School of Chemistry, University of St. Andrews. The syntheses of this microporous material [Sc₂(bdc)₃] are described elsewhere.^[1-3] The crystals received were synthesised by mixing scandium nitrate (Sc(NO₃)₃·3H₂O (Metall Rare Earth Limited, 99.9 %, 0.0768 g,) and H₂bdc, (Aldrich, 98 %, 0.0895 g) in DEF (Alfa Aesar, 98%, 6 mL). The mixture was heated at 463 K for 72 h. The resulting solid was washed with ethanol and dried at 333 K.

A colourless chip-shape crystal (0.15 x 0.13 x 0.10 nm³) of [Sc₂(bdc)₃] was glued to the end of glass fibre that was then glued to the internal wall of a capillary tube. The crystal was then activated in a glass capillary tube at room temperature and a pressure of 1.85 x 10⁻¹ mbarr for 48 hours prior to flame-sealing under vacuum. The capillary tube containing the crystal was mounted on a Riguka AFC12 diffractometer for which the incident Mo-K α radiation (λ = 0.71075 Å) X ray beam is generated by an *FR-E+ SuperBright* rotating anode generator with very high flux *Varimax* optics (70 μ m focus), operating at 2500 W power (45 kV, 55 mA). The diffracted beam was measured with an enhanced sensitivity (HG) Saturn 724+ 18 bit CCD detector. The diffractometer was also equipped with an Oxford cryostream Cobra so that the diffraction data can be collected over a variable temperature range (80 – 500 K).

In this work, the diffraction data of [Sc₂(bdc)₃] were collected over the temperature range of 100 – 500 K where the diffraction data over the temperature range of 100 - 200 K were collected at 25 K intervals and at 20 K intervals above 200 K up to 500 K. A representative example of the data collection strategy is provided for the 300 K data set for which a total of 164 frames were collected with an exposure time of 10s/ frame. The frames were integrated with the CrystalClear-SM Expert 2.0 r11 software package. The integration of the data

gave a total of 6053 reflections to a maximum 2θ value of 55° of which 1787 reflections were independent. The final unit cell constants were refined using 5674 reflection with $I > 10\sigma(I)$. The data were corrected for absorption using the semi-empirical calculation in the CrystalClear-SM Expert 2.0 r13 software package.

The initial structure model was taken from that reported previously using the space group $Fddd$ with $Z = 16$.^[4] The structure was refined by full-matrix least squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms positions were generated with ideal geometries and were fixed during the refinement process. Final full matrix least squares refinement on F^2 converged to $R1 = 0.0313$ ($I > 2\sigma(I)$) and $wR2 = 0.0765$ (all data) with $GOF = 1.063$. The asymmetric unit and the full structure of $[Sc_2(bdc)_3]$ are shown in **Figure 5.3** (a) and (b). The crystallographic data for the 300 K are summarized in **Table 5.1**. The final atomic coordinates, occupancies and equivalent isotropic displacement parameters are given in **Table 5.2**. Selected bond lengths and bond angles are given in **Table 5.3**. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 300 K are given in **Table 5.4**. The refinements of all data sets are given in the attached CD.



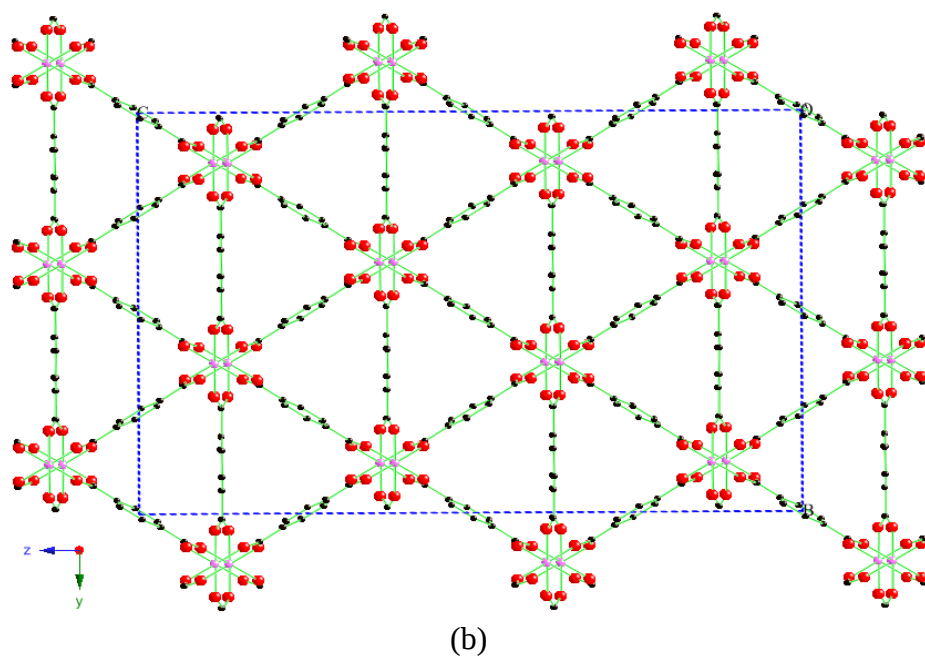


Figure 5.3 (a) The asymmetric unit of $[\text{Sc}_2(\text{bdc})_3]$ (b) The topology of the structure of $[\text{Sc}_2(\text{bdc})_3]$ viewed along the direction parallel to the a axis. The pink, red and black balls represent the scandium, oxygen and carbon atoms respectively.

Table 5.1 Crystal data for [Sc₂(bdc)₃] at 300 K

Empirical formula	C ₁₂ H ₆ O ₆ Sc
Formula weight	291.13
Temperature	300(2) K
Wavelength	0.71075 Å
Crystal system	Orthorhombic
Space group	<i>Fddd</i>
Unit cell dimensions (Å)	a = 8.7474(3) b = 20.7351(9) c = 34.357(2)
Volume (Å ³)	6231.6(5)
Z	16
Density (calculated)	1.241 Mg/m ³
Absorption coefficient	0.487 mm ⁻¹
F(000)	2352
Crystal size	0.15 x 0.13 x 0.10 mm ³
Theta range for data collection	3.09 to 27.48°.
Index ranges	-7 ≤ h ≤ 11, -22 ≤ k ≤ 26, -44 ≤ l ≤ 27
Reflections collected	5674
Independent reflections	1787 [R(int) = 0.0337]
Completeness to theta = 27.48°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9529 and 0.9305
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1787 / 0 / 88
Goodness-of-fit on F ²	1.063
Final R indices [I > 2σ(I)]	R1 = 0.0313, wR2 = 0.0765

R indices (all data)	R1 = 0.0379, wR2 = 0.0794
Largest diff. peak and hole	0.298 and -0.268 e.Å ⁻³

Table 5.2 Atomic coordinates and equivalent isotropic displacement parameters (U(eq)) (Å²) for 300 K. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)	Occupancy
Sc	0.3750	0.3750	0.1143(1)	0.015(1)	1
O1	0.5089(1)	0.3333(1)	0.706(1)	0.037(1)	1
O2	0.7453(1)	0.3343(1)	0.926(1)	0.048(1)	1
O3	0.2448(1)	0.2916(1)	0.1147(1)	0.044(1)	1
C1	0.1250	0.2638(1)	0.1250	0.031(1)	1
C2	0.1250	0.1917(1)	0.1250	0.034(1)	1
C3	0.2609(2)	0.1583(1)	0.1245(1)	0.058(1)	1
C4	0.6478(2)	0.3198(1)	0.677(1)	0.031(1)	1
C5	0.7006(2)	0.2834(1)	0.325(1)	0.034(1)	1
C6	0.8533(2)	0.2695(1)	0.278(1)	0.055(1)	1
C7	0.5971(2)	0.2641(1)	0.47(1)	0.055(1)	1

Table 5.3 Selected bond lengths (Å) and bond angles (°) for [Sc₂(bdc)₃] for 300 K.

Sc-O1 (x 2)	2.093(1)	O2 ⁵ -Sc-O3 ⁷	87.49(6)
Sc-O2 ⁵ (x 2)	2.047(1)	O2 ⁶ -Sc-O3 ⁷	91.96(6)
Sc-O3 (x 2)	2.071(1)	O2 ⁶ -Sc-O3	87.49(6)
C1-O3 (x 2)	1.247(2)	O3 ⁷ -Sc-O3	179.23(9)
C1-C2	1.494(3)	C4-O1-Sc	133.90(10)
C2-C3	1.375(2)	C1-O3-Sc	148.24(1)
C3-C3 ³	1.383(4)	C4-O2-Sc ⁴	167.54(13)
C4-O1	1.250(2)	O3 ² -C1-O3	124.9(2)
C4-O2	1.246(2)	O3 ² -C1-C2	117.6(1)
C4-C5	1.497(2)	O3-C1-C2	117.6(1)
C5-C6	1.376(2)	C3-C2-C3 ²	119.6(2)
		C3-C2-C1	120.2(1)
C7-C6 ¹	1.385(2)	C3 ² -C2-C1	120.2(1)
O2 ⁵ -Sc-O2 ⁶	87.34(8)	C2-C3-C3 ³	120.2(1)
O2 ⁵ -Sc-O3 ⁷	87.49(6)	C4-O1-Sc	133.9(1)
O2 ⁶ -Sc-O3 ⁷	91.96(6)	C4-O2-Sc ⁴	167.5(1)
O2 ⁶ -Sc-O3	87.49(6)	O1-C4-O2	123.8(1)
O3 ⁷ -Sc-O3	179.23(9)	O1-C4-C5	117.7(1)
O2 ⁵ -Sc-O1	179.56(5)	O2-C4-C5	118.5(1)
O2 ⁶ -Sc-O1	92.23(5)	C6-C5-C7	119.7(2)
O3 ⁷ -Sc-O1	92.41(6)	C4-C5-C7	120.3(1)
O3-Sc-O1	88.14(5)		
O1-Sc-O1 ⁷	88.19(7)		
O2 ⁵ -Sc-O2 ⁶	87.34(8)		

Symmetry transformations used to generate equivalent atoms:

(1) -x+3/2,-y+1/2,-z, (2) -x+1/4,y,-z+1/4, (3) x,-y+1/4,-z+1/4, (4) x+1/2,-y+3/4,-z+1/4, (5) x-1/2,-y+3/4,-z+1/4, (6) -x+5/4,y,-z+1/4, (7) -x+3/4,-y+3/4,z.

Table 5.4 Anisotropic displacement parameters (ADPs) ($\text{\AA}^2 \times 10^3$) for 300 K.

Atoms	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sc	15(1)	16(1)	15(1)	0	0	0(1)
O1	24(1)	57(1)	29(1)	-20(1)	2(1)	7(1)
O2	27(1)	82(1)	36(1)	-38(1)	-4(1)	1(1)
O3	30(1)	18(1)	83(1)	-2(1)	8(1)	-6(1)
C1	26(1)	16(1)	51(1)	0	-2(1)	0
C2	25(1)	15(1)	62(2)	0	2(1)	0
C3	22(1)	18(1)	135(2)	-5(1)	2(1)	-3(1)
C4	24(1)	43(1)	24(1)	-16(1)	1(1)	0(1)
C5	24(1)	52(1)	27(1)	-22(1)	-1(1)	4(1)
C6	26(1)	98(2)	40(1)	-45(1)	-8(1)	9(1)
C7	22(1)	98(2)	45(1)	-45(1)	-5(1)	12(1)

5.3 Results and discussion

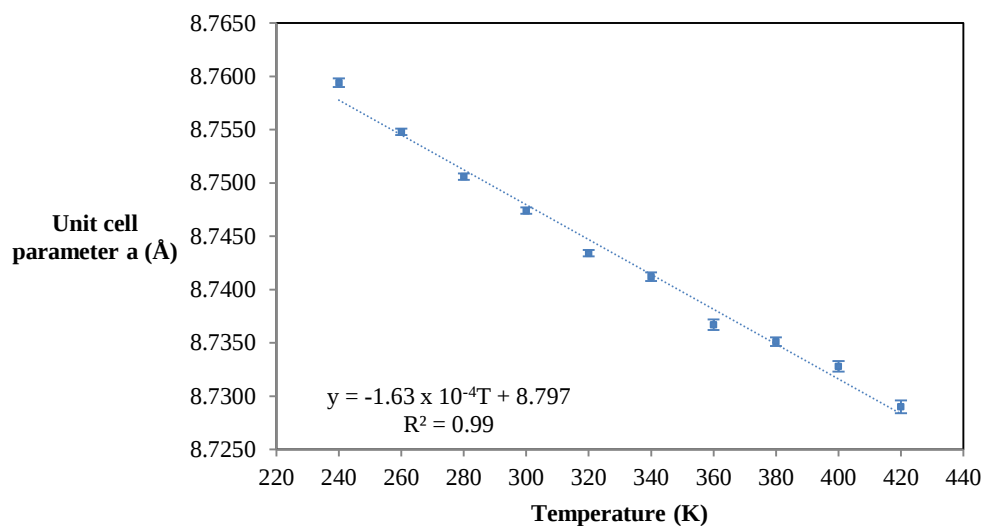
The ultimate aim of this chapter is to fully describe the mechanism behind the NTE behaviour of $[\text{Sc}_2(\text{bdc})_3]$; therefore, only the diffraction data over the temperature range of 240 – 420 K was investigated as the phase transition from the monoclinic phase to the orthorhombic phase occurs at 225 K. The mechanism of the phase transition has already been fully rationalised as reported previously.^[4] The diffraction data over the temperature range of 440 – 500 K were ignored due to the softening of the glue which results in the crystal movement. The unit cell dimensions and unit cell volume of $[\text{Sc}_2(\text{bdc})_3]$ from 240 - 420 K are listed in **Table 5.5**.

