

Lead-free ferroelectric glass-ceramics and composites

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SYMBOLS AND ABBREVIATIONS

Abbreviation	Name	Formula
BCZT	Barium calcium zirconate titanate based ceramics	$(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$
BT	Barium titanate-based ceramics	BaTiO_3
DSC	Differential scanning calorimetry	
DTA	Differential thermal analysis	
G1	Barium borosilicate glass (BBS)	$\text{BaO-B}_2\text{O}_3\text{-SiO}_2$
G2	Potassium and sodium-modified barium borosilicate glass	$\text{BaO-B}_2\text{O}_3\text{-SiO}_2\text{-K}_2\text{O-Na}_2\text{O}$
G3	Potassium-sodium and CuO-modified barium borosilicate glass	$\text{BaO-B}_2\text{O}_3\text{-SiO}_2\text{-K}_2\text{O-Na}_2\text{O-CuO}$
G4	Bismuth borosilicate glass	$\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-ZnO-SiO}_2$
HTCC	high temperature co-fired ceramic	
KBN	Potassium sodium niobate-Bismuth potassium sodium zirconate based ceramics	$0.96(\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3)\text{-}0.04(\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$
KNN	Potassium sodium niobate based ceramics	$(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$
LTCC	low temperature co-fired ceramic	
MLCC	multilayer ceramic capacitor	
SEM	Scanning Electron Microscopy	
EDS	Energy-dispersive X-ray spectroscopy	
XRD	X-Ray Diffraction	
SXPD	high-resolution synchrotron X-ray powder diffraction	

Constant	Name	SI Unit
a.u.	arbitrary unit	
C	capacitance	F (Farad)
E	electric field	kV mm ⁻¹
E _c	coercive field	kV mm ⁻¹
P	polarisation	C m ⁻²
P _{el}	electronic polarisation	C m ⁻²
P _{ion}	ionic polarisation	C m ⁻²
P _{or}	orientation polarisation	C m ⁻²
P _r	remnant polarisation	C m ⁻²
P _s	spontaneous polarisation	C m ⁻²
Q	electrical charge	C (coulomb)
t	tolerance factor	
Tanδ	loss tangent	
T _C	Curie temperature	°C
T _{cr}	crystallisation temperature	°C
T _g	glass transition temperature	°C
T _{O-T}	orthorhombic to tetragonal transition temperature	
T _{T-C}	tetragonal to cubic transition temperature	
V	voltage	V (volt)
ε _r	relative dielectric permittivity	

ABSTRACT

Lead-free ferroelectric glass-ceramics and composites

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Glass-ceramic composites and nanocrystalline glass-ceramics containing barium titanate (BT) or potassium sodium niobate (KNN) ferroelectric phases have been studied, with particular regard to their use as dielectric energy storage materials.

Barium borosilicate glass (BBS) was used as a sintering aid for BT and KNN, producing glass-ceramic composites. The temperatures required to achieve densification were reduced from 1400 to 1200 °C for BCZT (Ca, Zr-doped BT) and 1170 to 1050 °C for KBN (Bi, Na, K, Zr-doped KNN) by the use of glass additives. An unexpected observation, found in both BCZT and KBN systems, was the heterogeneous dissolution of dopant elements into the glass, inducing additional anomalies in the relative permittivity-temperature relationships. For BCZT, the orthorhombic-tetragonal phase transformation temperature shifted upwards to ≈ 50 °C, which was attributed to modification of the Ca/Zr ratio by preferential dissolution of Ca into the glass phase. Similarly, for KBN the dopant elements appeared to be leached into the liquid phase during sintering, resulting in relative permittivity-temperature characteristics similar to those of pure KNN.

A modified BBS glass having various KNN contents was prepared by the conventional melt-quenching method and then heat-treated to induce crystallisation, producing nanocrystalline glass-ceramics. It is shown that crystallisation of an intermediate barium niobate phase initiates at temperatures in the region of 650 °C; this is subsequently converted into perovskite KNN together with a second phase of $\text{Ba}_3\text{Nb}_5\text{O}_{15}$ at temperatures from 700 to 800 °C. The final crystallite size was in the region of 30 ± 7 nm.

The highest dielectric energy storage density of $0.134(4) \text{ J cm}^{-3}$ was obtained for a glass-modified BT ceramic at an electric field level of 5 kV mm^{-1} . However, the energy storage efficiency of the BT-based ceramics was relatively poor and they displayed a general tendency for saturation, indicating potentially poor performance at higher field levels. On the other hand, the KNN-based ceramics exhibited slightly lower energy storage density values, up to $0.108(1) \text{ J cm}^{-3}$, but with much improved linearity and energy storage efficiency. Therefore, the latter is considered to be more suitable as energy storage dielectrics. The BBS-KNN glass-ceramics yielded relatively low energy storage density, $0.035(2) \text{ J cm}^{-3}$, but the dielectric linearity and storage efficiency were similar to or better than those of the KNN ceramics, indicating good potential for use as energy storage dielectrics at very high electric field levels as a result of their nanocrystalline microstructures.

DECLARATION

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*To Dear
Mum
Dad
Wife*

أعزائي
أبي، أمي، زوجتي

1. Introduction

1.1 General Introduction

According to Kingery et al. (1976), any inorganic, non-metallic solid qualifies as a ceramic [1]. Inorganic dielectrics, semiconductors, and superconductors are, therefore, ceramics. Ceramics can be grouped as being either traditional or advanced in accordance with their properties and applications. Clay and silica are examples of traditional ceramics. Special engineering and processing techniques of ceramics are used to obtain advanced ceramics, which have shown superior mechanical, electrical, optical, and magnetic properties [2].

Nanocomposite materials can be obtained through the crystallisation of the grain-boundary glass phase in a ceramic matrix; the electrical and structural properties are improved with glass additives [3]. Over the last few decades, the field of electronic ceramics applications has been progressing. Some newer applications, such as in low temperature co-fired ceramics (LTCCs) and dynamic random access memories (DRAMs), utilise the material's dielectric properties. LTCC applications require the sintering temperature to be below the melting point of the electrode materials [4]. The chemical processes of adding glass and using starting materials with ultra-fine particle sizes improve the characteristics of ceramics at low sintering temperatures [5]. Glass additives can have useful effects on the dielectric constant due to their effect in broadening the diffusive phase transition at the Curie temperature, something that is desirable in the application of multilayer ceramic capacitors [6].

Glass-ceramics are ceramic materials that are produced through the controlled nucleation and crystallisation of glass through thermal treatment. Depending upon the chemical composition and microstructure of glass-ceramics, they can exhibit useful thermal, optical, chemical, mechanical, electrical, and magnetic properties. Useful composite materials can be produced by combining glass-ceramics and other materials, such as metals [7]. Low sintering temperatures and high relative permittivity are of primary importance in the manufacture of ferroelectric ceramics. Typical dielectric ceramic materials, such as barium titanate (BaTiO_3) and lead titanate zirconate (PZT), have found many applications in the electronics industry. Certain additives for BaTiO_3 and PZT, such as LiF and $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$, can reduce their sintering temperatures to around 900°C and improve their ferroelectric properties, making them suitable for a range of different electronic applications [8, 9].

There are many techniques that are used to prepare ferroelectric ceramics, including the conventional ceramic method, involving solid-state reactions, and wet chemical methods, which are generally used in the preparation of ceramic powders. Additionally, there is another method to obtain ceramic materials in the form of a film, referred to as Electrophoretic Deposition (EPD). EPD can be used in a wide range of novel applications for the processing of advanced ceramic films and coatings.

1.2 Aims and objectives

The main aim of this project was to determine the influence of glass additives on the structure and functional properties of lead-free ferroelectric ceramic solid solutions, employing two different synthesis methods involving either solid state reaction or the melt-quenching method. Barium titanate (BaTiO_3) (BT) and potassium sodium niobate ($\text{K}_x\text{Na}_{1-x}\text{NbO}_3$) (KNN) are typical lead-free ferroelectric ceramic materials, which were chosen as the majority crystalline components, while the barium borosilicate (BBS) system, $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$, was selected as the glassy component. By these means, it was intended to develop processing methods and chemical compositions to facilitate the fabrication of dense and homogeneous materials at reduced sintering temperatures, with potential for use in LTCC applications as thick film components.

For each system, the overall objective was to develop an understanding of the processing-microstructure-property relationships by evaluating the influence of chemical composition and processing conditions on crystal structure, microstructure, thermally-induced phase transformations, dielectric and ferroelectric properties. Hence, the processing parameters required to produce the optimum properties can be identified.

As the project evolved, it became evident that the most significant application for such materials was in the area of energy storage dielectrics for pulsed-power devices. In this area, improvements in microstructural homogeneity are vital to enable the extension of the applied electric field to higher levels. Therefore, a final objective of this research was to assess the potential of the glass-modified ferroelectric ceramics as energy storage dielectrics, identifying the advantages and disadvantages of each system.

2. Literature Review

2.1 Overview of ferroelectrics

This chapter aims to provide background information regarding the fundamentals of ferroelectrics and similar materials. Additionally, a brief explanation of the phenomena of piezoelectricity and ferroelectricity will be given.

2.1.1 Fundamentals of Ferroelectrics

Ferroelectric ceramics were discovered in the early 1940s, following the discovery of ferroelectricity in the preceding decades. It was found that unusually high dielectric constants in ceramic BaTiO_3 capacitors were associated with ferroelectricity. Since then, ferroelectric ceramics have been the focus of several multi-billion dollar industries, including those producing high-dielectric-constant capacitors and, later, those producing electro-optic light valves, positive temperature coefficient devices, and piezoelectric transducers. Two compositional systems, PZT and BaTiO_3 , have formed the basis of the materials that have dominated the industry throughout its history [10].