Table 5.5 Unit cell dimensions ($\text{\AA}$), unit cell volume ($\text{\AA}^3$), R(int) and R1 for $[\text{Sc}_2(\text{bdc})_3]$ from 240 - 420 K

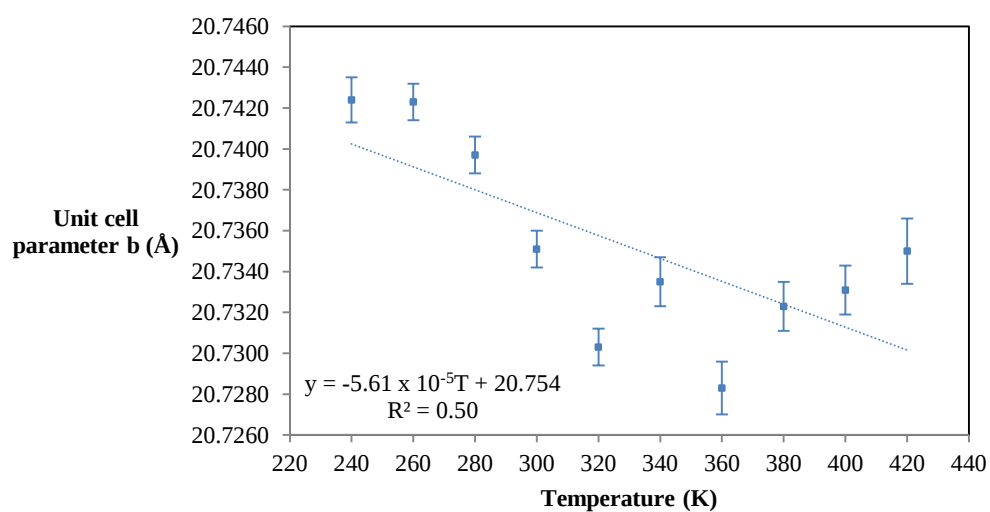
Temperature (K)	a	b	c	V	R(int)	R1
240	8.7594(4)	20.7424(11)	34.349(2)	6240.9(6)	0.0412	0.0349
260	8.7548(3)	20.7423(9)	34.355(2)	6238.7(5)	0.0346	0.0325
280	8.7506(3)	20.7397(9)	34.357(2)	6235.3(5)	0.0371	0.0325
300	8.7474(3)	20.7351(9)	34.357(2)	6231.6(5)	0.0337	0.0313
320	8.7434(3)	20.7303(9)	34.355(2)	6227.0(5)	0.0322	0.0317
340	8.7412(4)	20.7335(12)	34.373(2)	6229.6(6)	0.0557	0.0359
360	8.7367(5)	20.7283(13)	34.369(2)	6224.1(6)	0.0595	0.0358
380	8.7351(4)	20.7323(12)	34.378(2)	6225.8(6)	0.0606	0.0366
400	8.7328(5)	20.7331(12)	34.383(2)	6225.3(6)	0.0766	0.0377
420	8.7290(6)	20.7350(16)	34.396(3)	6225.5(8)	0.0775	0.0374

$[\text{Sc}_2(\text{bdc})_3]$ shows negative thermal expansion over the entire temperature range studied from 240 K – 420 K which agrees well with that reported

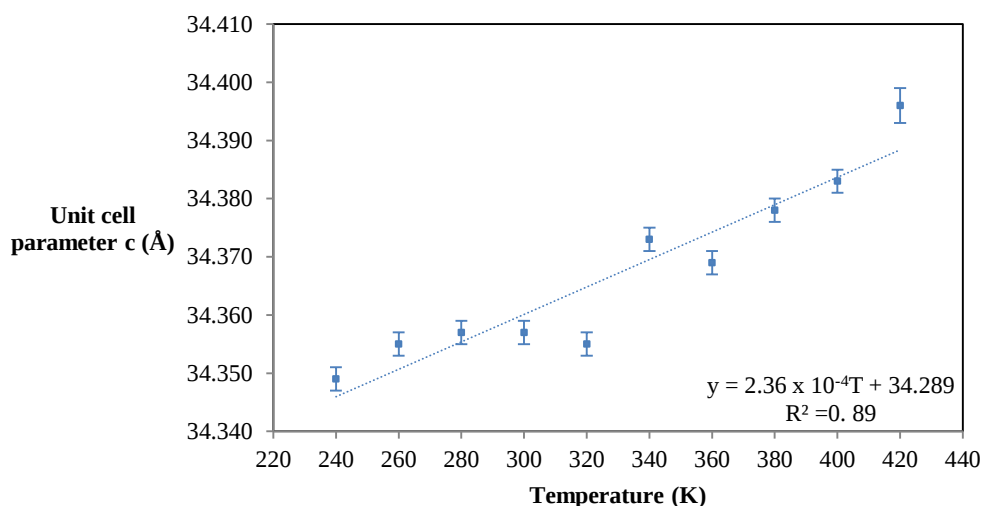
previously.^[4] The measured variations in lattice parameters and unit cell volume as a function of temperature of [Sc₂(bdc)₃] are shown in **Figure 5.4**.



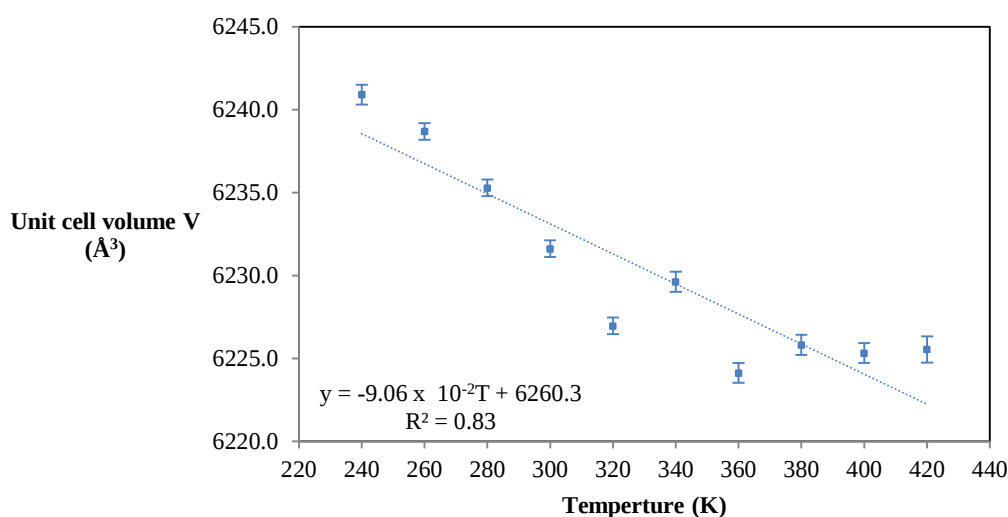
(a)



(b)



(c)



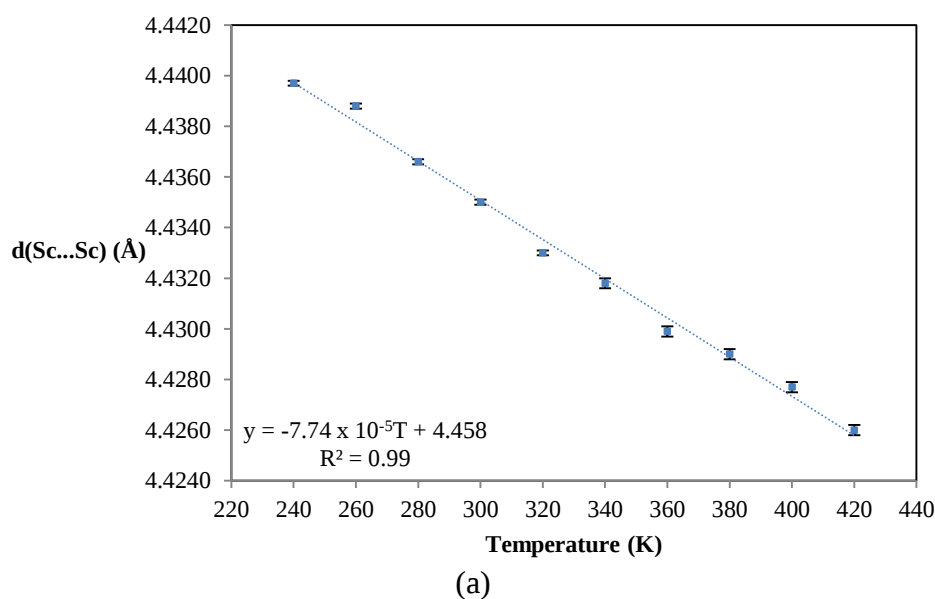
(d)

Figure 5.4 The temperature dependence of the unit cell dimension (a) a , (b) b and (c) c , and (d) the temperature dependence of the unit cell volume V . Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

A decrease in a ($-1.63 \times 10^{-4} \text{ Å K}^{-1}$) and b ($-5.61 \times 10^{-5} \text{ Å K}^{-1}$) and an increase in c ($2.36 \times 10^{-4} \text{ Å K}^{-1}$) is observed over the entire temperature range of 240 – 420 K. The coefficients of linear thermal expansion, calculated at 300 K, along a , b and c direction are $-1.86 \times 10^{-5} \text{ K}^{-1}$, $-2.71 \times 10^{-6} \text{ K}^{-1}$ and $6.87 \times 10^{-6} \text{ K}^{-1}$ respectively. Thermal contraction in the a axis direction has the greatest contribution to the overall unit cell volume contraction. The unit cell volume is

found to decrease by $\sim 15 \text{ \AA}^3$ over the entire temperature range studied and the overall volume contraction is represented by $V = -9.06 \times 10^{-2}T + 6260.3$ with a coefficient of thermal expansion $\alpha_v = -1.45 \times 10^{-5} \text{ K}^{-1}$. This coefficient is found to be lower than that reported recently,^[4] $\alpha_v = -2.4 \times 10^{-5} \text{ K}^{-1}$. The discrepancy may be possibly due to incomplete evacuation of the O_2 or N_2 guest molecules. However, the final structural refinement at each temperature indicates negligible residual electron density which means there is no evidence of ordered guest molecules in the internal void volume of the framework. In addition, the literature value of the coefficient of thermal expansion was calculated from the synchrotron powder X ray diffraction results which generally yield more accurate unit cell constants than that from single crystal X-ray diffraction.

Least squares structure refinements at each temperature allow one to elucidate the mechanism of the NTE behaviour of $[\text{Sc}_2(\text{bdc})_3]$. The contraction in the $[100]$ direction implies that the chain of isolated ScO_6 octahedra contracts as the temperature is increased. The distance between the adjacent non-bonding $\text{Sc}\dots\text{Sc}$, $d(\text{Sc}\dots\text{Sc})$ decreases as shown in **Figure 5.5 (a)**. A possible origin of this contraction is a concerted twisting motion of the three carboxylate groups of the bdc linkers about the $\text{C}-\text{C}_6\text{H}_4-\text{C}$ axis as illustrated in **Figure 5.5 (b)**.



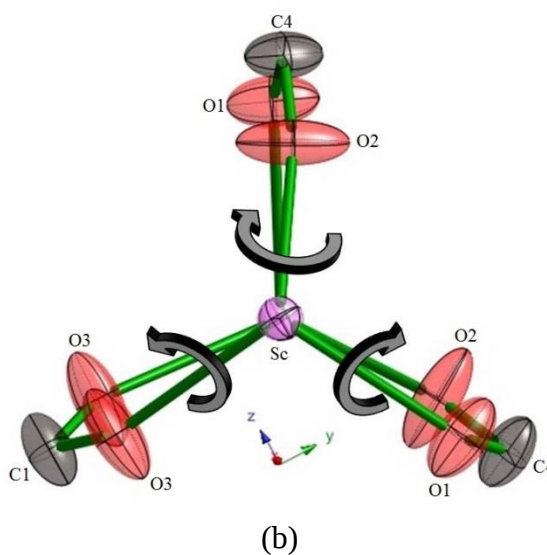
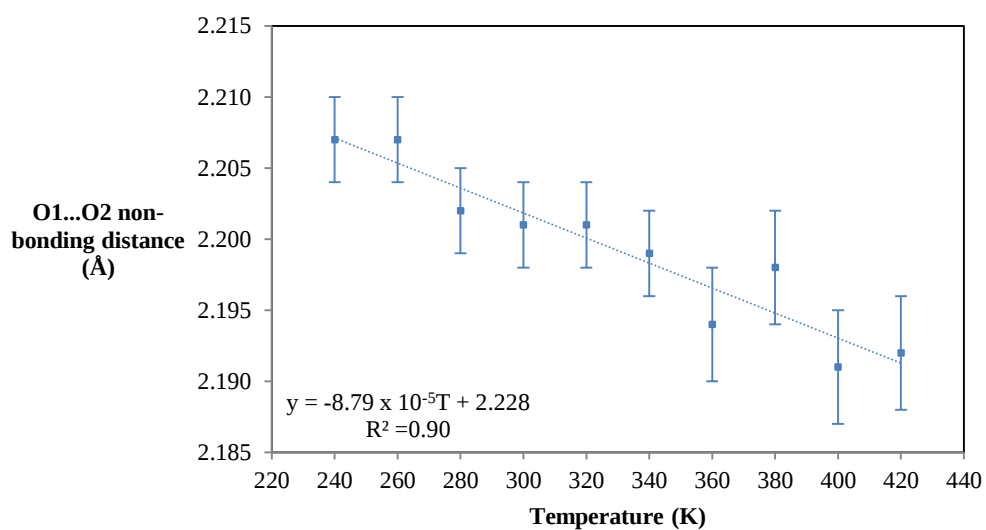
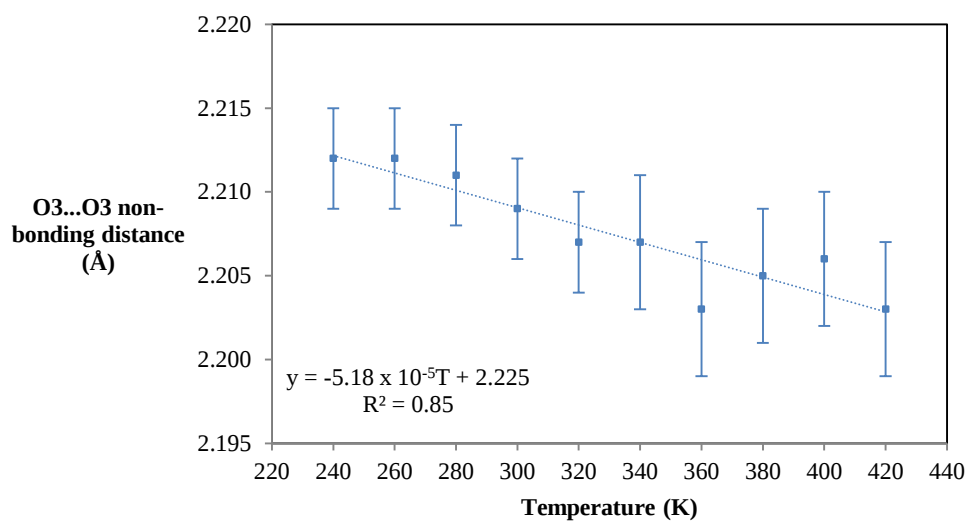


Figure 5.5 (a) The measured Sc...Sc non-bonding distance $d(\text{Sc} \cdots \text{Sc})$ as a function of temperature. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point. (b) Schematic representation of the twisting vibrational modes of the three carboxylate groups of the bdc linkers.

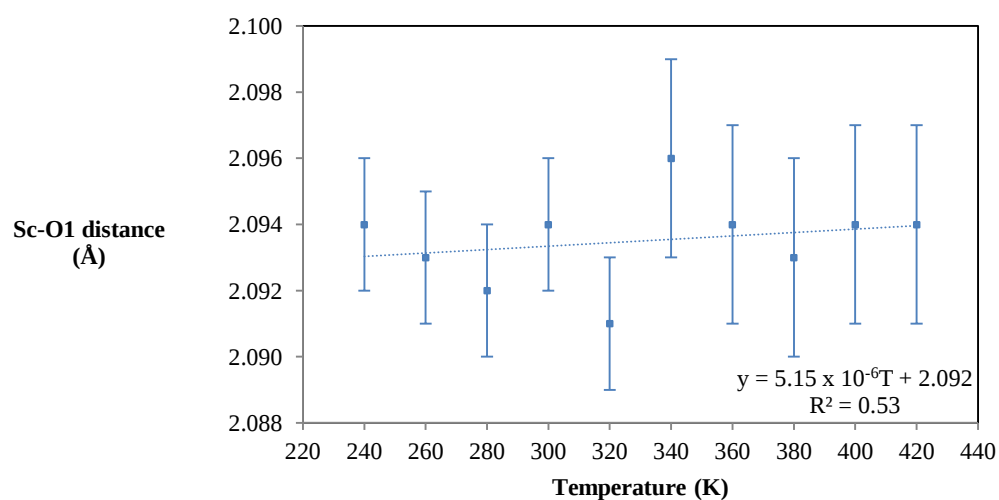
The expected accompanying changes of geometric parameters due to the twisting vibrational mode of the carboxylate groups of the bdc linkers would be decreases of the carboxylate O1...O2 and O3...O3 non-bonding distances, as shown in **Figure 5.6** (a) and (b) respectively, near constant of the Sc-O1, Sc-O2, Sc-O3, C4-O1, C4-O2 and C1-O3 bond distances and the O1-C4-O2 and O3-C2-O3 bond angle as shown in **Figure 5.6** (c) - (j) respectively. The expected behaviour is seen for the O1...O2 and O3...O3 non-bonding distances. All other geometric parameters remain essentially constant within the precision of these measurements. However, the overall trends of these eight of ten geometries do appear to have negative or zero expansion which supports the twisting vibrational modes of the carboxylate groups of the bdc linkers.



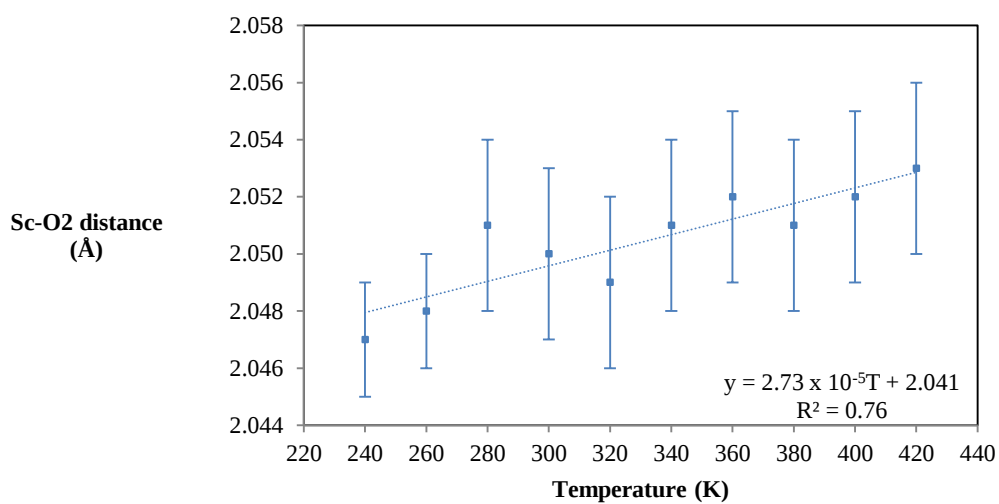
(a)



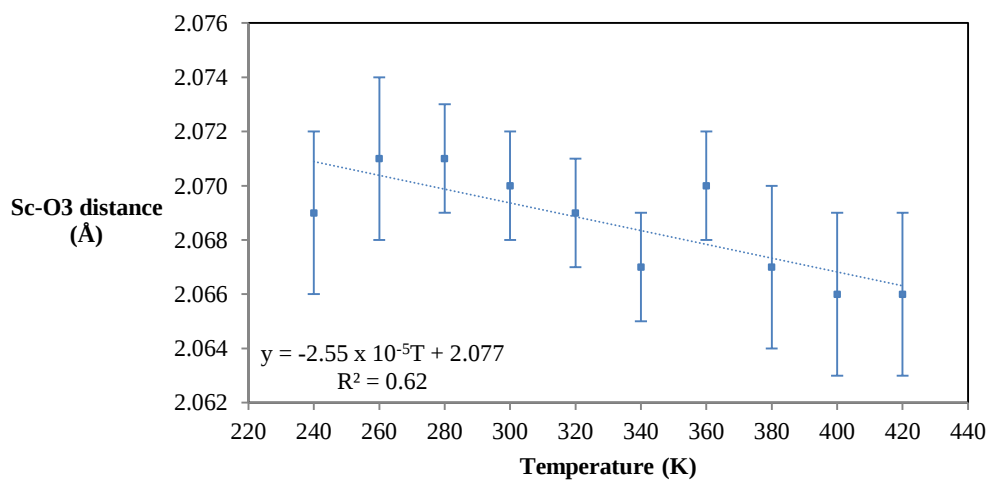
(b)



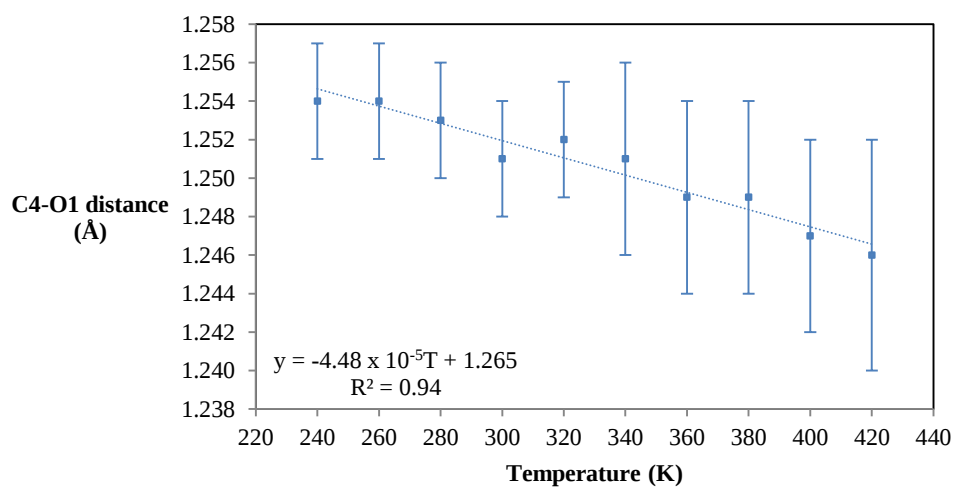
(c)