Ferroelectrics are insulating solids that have spontaneous polarisation. This means that they contain a permanent polarisation at the unit cell level, even in the absence of external electric fields. Additionally, ferroelectric materials exhibit the ability to alter the orientation of their polarisation between two or more directions when under the influence of external electric fields. In order to exhibit spontaneous electric polarisation, there must be a noncentrosymmetric arrangement of the ions and their electrons in these materials.

There are four primary mechanisms of electric field-induced polarisation that can contribute to the dielectric response, as shown in Figure 2.1. Each mechanism produces a short-range movement of charge that responds to the applied electric field and contributes to the overall polarisation. Initially, there is electronic polarisation (P_{el}) in which negatively charged electrons and positively charged nuclei are displaced in such a way that the electrons move towards the positive field and the nuclei move towards the opposite direction. Secondly, ionic polarisation (P_{ion}) occurs, in which there is relative displacement between cations and anions. Thirdly, there is orientation polarisation (P_{or}) in which the dipoles tend to align themselves with the field direction if the material contains complexes or molecules possessing permanent dipole moments. The net effect is the induction of a dipole moment within the solid. Lastly, there are interfaces or space charge polarisations (P_{sc}) in which a final source of polarisation is

the mobile charges which are present due to impedance by interfaces which occurs because they are not supplied to an electrode or discharged at an electrode [2, 11].

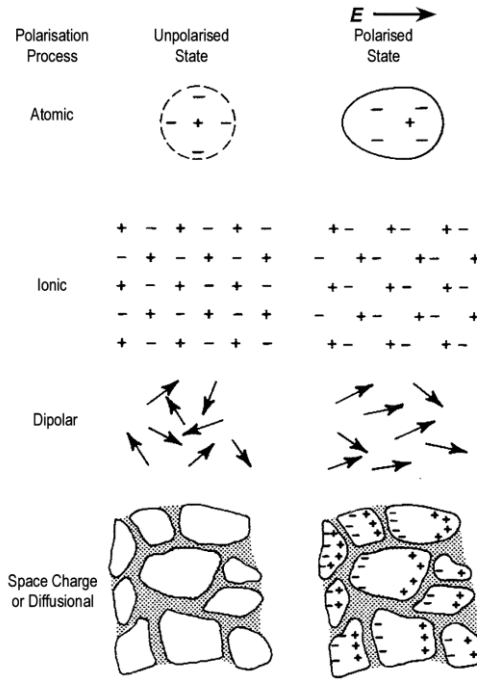


Figure 2.1 Schematic diagram showing different polarisation mechanisms in a material [2].

2.1.2 Phase transition and perovskite structure

Many ferroelectric materials have perovskite structures with a general chemical formula of ABO_3 , as shown in Figure 2.2 a-b. ABO_3 -type oxides are known to stabilise with a wide range of A (Pb, Ba, Ca, Sr) and B (Ti, Zr, Sn) ions, with A ions having larger ionic radii than B ions.

It is shown in Figure 2.2 (a) that when the A cation occupies the corner of the cubic unit cell, the B cation occupies the centre, and the oxygen anion occupies the face of the cubic unit cell that surrounds the B cation. Figure 2.2 (b) shows the perovskite structure as an octahedron with six O ions occupying the centres of the faces of the cubic unit cell. Different structural forms of the oxides exist and they are broadly classified as being either perovskite or ilmenite, grouped in accordance with their tolerance factors (t) that are calculated using the equation below.

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad 2-1$$

here R_A , R_B , and R_O represent the respective ionic radii for A, B, and O, respectively. In general, the perovskite-type structure is usually obtained when t is in the range $0.75 < t < 1$, as found in $BaTiO_3$. ABO_3 oxides with $t < 0.75$ have ilmenite-type structures,

such as in FeTiO_3 , CdTiO_3 , and those having $t > 1$ have a hexagonal structure, such as in CaCO_3 [11].

Ferroelectrics have typical properties which are essential for their use in electronic devices. High relative permittivity and low-loss dielectric characteristics are most important in multilayer ceramic capacitors (MLCC), which are widely used in electronic devices. There have been progressive developments in the manufacture of MLCCs to increase both the relative permittivity and the number of layers, as well as decreasing the layer thickness, t , according to equation 2-6 below [12, 13].

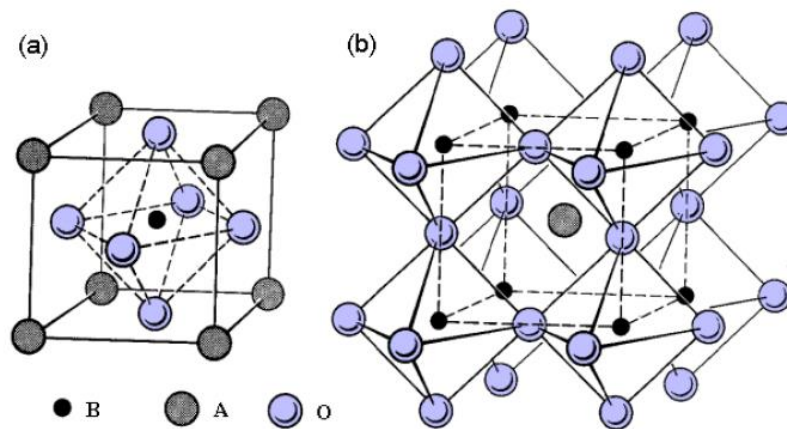


Figure 2.2 (a) Perovskite crystal structure, ABO_3 , and (b) octahedral chain, BO_6 , with the symmetrical centre [14].

Figure 2.3 and Figure 2.4 illustrate the changes in structure and dielectric properties of a typical ferroelectric as a function of temperature. Figure 2.3 (a) depicts BaTiO_3 ; the total positive charge of Ti^{4+} and Ba^{2+} is balanced by the negative charge of the oxide ions, O^{2-} . In this case, at high temperatures, this material has a paraelectric cubic perovskite structure. Figure 2.3 (b)-(c) show the transformations that occur in this material at a low temperature (below the Curie point, T_C). The material transforms from a cubic phase to a tetragonal phase material, showing ferroelectric properties. The Ti^{4+} and Ba^{2+} ions are shifted by small displacements relative to the oxygen octahedron. The cubic symmetry is broken by this shift and, as a result, the net dipole per unit cell produces the polarisation.

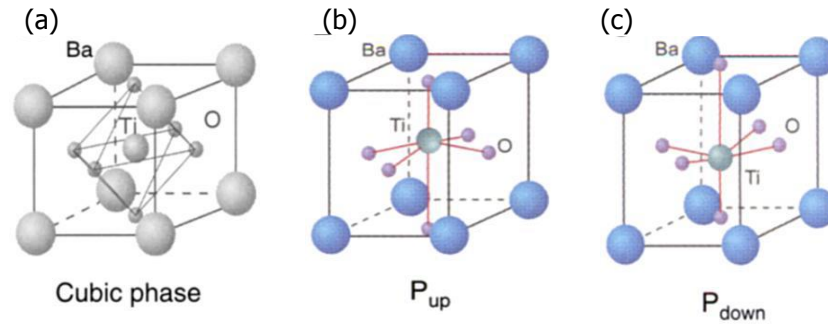


Figure 2.3 Perovskite structure of ferroelectric BaTiO₃. (a) cubic phase, paraelectric at high temperature. (b) and (c) tetragonal phase and ferroelectric at room temperature, with up- or down-oriented polarisation [11].

The properties of ferroelectrics are dependent upon the temperature at which they transform from the high crystal symmetry paraelectric to the lower symmetry ferroelectric phases. On cooling from temperatures above T_C , the relative permittivity, ϵ_r , increases with temperature and reaches a peak at the Curie point, decreasing below that. The temperature-dependent variations in ϵ_r above T_C are described by the Curie-Weiss law, according to the equation:

$$\epsilon_r = \frac{C}{T - T_C} \quad 2-2$$

where C is the Curie constant. As shown in Figure 2.4, some of the characteristics of ferroelectric materials, including thermal, optical, and physical properties, exhibit large changes at temperatures near to the Curie point [11, 15].

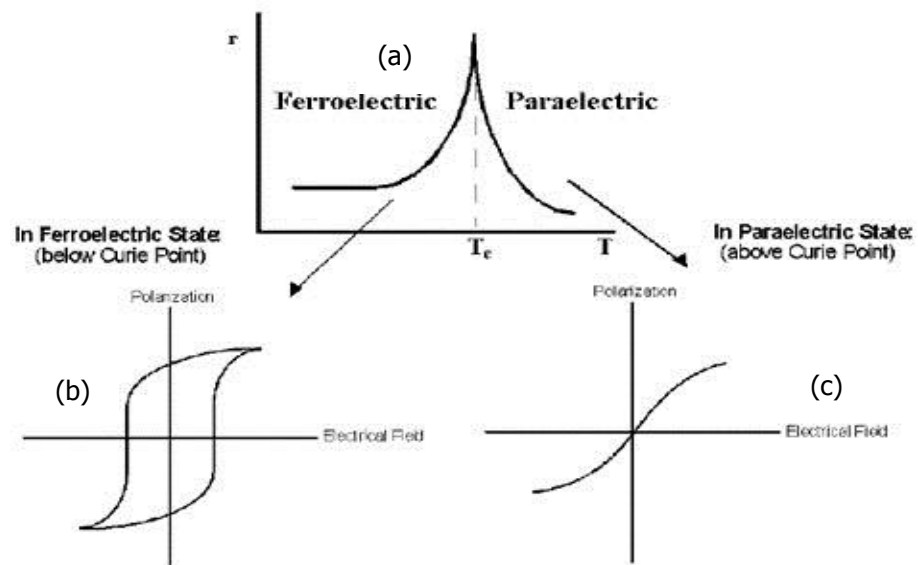


Figure 2.4 (a) The temperature is dependent on the relative dielectric constant of the polar material. (b)-(c) The change in P-E characteristics due to the transformation from ferroelectric and paraelectric [16].

2.1.3 Domain structure and ferroelectric hysteresis

Ferroelectrics are polar crystals with the ability to alter their polarisation direction upon the application of an external electric field. They exhibit spontaneous polarisation, even in the absence of external electric fields. In the unit cell, net permanent dipole moments are present in ferroelectric materials. In polycrystalline ceramics, the orientation of the dipole moments are random and therefore a net polarisation is not normally present after cooling through T_C in the absence of an external electric field.

The overall orientation of the dipole moments in polycrystalline and single crystal ferroelectrics are not completely random at the scale of the unit cell, since they form ordered groups, referred to as *domains*. Within the domains, there is a uniform alignment of dipoles, with neighbouring domains being separated by boundaries known as *domain walls*.

The direction of spontaneous polarisation in ferroelectrics can be altered through an applied electric field, as shown in Figure 2.5. With the increase of the electric field, the domains begin to align, giving rise to an increase and saturation in the polarisation at high field. In the absence of an external electric field, some of the domains remain aligned. Thus, the crystal displays remanent polarisation. If the field is reversed, the domains change direction. The direction of polarisation flips and produces a hysteresis loop when the external electric field alternates between negative and positive [2, 17].

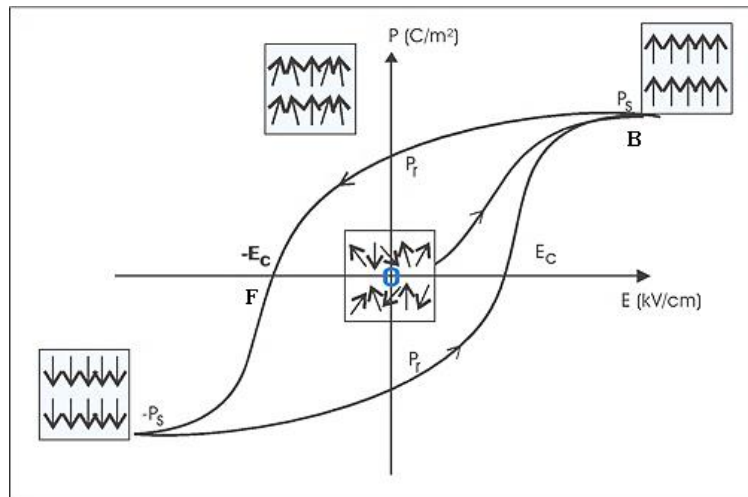


Figure 2.5 Illustration of the polarisation-electric field relation, P-E hysteresis loop, for a typical ferroelectric crystal [2].

2.1.4 Dielectric properties and capacitance

Materials that possess a high electrical resistivity are called dielectrics and can exhibit paraelectric, ferroelectric, pyroelectric, and piezoelectric behaviour. In the case of paraelectric and ferroelectric behaviour, an applied electric field induces a change in polarisation, while for piezoelectrics and pyroelectrics, the effect is due to the application of pressure or temperature, respectively [18].

Ferroelectrics are able to maintain the direction of their dipoles even upon removal of the external electric field. As seen in Figure 2.6 when a dielectric material is positioned between two parallel plates, the material becomes polarised due to the applied field. Dielectric materials have, therefore, significant technological implications and use.

The relative permittivity describes the flux density which arises through the application of an electric field on the insulator. The principal characteristic of a capacitor is that it is able to store an electrical charge, Q . The charge of a capacitor is given by the equation:

$$Q = CV \quad 2-3$$

where V is the applied voltage and C is the capacitance.

The capacitance contains both a geometrical and material factor. For a large plate capacitor area, A , and thickness, t , the geometrical capacitance in a vacuum is given by the equation:

$$C_0 = \frac{A\epsilon_0}{t} \quad 2-4$$

where ϵ_0 is the permittivity (dielectric constant) of a vacuum. If a dielectric material with permittivity ϵ is inserted between the capacitor plates, the capacitance would increase according to:

$$\frac{C}{C_0} = \frac{\epsilon}{\epsilon_0} = \epsilon_r \quad 2-5$$

where ϵ_r is the relative permittivity or relative dielectric constant. The capacitance itself is dependent upon ϵ_r , the area of the parallel plates, A , and the thickness of the dielectric material, t , according to:

$$C = \frac{\epsilon_0 \epsilon_r A}{t} \quad 2-6$$

For real (non-ideal) dielectric materials, which possess both polarisation (capacitive contribution) and charge transport (resistive contribution) processes, the concept of complex relative permittivity is used to describe the material:

$$\varepsilon_r = \varepsilon'_r - i\varepsilon''_r \quad 2-7$$

Where the real part ε'_r is the relative permittivity or dielectric constant and ε''_r is referred to as "relative loss factor", which is associated with the resistive loss, and i is the complex number [11, 15].

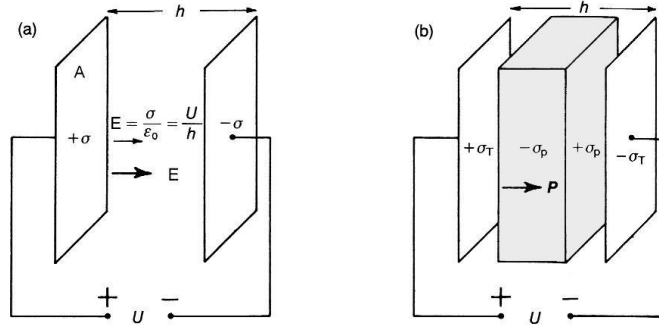


Figure 2.6 Schematic diagrams showing how charge can store on capacitor plates in a vacuum (a) and how a dielectric material (grey) in between them can play a role (b).

2.1.5 Energy Storage in Capacitors

Significant improvements over the last couple of decades in both the energy storage density and reliability of capacitors have been achieved through a combination of novel materials, diagnostic methods, and manufacturing techniques. Capacitors, inductors, and batteries are means through which electrical energy is stored. Figure 2.7 depicts a graph of the specific energy for different energy conversion and storage devices plotted against their specific powers [19].

The characteristics of energy-storage in four types of the most highly studied dielectric materials, namely, relaxor ferroelectrics, polymer-based ferroelectrics, antiferroelectric, and dielectric glass-ceramics were reviewed by Hao [20].

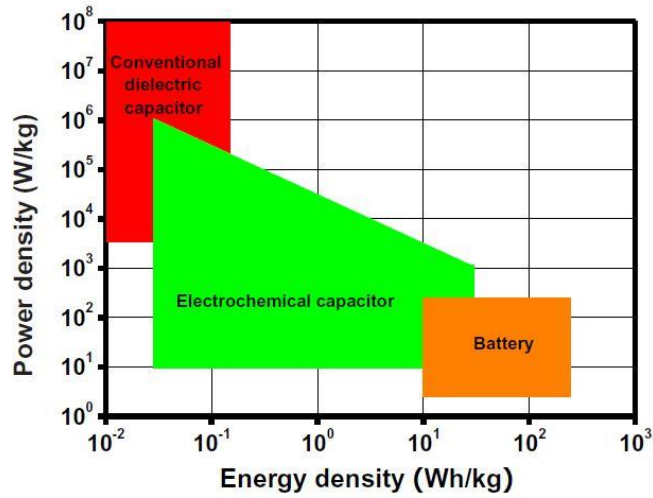


Figure 2.7 Diagram of power density as a function of energy density in different energy-storage devices [20].

The changes in polarisation upon the application of an electric field is a critical aspect of energy storage dielectrics. This response can be used to estimate the stored energy, which should exclude hysteresis losses. Dielectrics may be grouped into being either linear or non-linear, according to the relationship between the applied electric field and the polarisation. A simple equation (below) may be used to describe their behaviour [15].

$$D = \epsilon_0 E + P = \epsilon E \quad 2-8$$

Therefore:

$$P = \epsilon_0(\epsilon_r - 1)E = \chi \epsilon_0 E \quad 2-9$$

where χ is dielectric susceptibility and D is the dielectric displacement.

Energy density, U , is a measure of the energy stored per unit volume. For dielectrics, this can be obtained by the following relationship:

$$U = \int_0^{E_{\max}} P dE \quad 2-10$$

Using formula 2-10, the U values of the dielectrics can be obtained through the numerical integration of the area between the polarisation and curves for the electric-field polarisation (P - E) loops. Figure 2.8, shows that upon reaching the maximum electric field strength ($E_{\max}$), the polarisation approaches its maximum ($P_{\max}$) and the capacitor holds the electrical energy (U_{store}), as illustrated by the red and green areas.

The recoverable electrical energy density (U_{rec}) is released during the discharge process when the electrical field reduces from E_{max} to zero. This is represented by the green area in Figure 2.8. Therefore, an amount of the stored energy (the red segment surrounded by the loops) is dissipated during the process of depolarisation, denoted the hysteresis loss, U_{loss} . [20, 21].