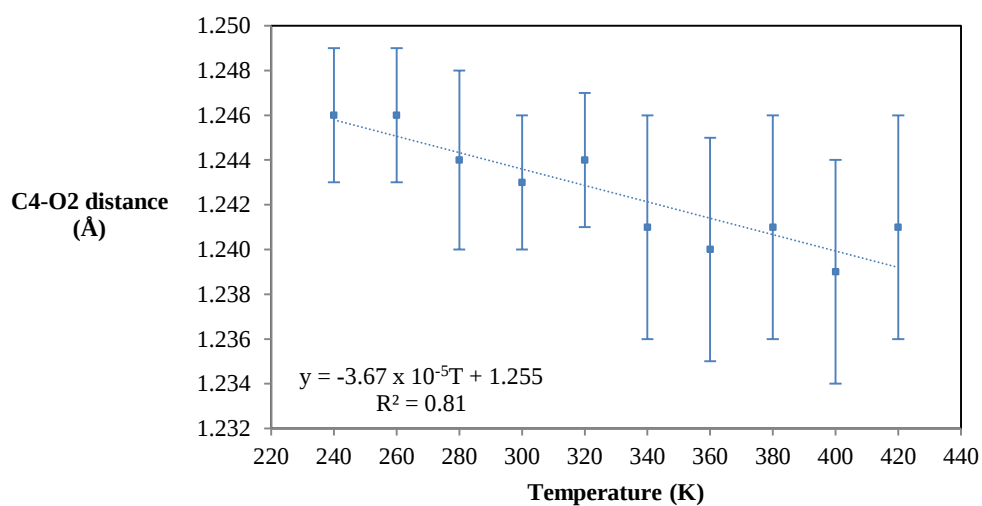
(d)



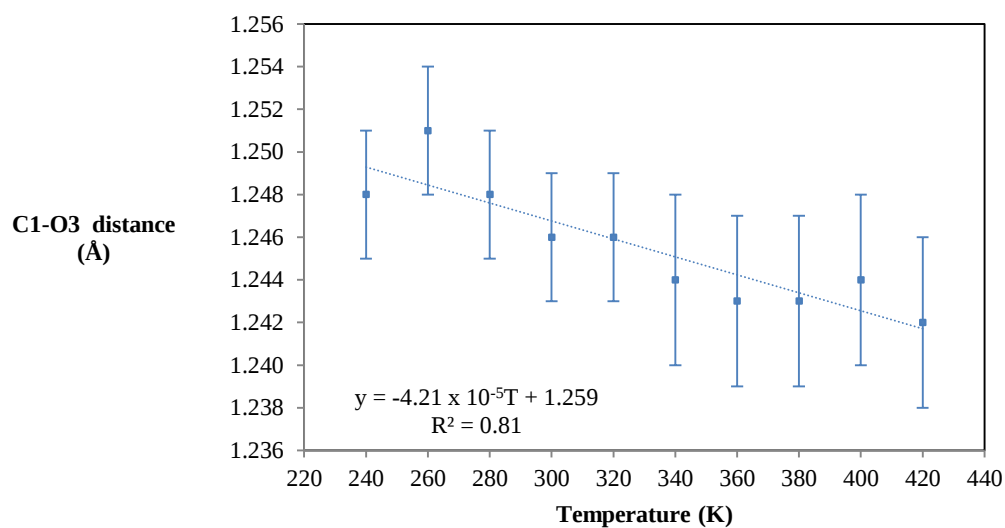
(e)



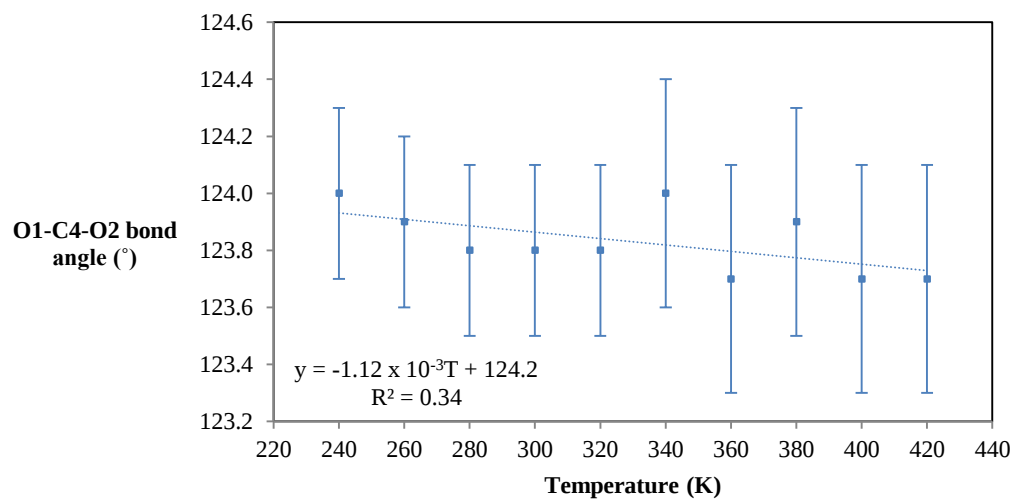
(f)



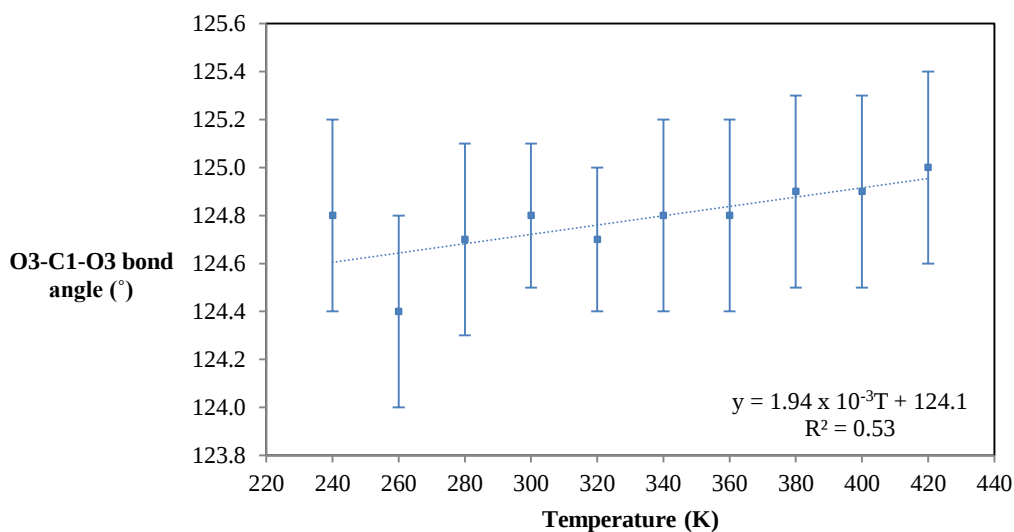
(g)



(h)



(i)

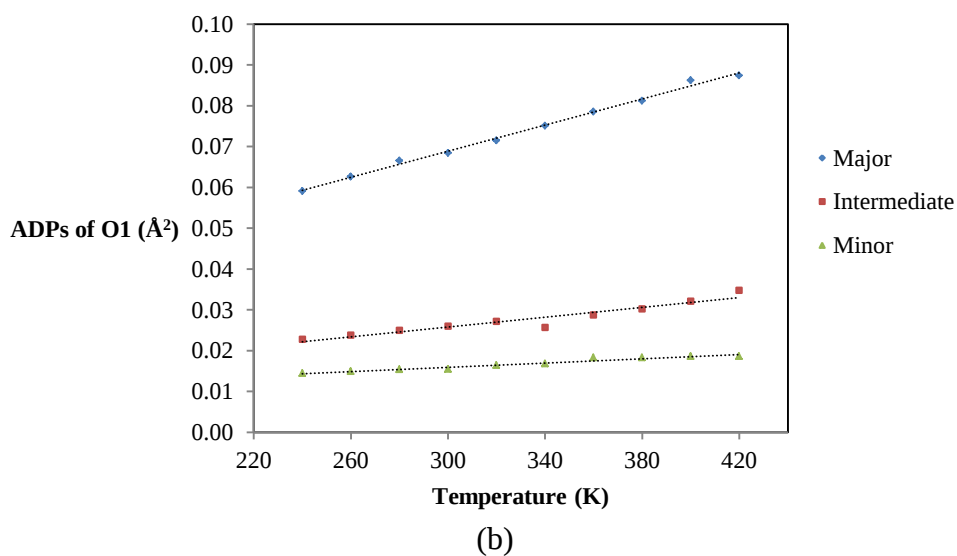
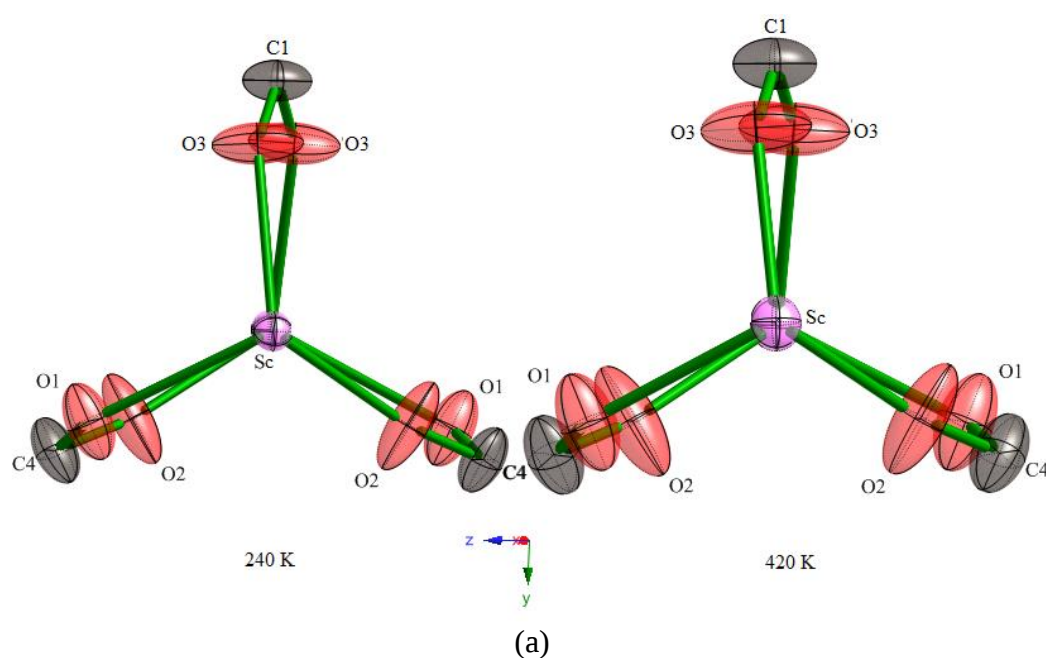


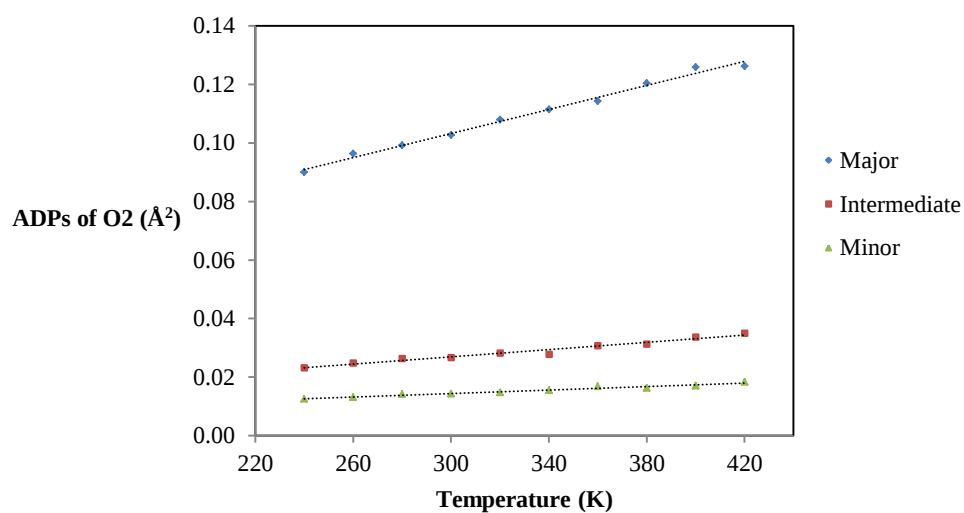
(j)

Figure 5.6 The temperature dependence of (a) the O1...O2 non-bonding distance (b) the O3...O3 non-bonding distances (c) the Sc-O1 bond distance (d) the Sc-O2 bond distance (e) the Sc-O3 bond distances (f) the C4-O1 bond distance (g) the C4-O2 bond distance (h) the C1-O3 bond distances (i) the O1-C4-O2 bond angle and (j) the O3-C1-O3 bond angles. Equations of the trend line and goodness of fit (R^2) are also provided on each plot. Estimated standard deviations are marked on each data point.

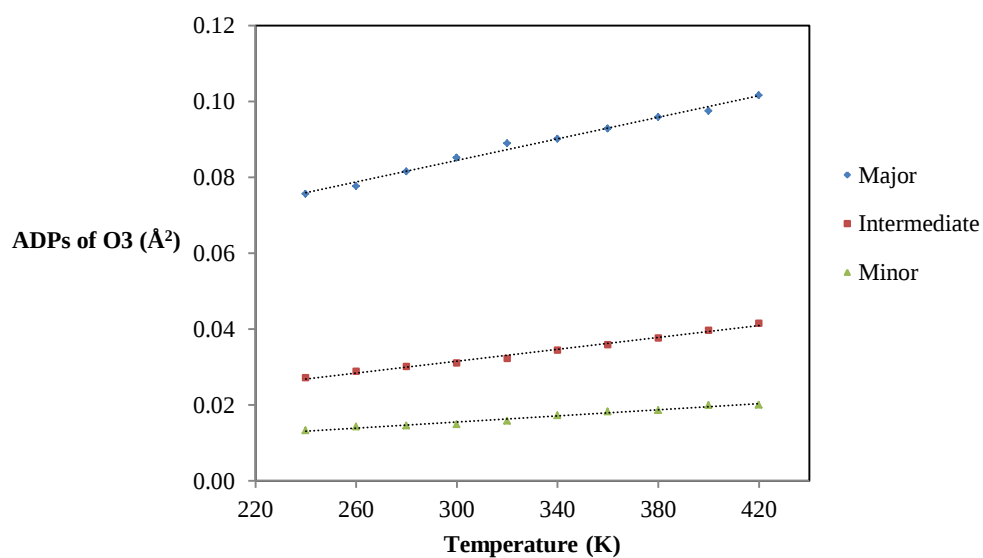
The increasing amplitude of the twisting vibrational mode of the carboxylate groups of the bdc linkers will also be indicated by the evolution of the anisotropic displacement parameters (ADPs) of the relevant atoms, such as O1, O2, O3, C4, C1 and all the carbon atoms of the benzene ring upon heating. The direction that the electron density is smear-out as the temperature is raised is illustrated by the amount of displacement in the direction of the axes of the thermal ellipsoid and relates to the direction of the vibrational mode of that particular atom. The framework of $[\text{Sc}_2(\text{bdc})_3]$ in the direction parallel to the a axis, drawn with thermal ellipsoid at 50% probability, at 240 K and 420 K are shown in **Figure 5.7** (a). The temperature dependences of the O1, O2, O3, C1 and C4 atoms are shown in **Figure 5.7** (b), (c), (d), (e) and (f) respectively, the rate of the temperature dependence of ADPs of all atoms are summarised in **Figure 5.7** (g) and a fragment of the two crystallographically different bdc linkers drawn with thermal ellipsoid at 50% probability, at 240 K and 420 K are shown in **Figure 5.7** (h) and (i).

The temperature dependence of ADPs shows that the direction that atoms vibrate is perpendicular to the O-C bond axis and the plane of the O-C-O group. This implies the occurrence of the transverse vibrational modes at this part of the bdc molecules which is the twisting mode as the ADPs of the O1, O2 and O3 oxygen atoms are greater than that of the C1 and C4 carbon atoms. As the temperature is increased, the magnitude of the transverse vibration is also increased, thus the isolated ScO_6 octahedra are drawn closer resulting in a decrease of $d(\text{Sc}\dots\text{Sc})$ distance.

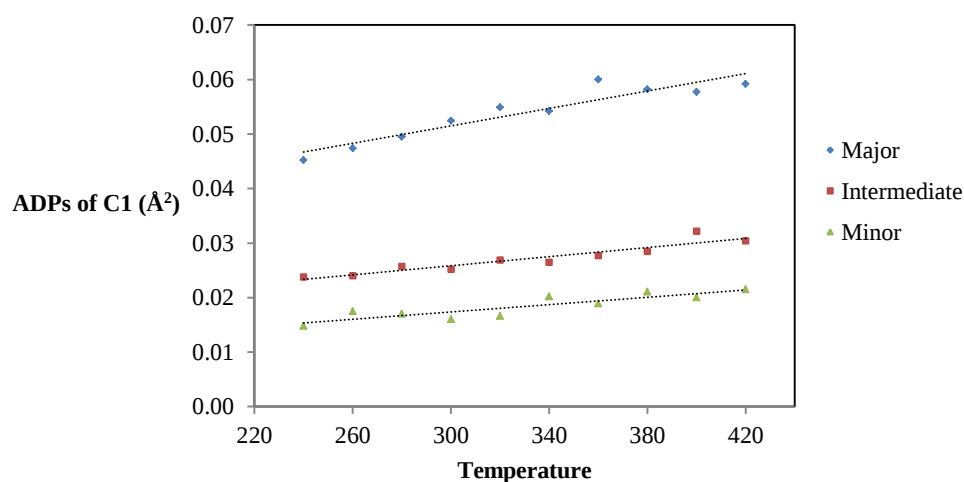




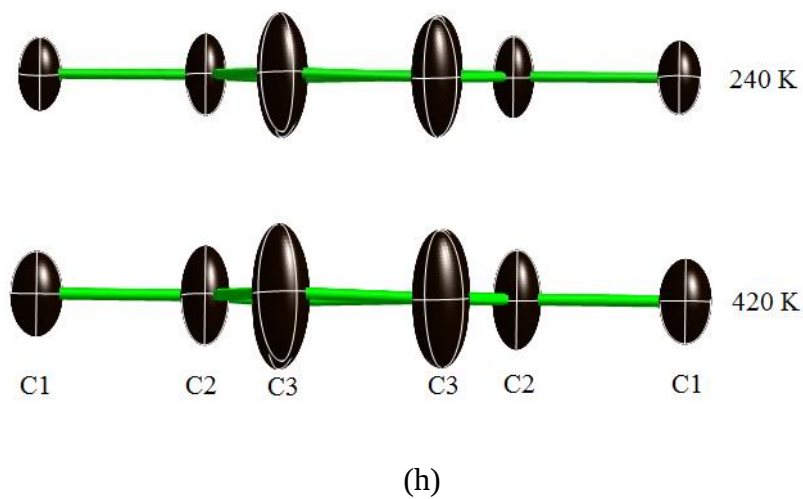
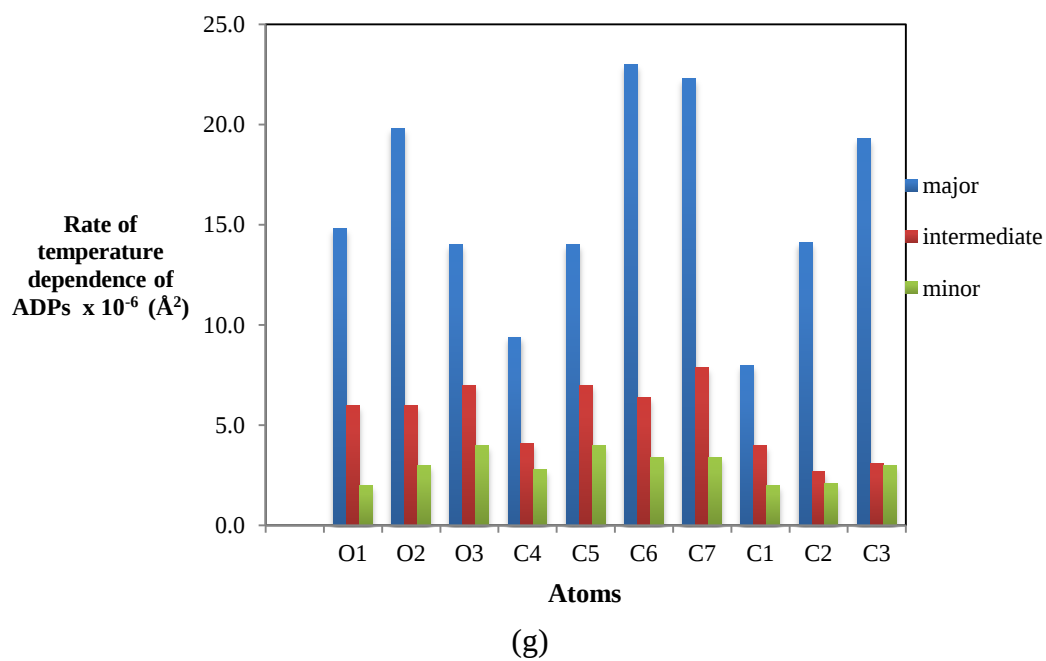
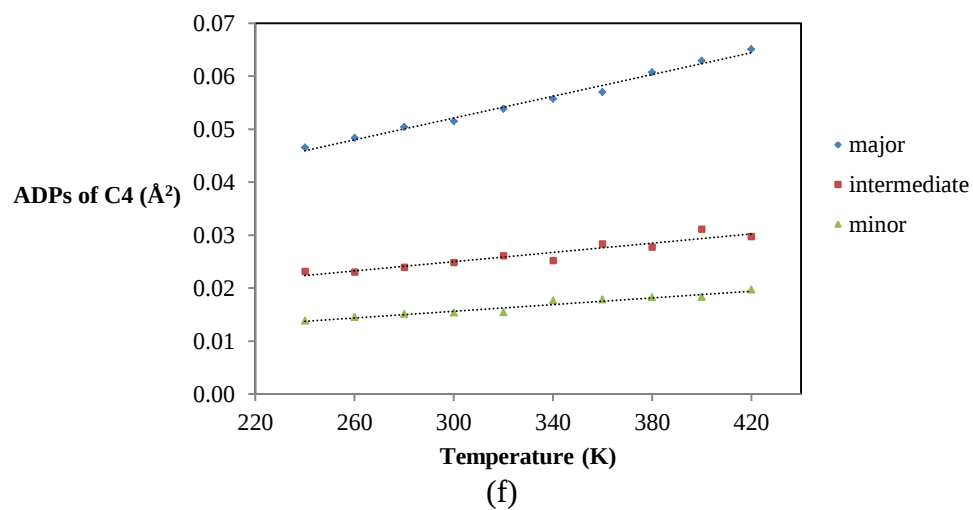
(c)



(d)



(e)