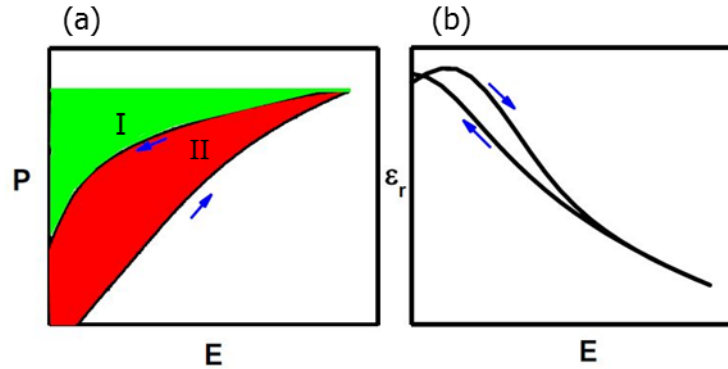


Figure 2.8 The typical dependence of (a) polarisation and (b) relative permittivity on the electric field of ferroelectrics in the first quarter shows the charge-discharge cycle. The area I (green shaded area) corresponds to the discharged or recoverable, energy density and area II (red shaded area) correspond to the energy density loss [20].

The above analysis indicates that there are three prerequisites to designing an effective dielectric material for practical use with high efficiency and high recoverable energy-storage density. These three requirements need to be satisfied simultaneously and are small remanent polarisation, large saturation polarisation, and a high electric breakdown field [22].

Figure 2.9 (a)-(d) depicts typical P-E loops and an illustration of the energy-storage of four types of dielectrics: (a) linear dielectric with constant permittivity (e.g. Al_2O_3 , glass), (b) antiferroelectric with zero net remnant polarisation (e.g. PbZrO_3), (c) ferroelectric with spontaneous polarisation (e.g. PbTiO_3 , BaTiO_3), and (d) relaxor ferroelectrics with nanosized domains, e.g. $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$.

Even though linear dielectrics often have lower energy losses and higher breakdown fields, small polarisation values resulting from the use of low-permittivity dielectrics can reduce their effectiveness for high-energy storage purposes, unless very high breakdown fields can be achieved.

Ferroelectrics generally have moderate electric field endurance and larger saturated polarisations, however, due to their larger remnant polarisations, they are often less efficient and have smaller energy-storage densities. Figure 2.9 demonstrates that antiferroelectrics and relaxor ferroelectrics are more attractive for high energy storage

due to their relatively moderate breakdown fields, smaller remnant polarisations, and larger saturated polarisations.

Novel manufacturing processes, such as the use of composite technology and glass-crystallisation techniques, have allowed for the production of ceramic-polymer composites and glass-ceramics. These materials could potentially combine the larger polarisations of ferroelectrics and the higher breakdown fields of linear dielectrics. Therefore, amongst the aforementioned four groups of dielectrics, namely, relaxor ferroelectrics, ceramic-polymer composites, glass-ceramics, and antiferroelectrics, the former two are generally thought to be the most useful for high energy storage purposes and therefore much research has been conducted on these two types of material [20, 23].

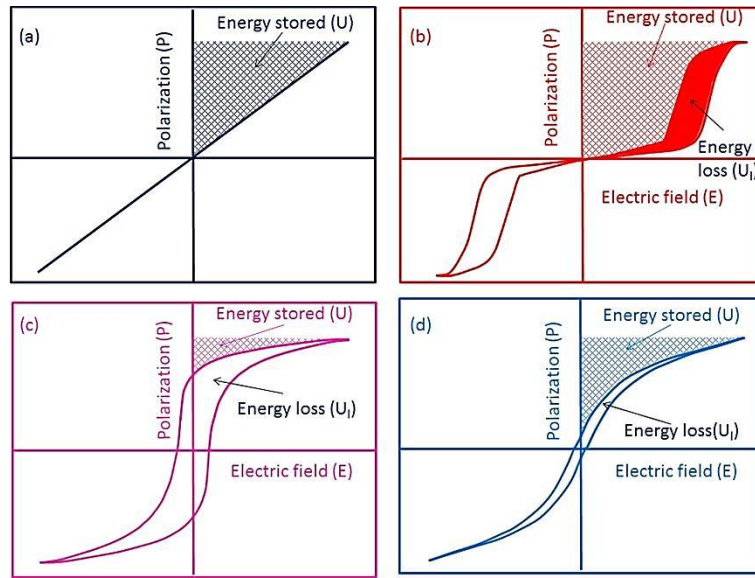


Figure 2.9 Schematic description of the energy storage characteristics of (a) linear dielectrics, (b) antiferroelectrics, (c) ferroelectrics, and (d) relaxor ferroelectric ceramics [23].

$\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) based materials have been widely used in energy storage applications because of their high dielectric constant. However, the environmental issues derived from the use of lead have encouraged many searches for more environmentally friendly materials.

The perovskite structure of BaTiO_3 , capable of high dielectric constant values, spontaneous polarization, low dielectric loss and ferroelectricity offers an alternative for lead-based capacitors. As mentioned earlier on, for energy storage applications a high dielectric breakdown strength is required to allow device miniaturization. It is well known that the energy storage properties of BaTiO_3 based ceramics can be improved by reducing the porosity [24], tuning the grain size [25], the addition of glass additives

[26], presence of secondary phases, etc. For example, the relative permittivity of BaTiO₃ increases as the grain size decreases [27], reaching a maximum of 5000 at grain sizes of about 0.8 to 1.1 μm [28]. This was attributed to domain size and stress effects. Further reductions in the grain size resulted in a rapidly decreased permittivity. Furthermore, the dielectric breakdown strength increases with decreasing grain size [29], being about 8.5 kV mm⁻¹ when the grain size is 3.5 μm [30].

The addition of glass additives to induce liquid phase sintering is a widely used technique to improve the energy storage capabilities of BaTiO₃ based ceramics. During the liquid phase sintering, a thin layer of the fluxing agent coats the BaTiO₃ grains leading to improved relative densities and reduced sintering temperatures. Until now, the use of several glass additives in BaTiO₃ ceramics has been proved to show promising results for energy storage applications. For example, Sarkar and Sharma [31] demonstrated that the addition of B₂O₃ and PbB₂O₄ to BaTiO₃ significantly reduced the sintering temperature to about 800 °C, which is suitable for commercial applications as multilayer capacitors. Moreover, they doubled the dielectric breakdown strength of BaTiO₃ by the addition of 10 mol% of PbB₂O₄ [31]. However, this improvement in the dielectric breakdown strength was accompanied by a small decrease in the dielectric constant.

The aliovalent substitution at the Ba²⁺ and/or Ti⁴⁺ sites in the perovskite structure of BaTiO₃ has been demonstrated [32] to be an effective approach to tailor the energy storage properties of BaTiO₃ to meet industrial application requirements. Recently, Puli et al [33] investigated the dielectric, ferroelectric and energy density properties of (1-x){BaZr_{0.2}Ti_{0.8}O₃}-x{Ba_{0.7}ZCa_{0.3}TiO₃} where x= 0.1, 0.15 and 0.20, hereinafter denoted BCZT. They reported a dielectric of the permittivity of 8400 when x=0.15 and a low loss (tan δ) of 0.014 in samples sintered at 1600 °C. Figure 2.10 shows the discharge energy density, charge energy density, and energy storage efficiency reported by Puli and co-workers, measured at a maximum electric field of 80 kV cm⁻¹ [33]. They achieved an energy storage efficiency of about 70 % when x= 0.15.

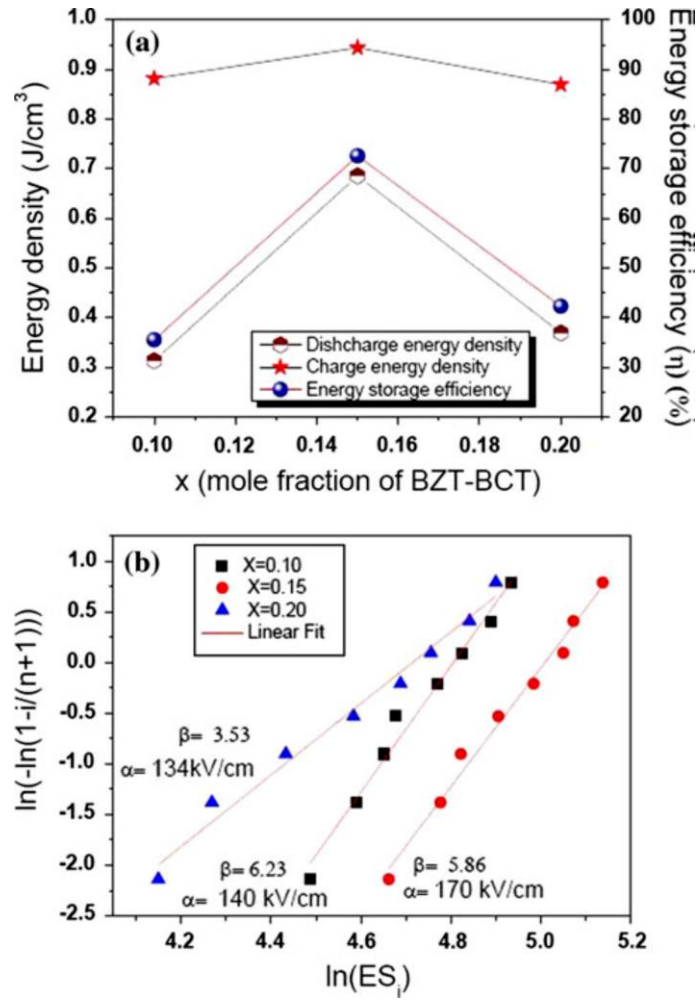


Figure 2.10 (a) Composition dependence of recoverable energy density (U_{rec}), stored energy density (U_{stor}), and energy storage efficiency (η %) of $(1-x)\{BaZr_{0.2}Ti_{0.8}O_3\}-(x)\{Ba_{0.7}ZCa_{0.3}TiO_3\}$ where $x=0.1, 0.15$ and 0.20 (b) Weibull plots of the breakdown strength of BCZT ceramics sintered at 1600 °C [33].

Wang et al [34] achieved an energy density of $0.52 J cm^{-3}$ in a $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ ceramic prepared by the sol-gel method. They attributed it to the improved microstructure compared to that obtained by the conventional solid-state reaction method.

In order to simultaneously attain high dielectric breakdown strength, high energy density and a high dielectric constant in a material, the glass-ceramic concept has been devised. Here, the high dielectric breakdown of the linear dielectric (glass) and the high dielectric constant/large polarization typical of ferroelectric ceramics are combined in a nanostructured composite-type material.

Puli et al. [35] followed the glass-ceramic approach to improve the energy storage properties of BCZT ceramics. They added 15 wt% of two different alkali-free glass compositions, namely $0.1BaO+0.4B_2O_3+0.5ZnO$ and $0.3BaO+0.6B_2O_3+0.1ZnO$, to

BCZT, They reported a slight improvement in the dielectric breakdown field to about 28 kV mm^{-1} but a lower energy density compared to glass-free BCZT. The low energy density values reported were attributed to the low relative permittivity values (≈ 270) for glass-ceramic composition.

Another lead-free perovskite material that exhibits useful ferroelectric properties is the solid solution system potassium-sodium niobate (KNN). The solid solution in the binary system $\text{KNbO}_3\text{-NaNbO}_3$ crystallises as an orthorhombic perovskite, [36], with the composition around $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ being the most popular due to its closeness to the morphotropic phase boundary (MPB) which occurs at about 52.5% Na [37]. The solid solution $(\text{K,Na})\text{NbO}_3$ exhibits ferroelectric behaviour which diminishes at high sodium additions until it completely disappears due to the nonpolar, antiferroelectric end-member NaNbO_3 [38, 39]. The dielectric constant of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ at room temperature is about 290 [38] and reaches 990 at 473 K. The use of additives to reduce the grain size and to improve the energy storage abilities of KNN ceramics has shown promising results. Qu et al [40] achieved an energy storage density of 2.48 J cm^{-3} and a breakdown strength of 29.5 kV mm^{-1} by reducing the grain size of KNN to $0.5 \mu\text{m}$ through the addition of $\text{Sr}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (SSN), although they reported the presence of porosity at the grain boundaries. Highly dense KNN-SSN samples were achieved through the addition of 0.5 mol% ZnO, leading to a breakdown strength of 40 kV mm^{-1} and an energy storage density of 2.6 J cm^{-3} [41].

2.1.6 Piezoelectricity

A dimensional change is seen in some polar dielectric materials upon exposure to an external electric field; this is illustrated in Figure 2.11. This phenomenon is referred to as the *converse piezoelectric effect* and it can be observed in polycrystalline ferroelectrics after application of a high electric field to induce a remanent polarisation.

On the other hand, the *direct piezoelectric effect* describes the changes in polarisation induced by the application of stress to deform the lattice of crystalline materials without fracturing it. Piezoelectricity was discovered over a century ago and it has many current uses [15, 37].

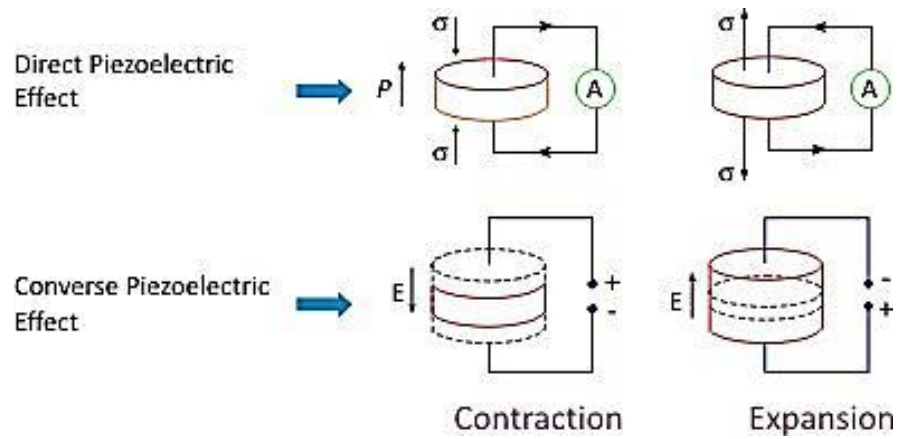


Figure 2.11 The direct and indirect piezoelectric effects [15].

Many different piezoelectric coefficients can be measured in a ceramic material. These coefficients are denoted, generically, as d_{ij} , where i and j represent the electric field/dielectric displacement and mechanical stress/strain, respectively. An example of this is the transverse piezoelectric coefficient, d_{31} , which represents the field aligned along the polar axis and the stress/strain perpendicular to it (Figure 2.12) [42]. d_{33} is the most widely studied piezoelectric coefficient and it represents the field and stress/strain being measured along the polar axis [15]. It is delineated by equation 2-11, where Q , F , and V are the induced charge, applied force, and induced voltage, respectively, and C is the capacitance [43].

$$d_{33} = \frac{Q}{V} = \frac{CV}{F} \quad 2-11$$

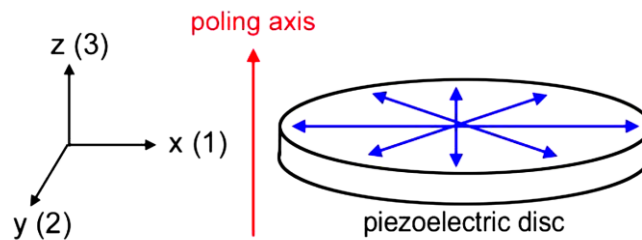


Figure 2.12 Schematic labelling the reference axes and planes of piezoceramics.

2.1.7 Ferroelectric and piezoelectric applications

Due to its low losses and high electromechanical coupling, PZT is a ferroelectric ceramic material that has been used for many years. However, the ferroelectric properties of PZT degrade with increases in temperature and pressure, and as such, its availability for high-temperature and high-pressure devices is limited.

As mentioned before, T_C is the transition temperature at which the ferroelectric to paraelectric phase transformation occurs. The working pressure changes in accordance with the composition, as shown in the diagram regarding the ceramic phase Figure 2.21 [11].

Ferroelectric and piezoelectric materials are, broadly, transducers, as they convert one form of energy into another. There are four main categories of piezoelectric transducers, which are normally denoted as *generators*, *actuators*, *sensors*, and *transducers*, with the latter referring (in a narrow sense) to a combined generator and sensor function. The global market share of these piezoelectric devices is expected to undergo a compound annual growth rate of 13.2% and rise to 38.4 billion US dollars by 2017 [44].

Hong et al. [45] identified eleven broad types of devices, which were ultrasonic motors, actuators, Langevin actuators, resonators, transducers, piezoelectric transformers, piezoelectric generators (including energy harvesters), piezoelectric sensors and accelerators, acoustic devices, sonars for military and civilian use nine broad application fields cover the primary uses of these devices. These fields are: information technology/robotics, precision machines, biomedical processes, non-destructive testing and measuring of transducers, ecological/energy harvesting, acoustic devices and resonators, sonars (for both military and civilian use), piezoelectric sensors, and a group comprising ultrasonic cutting and welding, gas ignition, and other uses [45].

The progress made in the development of low loss, high dielectric constant materials allows for the future miniaturisation of electronics. The high dielectric constant is also an essential component in many other applications of these materials, including memory storage and high power, high energy capacitors for hybrid vehicles [46].

Pulsed ceramic capacitors (also simply called ceramic capacitors) have drawn much interest as they have superior energy densities and faster discharge rates than normal capacitors, and so they have a huge potential to be used as energy storage devices.

'Future Electronics Company' a global supplier of electronic components and electromechanical products, possesses full multilayer ceramic capacitors (MLCCs) that can be used as multilayer ceramic chip capacitors, high voltage ceramic capacitors, or any other kind of multilayer ceramic capacitors. A broad classification can be used to divide MLCCs into two types: MLCCs with high relative permittivity and MLCCs for temperature compensation. The latter uses a paraelectric composition comprising

calcium zirconate (CaZrO_3) and titanium oxide (TiO_2), making it unsuitable for high value capacitors due to the low relative permittivity (about 20 to 300).

Barium titanate (BaTiO_3) is used as the primary material as the dielectric in MLCCs with high relative permittivity. It can produce capacitors that have high capacitance but are small in size due to its large relative permittivity, in the range 1000 to 20,000. However, the strong temperature-dependence of permittivity means that caution is advised when using it for time-constant circuits [47, 48].

2.2 Ferroelectric ceramic systems

2.2.1 Barium titanate-pure and modified

BaTiO_3 is an important ferroelectric material used in many processes and applications in electronics, due to its typical perovskite structure and specific characteristics, such as a high dielectric, ferroelectric, and piezoelectric properties.