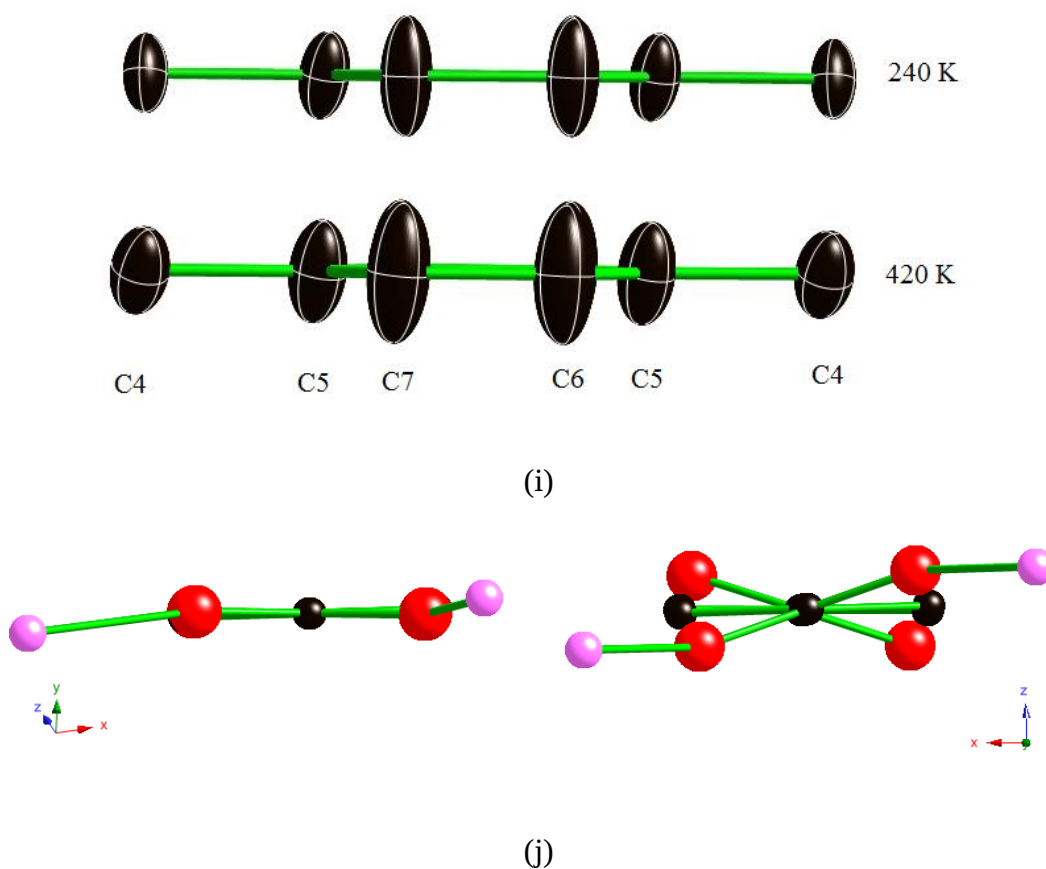


Figure 5.7 (a) A schematic illustration shows the concerted twisting mode of the carboxylate group of the bdc linkers and the evolution of the ADPs of the relevant atoms. The temperature dependence of ADPs of (b) the O1 oxygen atom (c) the O2 oxygen atom (d) the O3 oxygen atom (e) the C1 carbon atom and (f) the C4 carbon atom and (g) the rate of the temperature dependence of all constituent atoms. Anisotropic displacement parameters, represented by thermal ellipsoids set at 50% probability, at 240 K and 420 K (h) for a fragment of the bdc linker lying in the *b* axis direction and (i) for a fragment of the bdc linker lying in the direction parallel to the {011} plane where hydrogen atoms are omitted for clarity. (j) the alignment of the two crystallographically different bdc linker in the framework where the left illustration represents the bdc linker lying in the direction parallel to the {011} plane and the right illustration represents the bdc linker lying in the *b* axis direction. The pink, red and black balls represent the Sc, O and C atoms respectively.

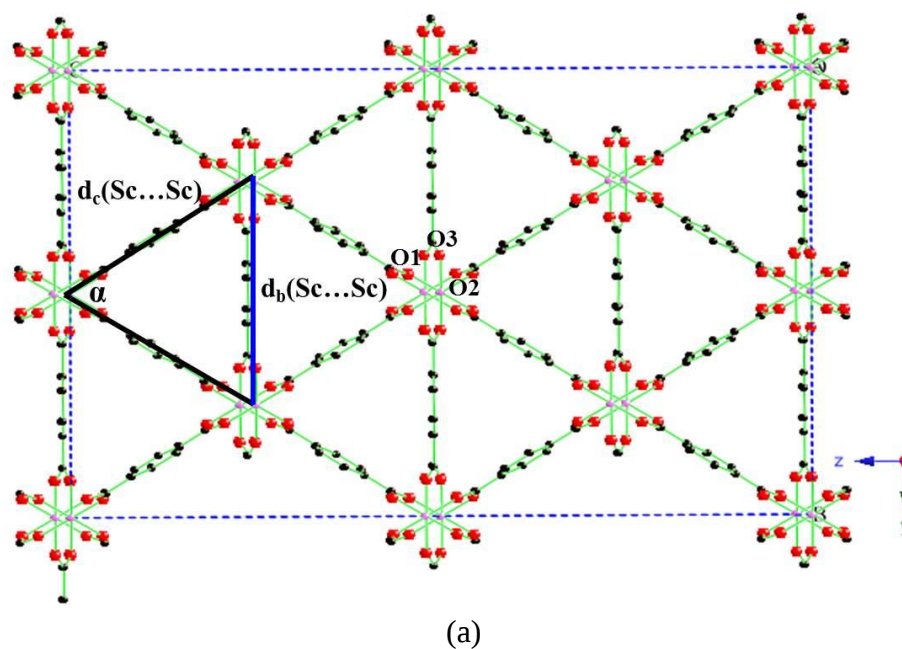
In addition, the decrease of the Sc...Sc non-bonding distance is found to be more likely influenced by the changes of the O3-C1-O3 carboxylate group than the changes of the O1-C4-O2 carboxylate group. With regardless of the precision of the measurements, this argument is supported by the greater changes observed in the Sc-O3 and O3-C1 bond distances and the O3-C1-O3 bond angle than those

of the O1-C4-O2 carboxylate groups as shown in **Figure 5.6**. This is possibly due to the difference in the alignment of the two types of the bdc linkers. The bdc linker lying in the *b* axis direction contains the O3-C1-O3 carboxylate group and aligns in a non-planar manner as shown in **Figure 5.7** (j) resulting in a breaking of π - bonding system of the benzene ring of the bdc linker. This may possibly make the twisting motion of the O3-C1-O3 carboxylate group of this bdc linker more favourable. In contrast, the bdc linker containing the O1-C4-O2 carboxylate group aligns in a planar manner which means the twisting motion of the O1-C4-O2 carboxylate group is more difficult. From all above arguments, the rate of change of ADPs of the constituent atoms of the bdc linker lying in the *b* axis direction would be expected to increase in a greater rate than the other. However, the experimental results as shown in **Figure 5.7** (g), (h) and (i) are not as expected. This again may be due to the precision of the measurements. Or, the changes of the geometries of the Sc-O1-C4-O2-Sc fragment might be due to the static distortion more than the dynamic vibration.

Contractions along the one dimensional inorganic component in both $[\text{Sc}_2(\text{bdc})_3]$ and in the $[\text{Al}(\text{OH})(\text{bdc})]$ member of the MIL-53 family are similar because they occur as a consequence of the twisting vibrational mode at the carboxylate groups of the bdc linkers. However, the coefficients of thermal expansion along this direction in the two materials are significantly different. For instance, this value is found to be $-9.44 \times 10^{-7} \text{ K}^{-1}$ for $[\text{Al}(\text{OH})(\text{bdc})]$ and $-1.86 \times 10^{-5} \text{ K}^{-1}$ for $[\text{Sc}_2(\text{bdc})_3]$ where the latter is ~ 20 times larger than the former. The differences between these two systems are the constituent metal cation and the fashion of the connectivity between the MO_6 octahedra. If the effect of the constituent cations is discounted, it can be concluded that the addition of a degree of freedom along the chain of MO_6 octahedra in $[\text{Sc}_2(\text{bdc})_3]$ enhances the effect of the transverse vibrational mode and hence the contraction. This is because, in $[\text{Sc}_2(\text{bdc})_3]$, the chain of ScO_6 octahedra are made by the ScO_6 octahedra being linked by the carboxylate group of the bdc linker in a fashion that each ScO_6 is kept isolated. Hence, the twisting motion at the carboxylate group will fully affect the ScO_6 octahedra and lead to a significant change along this direction. While in

the MIL-53 topology, the effect of this vibrational mode is reduced due to the presence of the M-OH-M linkage joining each MO_6 octahedra together.

Thermal contraction along the b axis direction and thermal expansion along the c axis direction are observed over the temperature range studied. The mechanism behind this behaviour may be explained by considering one of the rhombus-shaped channels in the (100) plane similar to that considered for the members of the MIL-53 family, as shown in **Figure 5.8** (a), that is bound by four bdc ligands with the Sc atoms at the vertices of the rhombus. In case of $[\text{Sc}_2(\text{bdc})_3]$, however, the two Sc vertices in the b axis direction are additionally linked by the bdc ligand.



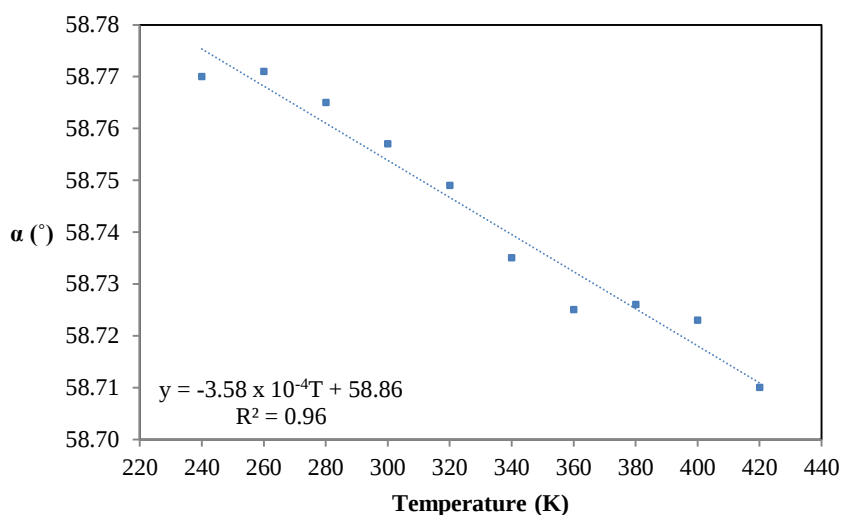
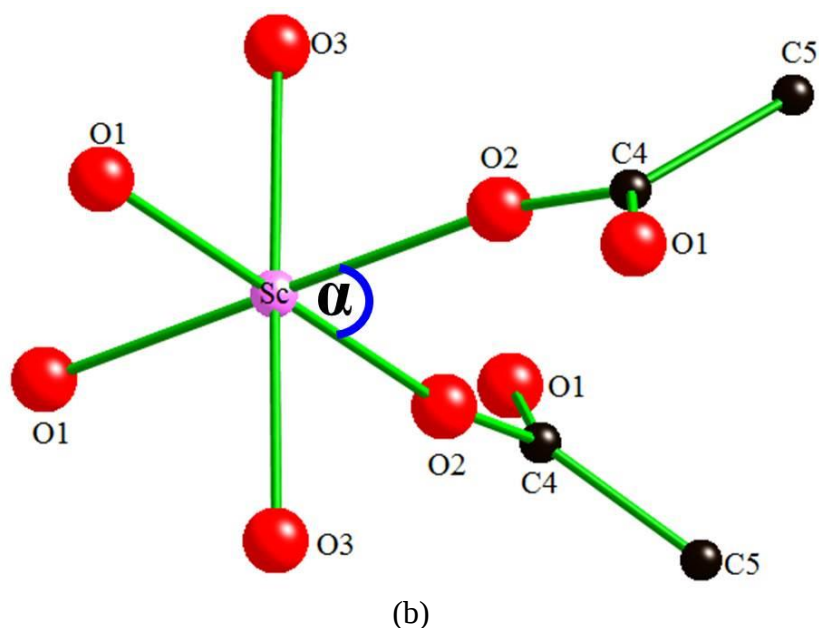
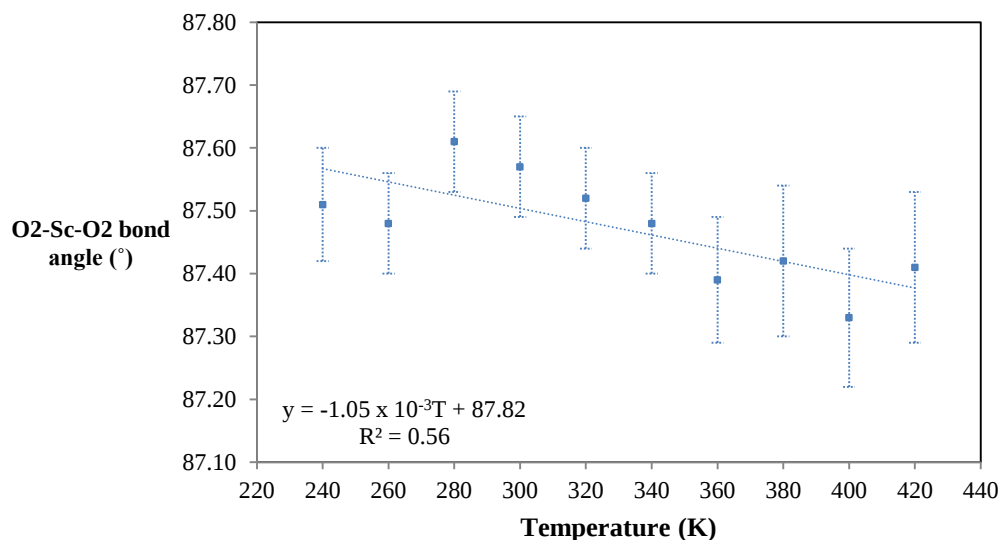