2.2.1.1 Structure and phase transitions

BaTiO_3 has a typical perovskite structure, where the unit cell is a cubic above the Curie point. The paraelectric cubic phase transforms to ferroelectric tetragonal at temperatures below the Curie point (around 130°C). Generally, these two phases are the most important in BaTiO_3 . Changes in the crystal structure of BaTiO_3 are dependent upon the temperature, as can be seen in Figure 2.13. There are four phase transformations that occur in BT due to temperature changes with transformations to orthorhombic and rhombohedral occurring at 0°C and -90°C , respectively [2, 15].

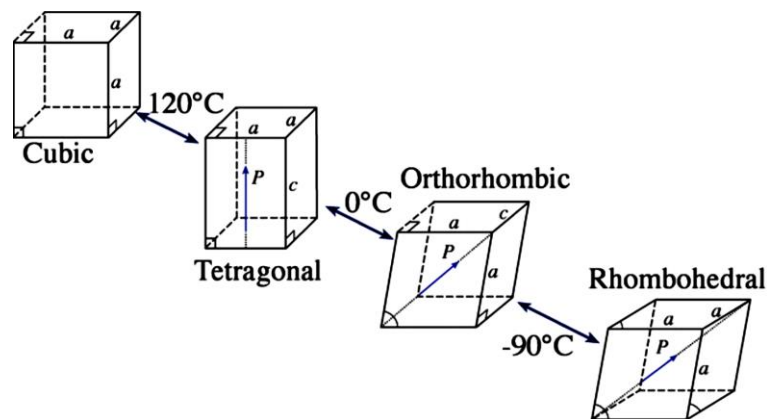


Figure 2.13 The phase structures of BaTiO_3 [2].

The phase diagram for the BaO-TiO_2 system is shown in Figure 2.14. The intermediate compound at the ratio 1:1 of BaO-TiO_2 in the phase diagram is BaTiO_3 . The mechanism of BaTiO_3 solid-state formation is the reaction between the BaCO_3 and TiO_2 [17, 49].

Generally, the rapid formation of BaTiO_3 nuclei was observed at a temperature between 600 and 800 °C. The formation of single-phase perovskite BT phase is observed at a temperature of 900 °C, which is in general agreement with the results that have been obtained in the present study [49, 50].

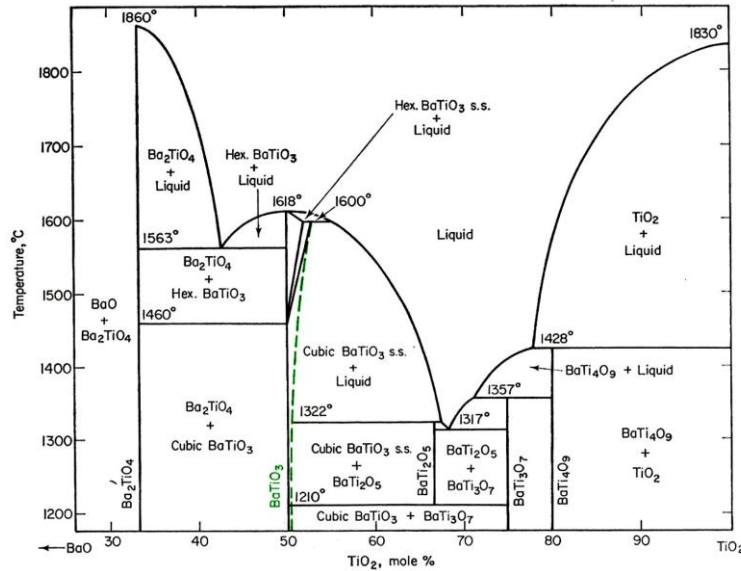


Figure 2.14 The phase diagram of the BaO-TiO₂ system [17].

The effect of grain size on the structure of BaTiO_3 has been recorded. Below a certain critical size, the properties of ferroelectric BT ceramics become more dependent on the grain size due to the tetragonality decreasing with decreasing particle size [51]. Many studies indicate that to produce sufficient ferroelectric behaviour in BaTiO_3 , the grain size should remain approximately 50 nm. Deng et al. [52] mentioned that the critical grain size for polycrystalline BaTiO_3 ceramics is less than 50 nm. The effect of grain size on relative permittivity was described by Zheng et al. [25] and Fang et al. [51]; it was shown that the decrease in grain size from 115 μm to 0.94 μm led to an increase in the relative permittivity values from 2640 to 4045.

Figure 2.15 shows the relative permittivity versus temperature curves of BaTiO_3 ceramics with a grain size ranging from 70 nm to 1700 nm after the work of Frey et al [53]. It can be observed that the relative permittivity increase as the grain size increases from 30 to 1700 nm. They observed a ferroelectric anomaly at the Curie temperature even for ceramics with a grain size less than 100 nm, but there was no significant shift in the Curie temperature when the grain size was below 2 μm. The pioneering work of Arlt et al [28] reported an enhanced dielectric constant when the grain size decreased from 10 μm to 0.3 μm, which was attributed to a decrease in the width of the equilibrium domain wall.

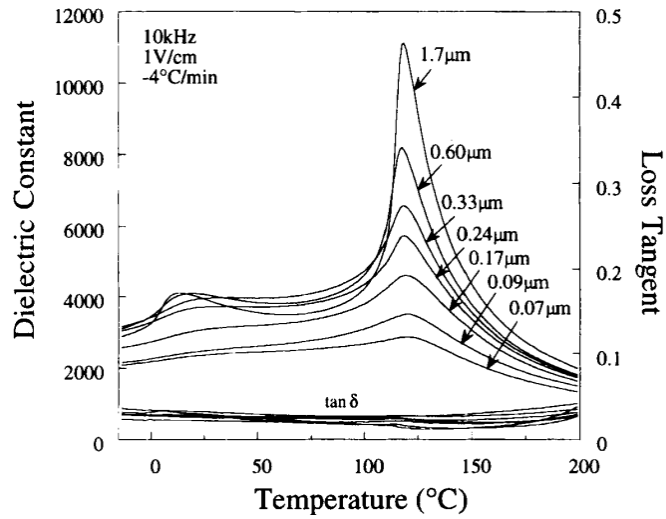


Figure 2.15 Relative permittivity versus Temperature curve of BaTiO₃ ceramic with a grain size of 70 to 1700 nm [53].

Yao et al [54] studied the dielectric properties of BaTiO₃ glass ceramics prepared via sol-gel reaction and annealed at different temperatures in air for 1 hour. They observed an increased relative permittivity with increasing temperature, reaching a maximum of 7900 when annealed at 1300 °C, as can be observed in Figure 2.16.

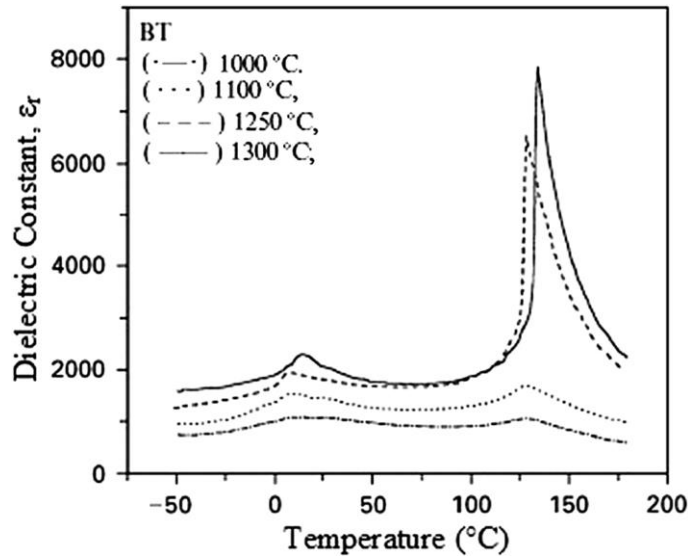


Figure 2.16 Relative permittivity versus temperatures curve of BaTiO₃ glass ceramics annealed at different temperature for 1 hour in air. Image taken from Yao et al [54].

2.2.1.2 Modified BaTiO₃

Isovalent substitutions at the Ba²⁺/Ti⁴⁺ sites have been widely reported to shift the Curie temperature of BaTiO₃ ceramics. For example, Mitsu et al [55] reported an increased Curie temperature up to 136 °C for Ca_xBa_{1-x}TiO₃ ceramic when x increases from 0 to 0.08, followed by a reduction at higher substitution levels. The substitution of Sr²⁺ in the Ba²⁺ site leads to a decrease of the Curie temperature to 90 K with increasing Sr²⁺ concentration [56] due to the smaller ionic size of Sr²⁺. Figure 2.17 shows the influence of typical substituents on the phase transformation temperatures.