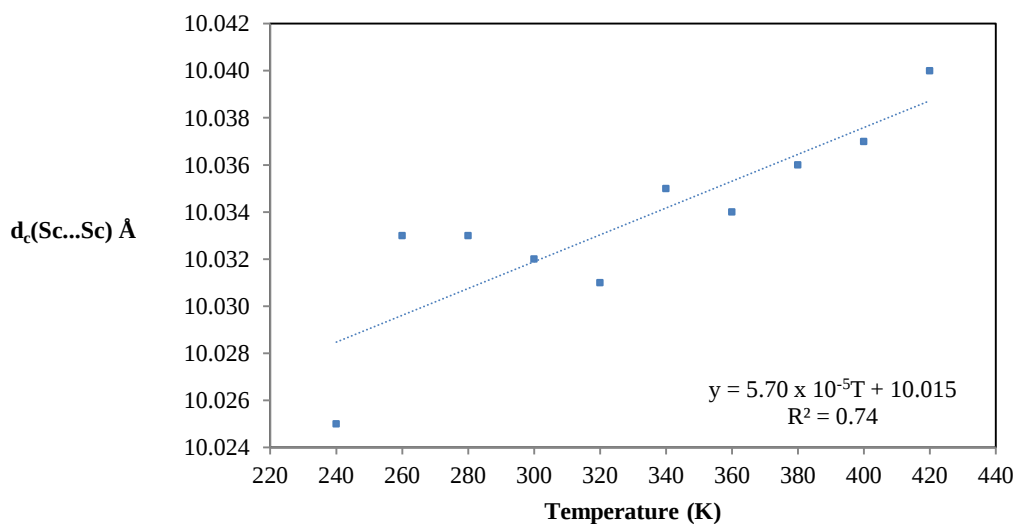
Figure 5.8 (a) The framework of $[\text{Sc}_2(\text{bdc})_3]$ viewed along the $[100]$ direction showing the rhombus-shaped channel that is made of four bdc ligands binding four infinite chains of ScO_6 octahedra together. The rhombus-shaped channel is cut by the additional connection between the two Sc vertices along the b axis direction. (b) A schematic showing the internal rhombus angle, α . (c) The variation of the internal rhombus angle α as a function temperature.

Similar to the members of the MIL-53 family, the rotation of the bdc linkers around the $\text{Sc}\dots\text{Sc}$ chain running through the core of isolated ScO_6 octahedra is observed and is reflected through the linear decrease of the internal rhombus angle, α , defined in **Figure 5.8** (a) and (b) and the change of the internal

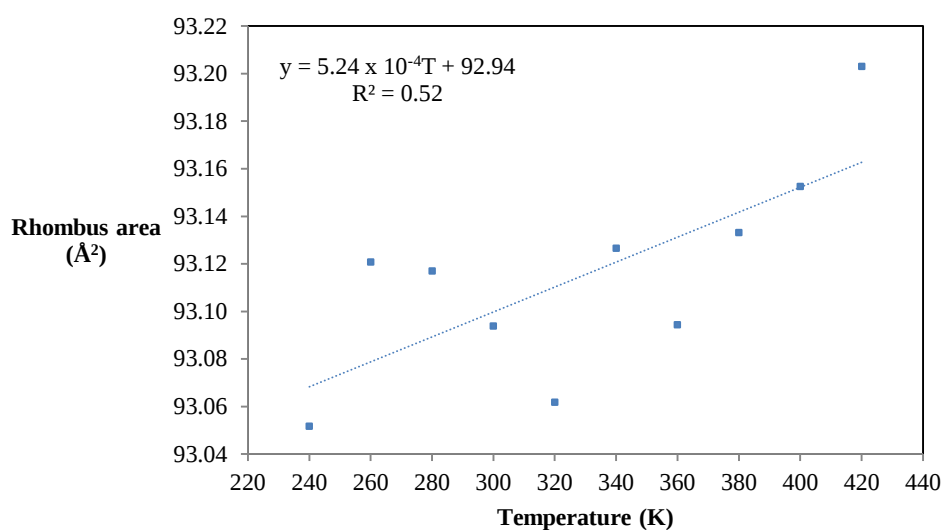
O2-Sc-O2 internal angle as shown in **Figure 5.9** (a). This indicates that the ScO_6 is not completely rigid. However, the total angular variation of α by a degree of $\sim 0.06^\circ$ is significantly smaller than those for the members of the MIL-53 family. This may be due to the presence of the additional connection between the two vertices along the b axis direction which prevents the rotational mode of the bdc linker around the chain of ScO_6 octahedra.



(a)



(b)



(c)

Figure 5.9 (a) The decrease of the O2-Sc-O2 bond angle as a function of temperature. (b) The variation of the $d_c(\text{Sc} \dots \text{Sc})$ non-bonding distance as a function of temperature. (c) The variation of the rhombus area as a function of temperature.

Interestingly, the side of the rhombus increases in length during this process with a distance, $d_c(\text{Sc} \dots \text{Sc})$ as defined in **Figure 5.8** (a) and the temperature dependence of the side of the rhombus is shown in **Figure 5.9** (b). The combination of the variation of the internal rhombus angle α and the $d_c(\text{Sc} \dots \text{Sc})$ distance yields an increase of the area of the rhombus over the entire temperature range, as shown in **Figure 5.9** (c), which is outweighed by the greater magnitude of the contraction along the a axis direction resulting in the volume contraction as the temperature increases.

The $d_b(\text{Sc} \dots \text{Sc})$ distance along the b axis direction, as defined in **Figure 5.8** (a) is seen to decrease upon heating as shown in **Figure 5.10** (a). This is combined contributions from the contractions of the Sc-O3 bond distance and the C1-O3 bond distance which outweigh the expansion of the C1...C1 non-bonding distance. The first two former geometric parameters are shown in **Figure 5.6** (e) and (h) respectively while the latter is shown in **Figure 5.10** (b).

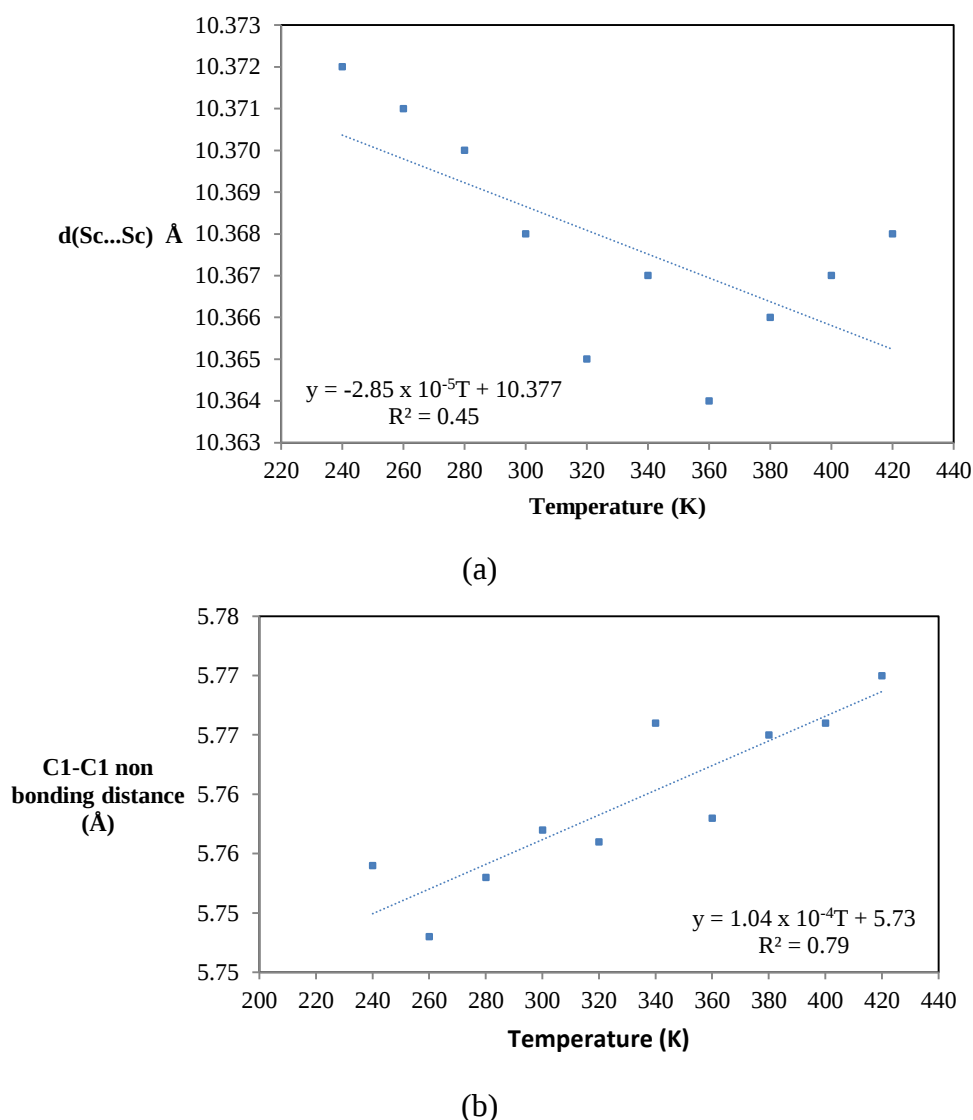


Figure 5.10 (a) The temperature dependence of the $d_b(\text{Sc}\dots\text{Sc})$ non-bonding distance. (b) The temperature dependence of the C1...C1 non-bonding distance.

The variation in the (100) plane of $[\text{Sc}_2(\text{bdc})_3]$ is attributed to the “wine rack” thermo-mechanical mechanism. However, the “wine rack” feature in $[\text{Sc}_2(\text{bdc})_3]$ is different from the members of the MIL-53 family. In $[\text{Sc}_2(\text{bdc})_3]$, the framework on the (100) plane compresses along the b axis direction while in the member of the MIL-53 family, the framework compresses along the c axis direction. This difference is illustrated in **Figure 5.11**. The origin of this significant different behaviour in the (100) plane of $[\text{Sc}_2(\text{bdc})_3]$ and the members of the MIL-53 family is due to the presence of the additional connection between

the two vertices along the b axis direction by the bdc linkers which physically inhibit the thermo-mechanical behaviour of the framework.

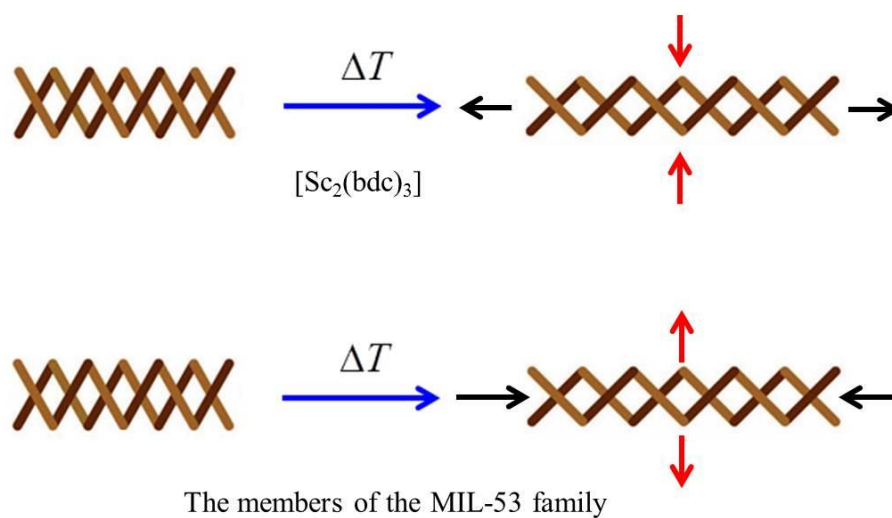


Figure 5.11 The “wine rack” thermo-mechanical mechanism observed in $[\text{Sc}_2(\text{bdc})_3]$ in comparison with that in the members of the MIL-53 family.

5.4 Conclusion

The mechanism behind the NTE behaviour of $[\text{Sc}_2(\text{bdc})_3]$ is attributed to a significant decrease in distance along the one dimensional inorganic chain which occurs as a result of the twisting vibrational mode of the carboxylate groups of the bdc linker that link the isolated ScO_6 octahedra together. The flexibility of the one dimensional inorganic chain is found to greatly dominate the expansion/contraction in the MOF material as it increases the flexibility along the inorganic chain so that a wide variety of vibrational modes become possible. The connectivity of the framework has a great influence on the thermal behaviour of the MOF material. A “wine rack” thermo-mechanical mechanism is found to be restricted by the presence of the additional connectivity that bisects the rhombus channel. This shows that the thermal behaviour of the MOF materials can be designed by considering the structural building units of the framework.

5.5 References

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6. Conclusion

6.1 Conclusion

In this thesis, the thermoresponsive behaviour of nine metal dicarboxylate MOFs was investigated and six of these materials were found to show NTE behaviour. These include four materials with a UiO-66 framework topology: $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bdc})_{12}]$, $[\text{Zr}_6\text{O}_6(\text{bpdc})_{12}]$ and $[\text{Zr}_6\text{O}_6(2,6\text{-ndc})_{12}]$ and two members of the MIL-53 family: $[\text{AlF}(\text{bdc})]$ and $[\text{VO}(\text{bdc})]$. The NTE behaviour of $[\text{Sc}_2(\text{bdc})_3]$ has already been discovered and two members of the MIL-53 family: $[\text{Al}(\text{OH})(\text{bdc})]$ and $[\text{Cr}(\text{OH})(\text{bdc})]$, show positive thermal expansivity. The variation of the coefficients of expansivity of all metal tri- or dicarboxylate NTE MOFs reported to date and all the MOFs studied in this work as a function of the temperature is shown in **Figure 6.1**.

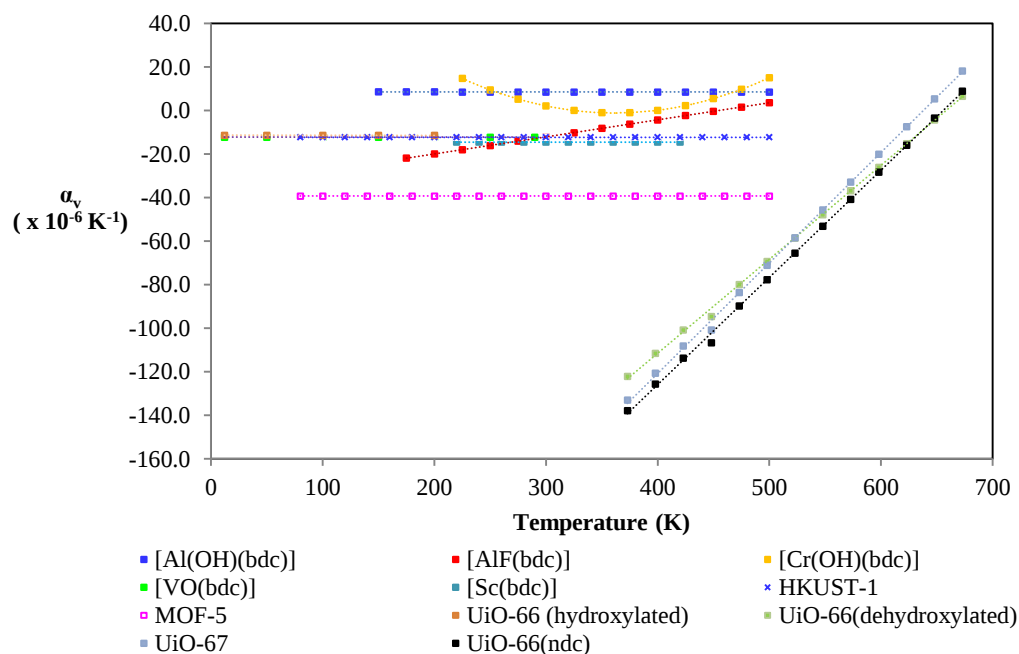


Figure 6.1 The variation of the coefficients of volume expansivity of the MOFs studied in this thesis, HKUST-1 and MOF-5 as a function of the temperature.

Within this research, [VO(bdc)] is found to be the best candidate material for use in the formation of a hybrid polymer composite as it offers a constant value of the coefficient of thermal expansion over the entire range of the temperature studied. Moreover, there is no occurrence of a phase transition over the observed temperature range which means it can be used as a suitable component in the formation of composites with polymers. [Zr₆O₄(OH)₄(bdc)₁₂] shows NTE behaviour with a coefficient of thermal expansion close in value to [VO(bdc)], but only over the temperature range of 12 -200 K before exhibiting positive thermal expansion which reduces its suitability for this application. [Sc₂(bdc)₃] shows the greatest constant value of the coefficient of thermal expansion over the observed temperature range of 240 – 420 K, but again its phase transition at 225 K makes it an unsuitable composite component. The other NTE MOFs which are [AlF(bdc)], [Zr₆O₆(bdc)₁₂] [Zr₆O₆(bpdc)₁₂] and [Zr₆O₆(2,6-ndc)₁₂] may only be applicable for certain composites as their coefficients of thermal expansion vary with temperature.

The presence of the bdc linker is found to have a great influence on the NTE behaviour. There are two distinct types of vibrational mode of the bdc linker which are found to dominate the NTE behaviour of MOFs, including the twisting motion of the carboxylate groups and possibly the bending modes of the C-C₆H₄-C fragment of the bdc linker. The latter motions are not evident in this work, although they have been suggested to be the important contributors in NTE behaviour of HKUST-1 and MOF-5. This might be due to the limitations in precision of our structure refinements. The twisting motion of the carboxylate groups of the bdc linker is found to be the main contributor driving the NTE behaviour in UiO-66 and [Sc₂(bdc)₃] studied in this work, as this motion introduces a concerted rocking motion of the inorganic components. Alteration of the structure and length of the organic linkers is found to have a small effect on the magnitude of the expansivity coefficient, although there is no direct relation between the length of the linker and the decrease of the expansivity coefficients. In addition, it is believed that the NTE behaviour is dependent on the nature of the organic linker which possesses specific vibrational modes.

New NTE MOFs containing one-dimensional inorganic components have been discovered and reported for the first time in this work. The magnitude of the coefficient of thermal contraction of MOFs containing one dimensional inorganic component appears to be lower than that of MOFs containing zero dimensional inorganic components. This is because the thermal behaviour along each direction in MOFs containing zero dimensional inorganic clusters occurs independently and each direction contains the relative flexible organic linker. Therefore, the presence of the vibrational modes of the bdc linker will greatly affect the thermal behaviour of these MOFs. While, in the systems containing one dimensional inorganic components like the members of the MIL-53 family and $[\text{Sc}_2(\text{bdc})_3]$, the thermal behaviour along each direction more correlates which restricts dynamic motion more and the bending in the direction along the linker is more restrictive as it does not contain the full organic linker.

The NTE behaviour in MOFs containing one dimensional inorganic components is greatly dominated by the flexibility of the particular inorganic component which depends on the connectivity of the constituent metal-centred octahedra and the rigidity of the octahedra themselves. The more flexibility within the chain of octahedra means the greater magnitude of thermal contraction being observed. For instance, the magnitude of thermal contraction along the chain of octahedra of $[\text{Sc}_2(\text{bdc})_3]$ is much greater than that of the members of the MIL-53 family. This is because in $[\text{Sc}_2(\text{bdc})_3]$ the constituent metal-centre octahedra are linked by three carboxylate groups while in the MIL-53 type framework, one of the linking carboxylate group is replaced by a single atom X. The rigidity of the metal-centred octahedra is compositionally dependent as found in the MIL-53 type framework and increases if the metal-centre octahedra contain either high electronegativity anions or high oxidation state metal ions. The rigidity of the octahedra plays an important role in determining the NTE behaviour of the MIL-53 materials as it appears to dominate the changes in the plane of the pore opening of the framework. The rigidity of the octahedra influences the thermoresponsive behaviour of the MIL-53 materials by determining which of two important motions is dominant, the rotation of the bdc linker about the -M-X-M- core of the chain of the $\text{MO}_4(\text{X})_2$ octahedra or the “knee cap” bending motion of the

carboxylate group of the bdc linker about the O...O vector. In addition, the rigidity of the metal-centre octahedra is also found to determine the occurrence of a “breathing” phase transition at low temperature with more rigid metal-centred octahedra not exhibiting such a transition.

The mechanism responsible for the NTE of MOFs is determined by the thermo-mechanical behaviour of the framework which is influenced by the structural connectivity. It is likely that the degree of freedom of the framework dominates the variety and magnitude of the vibrational modes exhibited by the bdc linker. For instance, the expansivity coefficient of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ is smaller than that of MOF-5. The $\text{Zn}_4\text{O}(\text{CO}_2)_6$ inorganic cluster of MOF-5 has a coordination number of six whereas the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inorganic cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$ has a coordination number of twelve and the transverse vibrational modes of the bdc linker in the direction perpendicular to the C-C₆H₄-C axis are not evident in $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}]$. The more connected the framework is means the more restriction of the vibrational modes of the bdc linkers. Moreover, in the cases of the MIL-53 materials and $[\text{Sc}_2(\text{bdc})_3]$, the presence of an additional bdc connecting linker in the plane of the pore opening of $[\text{Sc}_2(\text{bdc})_3]$ appears to restrict the mechanical changes in such plane resulting in an opposite framework compression direction in the plane of the pore opening compared to the MIL-53 type MOFs.

In summary, it is evident that the NTE behaviour of all candidate materials is greatly dependent on the inorganic clusters rather than the organic linkers. The greater size of the inorganic cluster means the greater effect of the NTE behaviour to be observed. In addition, the connectivity and the flexibility of the inorganic clusters are also found to dominate the NTE behaviour due to a wide variety of possible vibrational modes occurring in the clusters which consequently causes a decrease in size of the inorganic clusters and hence NTE behaviour.

A compilation of all the results in this work indicates that NTE behaviour results from a complex combination of all contributions from each constituent unit of the structural framework. Design and controlling of NTE behaviour at the microscopic level is theoretically possible but not as simple in reality. In addition,

the experimental results of this work are found to partially support the idea, proposed by Goodwin *et al.*, that is the NTE behaviour can be intrinsically designed by considering the individual structural units of the framework.

6.2 Future plan

The work of this thesis can be extended both experimentally and theoretically. The following list contains plausible further areas of study:

- Synthesis of MOFs with zero expansivity coefficient. The expansivity coefficient of [AlF(bdc)] may be increased to a near zero value by an addition of the –OH groups into the structural framework in order to form the chain of octahedra units with a –Al-OH-Al-F-Al- core. Introduction of the -OH group in the framework may reduce the rigidity of the one dimensional inorganic chain and hence increase the expansivity of [AlF(bdc)]. In addition, this may enable the expansivity coefficient to be varied by varying the ratio between the amount of the OH group and the F atoms incorporated in the core of the chain of the inorganic octahedra.
- Control of the overall expansivity coefficient of polymer composites. According to this work, the number of NTE MOFs has now been increased from two to eight materials while the performance of these materials in hybrid polymer composite in order to control the expansivity coefficient of the composite to a desired value has not yet been tested. [VO(bdc)] may be the best candidate to be used in formation of this composite in combination with a polymer that exhibits thermal expansion with a constant expansivity value.
- Molecular dynamic simulations of the thermoresponsive behaviours of the four members of the MIL-53 family. The full understanding of the physical origin of the thermal behaviour of the four MIL-53 materials may be fulfilled by further computational work. This

may be done by considering the effect of each constituent unit of the structural framework on the overall thermal behaviour of the particular material.