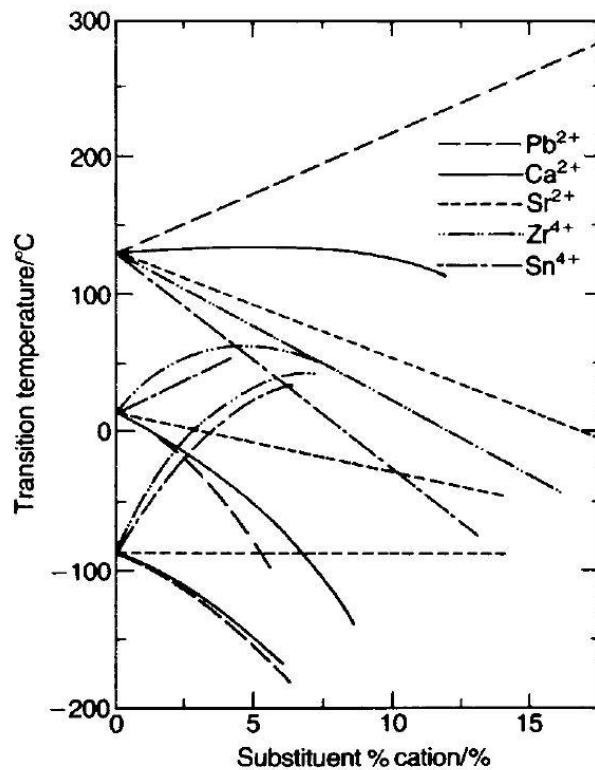


Figure 2.17 Transition temperature versus concentration of isovalent substituents (x) mol% in Ba site of BaTiO₃ [15].

Other studies showed that the Sr²⁺ additive led to a decrease in the Curie point, whilst the Ca²⁺ additive led to a decrease in the dielectric constant [57]. The effect of MnO₂ doping in BaSrTiO₃ was studied by Wang et al. [58] who found that the dielectric constant and dielectric loss increased with increasing MnO₂ in BaSrTiO₃.

Recently, attention has been directed towards Ba(Ti_{0.8}Zr_{0.2})O₃(Ba_{0.7}Ca_{0.3})TiO₃ (BCZT) because it has a large piezoelectric coefficient ($d_{33} > 500$ pC/N but low T_c) at high sintering temperature ≈ 1500 °C [59]. Furthermore, BCZT is an environmentally-friendly material because it is a lead-free piezoelectric ceramic [60]. Nevertheless, the pure perovskite phase for BCZT can only be achieved at very high calcination

(≈ 1350 °C) and sintering (≈ 1500 °C) temperatures, which is extremely high for some of the practical applications. The high preparation temperature of BCZT is reported as causing crystal distortion, hard domain wall rotation, high internal stress and inferior electrical properties [60-62].

Liu and Ren [59] reported the phase diagram of the $(1-x)\{\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\}$ - $(x)\{\text{Ba}_{0.7}\text{ZCa}_{0.3}\text{TiO}_3\}$ (BZT-BCT) pseudo-binary system. In this study [59], raw powders were calcined at 1350 °C and then sintered in air at 1450-1500 °C. The ϵ_r -T relationships were measured from -200 to 200 °C for all values of x , while the changes in crystal structure as a function of composition was determined by XRD. The phase diagram and ϵ_r -T curves of selected compositions reported by Liu et al [59] are shown in Figure 2.18.

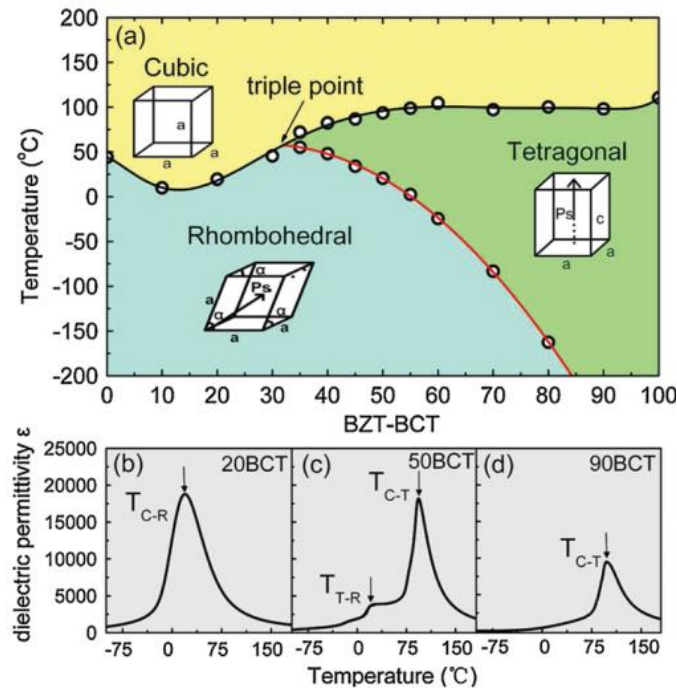


Figure 2.18 (a) Phase diagram of the BZT-BCT pseudobinary system and dielectric constant versus temperature curves for $x =$ (b) 0.2 (c) 0.5 and (d) 0.9. [59].

They observed [59] the presence of a Cubic-Rhombohedral-Tetragonal (C-R-T) triple point at about $x=0.32$ and at 57 °C (see Figure 2.18), this C-R-T triple point has been widely reported in Pb-based ferroelectric materials [63]. They reported the highest spontaneous polarization, $P_s \approx 20 \mu\text{C cm}^{-2}$, the highest remanent polarization, $P_r \approx 15 \mu\text{C cm}^{-2}$, the lowest coercive field, $E_c \approx 0.168 \text{ V mm}^{-1}$, and the highest relative permittivity, $\epsilon \approx 3060$, for $x=0.5$ (denoted 50BCT). The properties of this materials were said to be comparable to those reported for Pb-based systems. The outstanding properties of the $x=0.5$ composition reported by Liu et al [59] attracted further

research. In 2013, Keeble et al. [64], revisited the pseudo-binary system and reported an intermediate orthorhombic phase for compositions beyond $x=0.5$ by means of high resolution synchrotron diffraction, as shown in Figure 2.19.

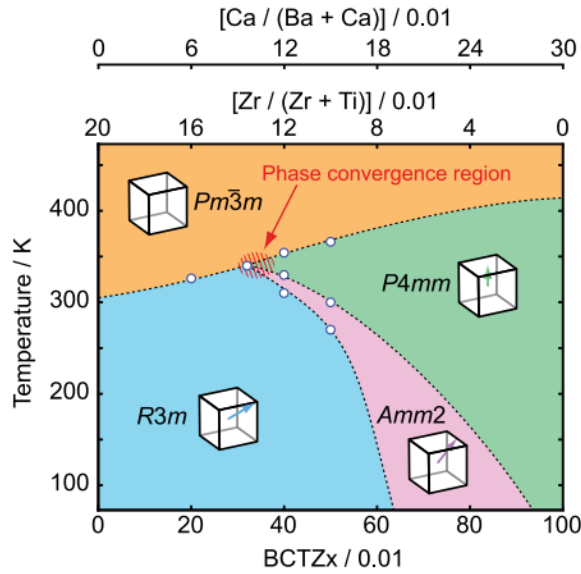


Figure 2.19 Phase diagram of the BZT-BCT pseudo-binary system reported by Keeble et al [64], in contrast to the phase diagram reported by Liu et al [59] a tetragonal to orthorhombic (T-R) transition was observed. The image is taken from Keeble et al [64].

Singh et al [65] studied a slightly different composition in the BZT-BCT pseudo-binary system. These were prepared according to the formula $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.05}\text{Ti}_{0.95})\text{O}_3$ where $x = 0.03, 0.05, 0.08, 0.10, 0.12$. They also reported an intermediate orthorhombic phase and the coexistence of tetragonal ($P4mm$) and orthorhombic ($Pmm2$) phases when $0.05 \leq x \leq 0.10$ at room temperature. In this region, the dielectric and piezoelectric properties were optimized due to the increased number of possible orientations of spontaneous polarization. Their [65] dielectric measurements showed that increasing Ca^{2+} content (x) leads to a decrease of the tetragonal to orthorhombic (T-O) and rhombohedral to orthorhombic (R-O) transitions, but retains the same cubic to the tetragonal (C-T) transition temperature.

A similar composition, $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ was studied by Asbani et al [66], who reported a large *electrocaloric responsivity* ($\Delta T/\Delta E$) of $0.34 \times 10^{-6} \text{ K m V}^{-1}$ at 386 K when $x=0.04$ by, which is one of the largest values reported for Pb-free materials.

Hao et al [67] prepared $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics by three different methods, namely spark plasma sintering, two-step sintering, and normal sintering (one step sintering). This lead to samples with different microstructures and grain sizes in the range of 0.4 to 32.2 μm . The effect of the grain size on the dielectric properties of the

BCZT ceramics was reported and is shown in Figure 2.20. Smaller grain sizes resulted in a shift of the T_C and T-R transitions towards higher temperatures and led to enhanced relaxor ferroelectric behaviour. Samples with larger grain size ($>10\text{ }\mu\text{m}$) exhibited enhanced piezoelectric properties ($k_p > 0.48$, $k_t > 0.46$ and $d_{33} > 470\text{ pC N}^{-1}$). It was observed that large grain sizes have a detrimental effect on the thermal stability of the material and enhance the resistance to thermal depoling due to the internal mechanical stresses and the movement of 180° and 90° domain walls.

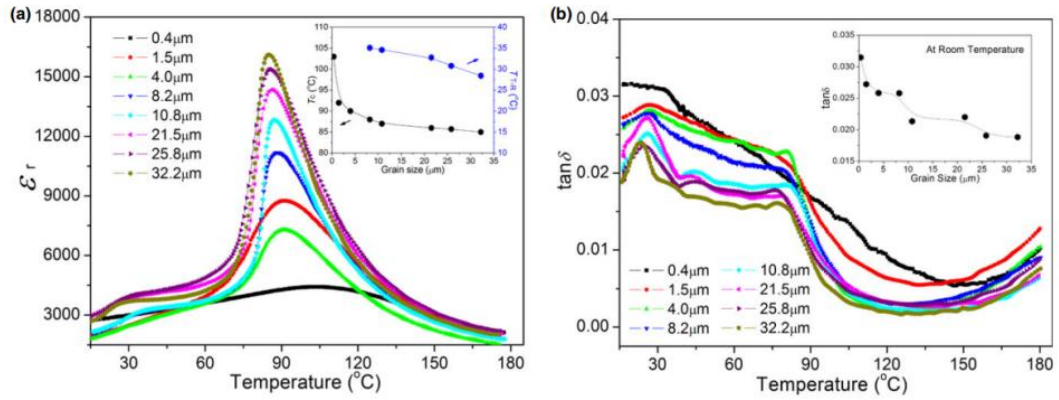


Figure 2.20 (a) Relative permittivity and (b) loss tangent ($\tan\delta$) versus temperature curves of BCZT ceramics prepared by different sintering methods and with different grain sizes. The insets in (a) and (b) show the dependence of T_C , T-R transition and $\tan\delta$ as a function of grain size [67].

2.2.2 Lead titanate

Lead titanate (PbTiO_3) is a ferroelectric ceramic that has a perovskite structure with a high T_C of 490 $^\circ\text{C}$. The cubic paraelectric phase of PbTiO_3 transforms to a tetragonal ferroelectric phase below the Curie temperature of 490 $^\circ\text{C}$. This phase transition is accompanied by a large transformation strain, which leads to the cracking of ceramic PbTiO_3 bodies upon cooling from the sintering temperature to room temperature [68], [69]. The strain can be reduced by introducing modifiers such as Sr^{2+} , Ca^{2+} , Sn^{4+} , and Ba^{2+} , which reduce the tetragonal c/a ratio from 1.06 to lower levels, depending on the dopant concentration [68]. The effect of Mn doping in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system was studied to investigate the domain stability in this system compared with that of the lead-free $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ system. The results showed that the lead-containing system had better domain stability and stronger defect dipole interactions than the lead-free system [70].

PbTiO_3 in glass-ceramic form has been studied to reduce the cracking observed in PbTiO_3 . The glass-ceramic samples showed high dielectric properties which can be harnessed for electronic applications. The effect of SiO_2 and B_2O_3 on PbTiO_3 -based

glasses was studied by Deshpande and Golezardi [71, 72]. By adding 2.5 mol% of SiO_2 , the glass-ceramic sample exhibited an optimum relative permittivity of 143, which decreased to 87 with 5 mol% SiO_2 content [71]. Furthermore, the effect of the addition of 0.05 to 0.1 Bi_2O_3 a nucleating agent into $\text{PbO-TiO}_2\text{-B}_2\text{O}_3\text{-SiO}_2$ glasses reported by Golezardi et al. [72]. Here the highest relative permittivity value was 390 for the glass-ceramic sample having 0.5 mol% of Bi_2O_3 , with grain size in the range of 20 to 25 nm.

2.2.3 PZT-pure and modified

Perovskite structured lead zirconate titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), is a common piezoelectric material that has been successfully used as ferroelectric and piezoelectric material since its initial industrial applications around 50 years ago. PZT is a binary solid solution of orthorhombic antiferroelectric PbZrO_3 with ferroelectric tetragonal PbTiO_3 . PbTiO_3 undergoes a simple phase transition from a paraelectric cubic to a ferroelectric tetragonal phase at a temperature of 490 °C, while PbZrO_3 behaves in a more complex manner, transforming from cubic to an antiferroelectric orthorhombic phase at a temperature of 240 °C [69].

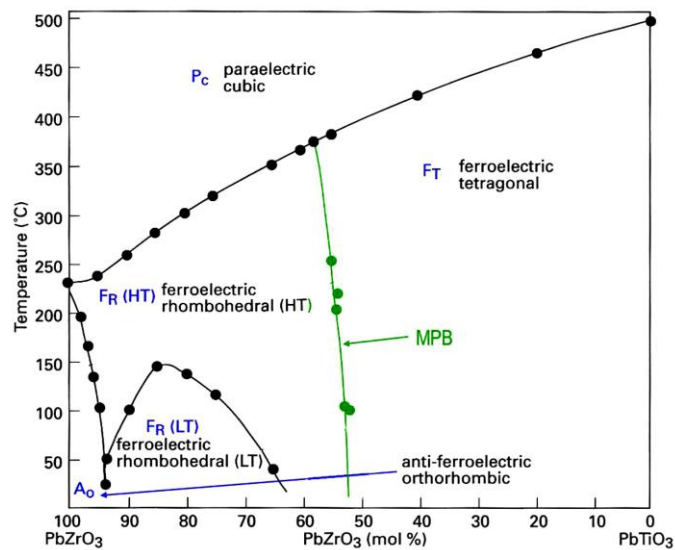


Figure 2.21: Phase diagram of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ system [73].

Figure 2.21 shows the phase diagram of the solid solution system $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$. At high temperatures, PZT has a cubic perovskite structure which is paraelectric. Upon cooling below the T_c line, the structure undergoes a phase transition to a ferroelectric tetragonal or rhombohedral phase. The solid solution has a wide range of ferroelectric phase transition temperatures and two different ferroelectric structures, depending upon the Zr:Ti composition ratio. The morphotropic phase boundary (MPB) separating the two ferroelectric tetragonal and orthorhombic phases have a room temperature

composition of Zr:Ti at $\approx 52/48$. PZT ceramics with the MPB composition display excellent piezoelectric properties.

There are many studies about adding modifiers, such as Ba, La, Na, and Bi into PZT. The goal of using these additives is generally to improve the functional properties. Isovalent dopants (Sr^{2+} , Ba^{2+}) generally act to reduce T_C and E_c , while donors (La^{3+} , Nb^{5+}) and acceptors (K^+ , Fe^{3+}) are employed to produce *soft* and *hard* PZT ceramics, respectively, creating materials that exhibit a wide range of ferroelectric and piezoelectric properties [74]. Pdungsap et al. [75] studied the effects of La doping in PZT. They found that the microstructure showed dense grains with increased La contents; at the same time, a decrease in average grain size was noted, which led to an increase in the dielectric constant. The solid-state reactions in PZT-BaTiO₃ have been studied [76]. The results show some development in the microstructure of ceramics, as well as the tetragonality, is increased with increasing BaTiO₃ content and the dielectric curve broadens.

2.2.4 KNN - pure and modified

Potassium sodium niobium, $(\text{K}_{1-x}\text{Na}_x)\text{NbO}_3$, (KNN) is an environmentally friendly lead-free piezoelectric material that has been developed as a possible replacement for PZT-based materials. KNN has a perovskite structure with a high T_C (420 °C) and piezoelectric coefficients. Therefore, KNN is amongst the most favoured lead-free ferroelectric ceramics and is considered suitable for some applications.

2.2.4.1 Structure and phase transitions

KNN is a pseudo-binary solid solution of KNbO_3 and NaNbO_3 compounds, which are shown in Figure 2.22. Many phases occur in this system; there are three ferroelectric phases: tetragonal, orthorhombic, and monoclinic, as well as an orthorhombic antiferroelectric phase [69].

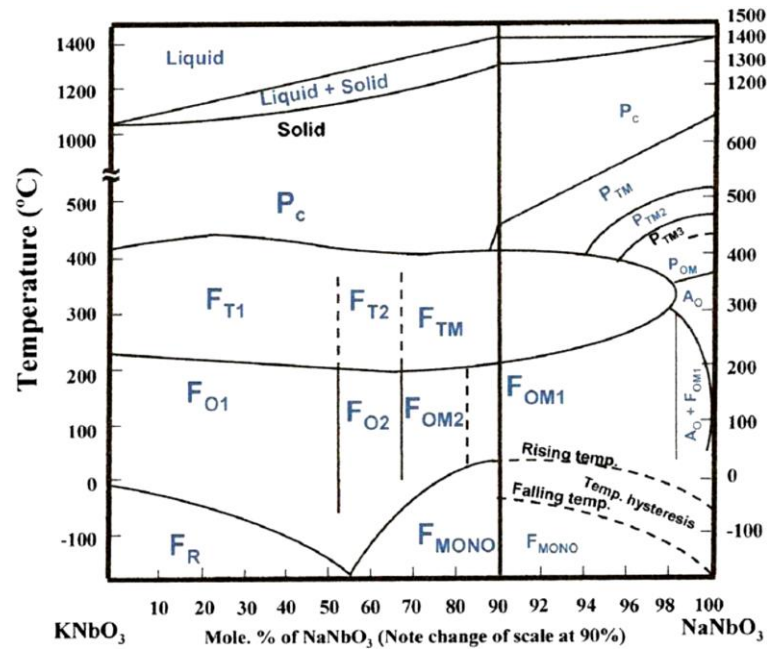


Figure 2.22 Phase diagram of the pseudo-binary KNbO_3 - NaNbO_3 system [69].

There are two transformations of KNN which are dependent upon the temperature. On heating from room temperature to 220 °C, KNN transforms from an orthorhombic to tetragonal phase. The second transition is from the tetragonal to cubic phase at 420 °C [69, 77]. According to the phase diagram of KNN, the MPB for this system occur at a Na:K ratio of approximately 1:1. At this ratio, the KNN shows good piezoelectric, ferroelectric, and electromechanical properties. The results of Priya and Nahm [69] and Kumar et al. [78] demonstrate that KNN is a suitable ceramic material for dielectric and piezoelectric applications.

The effects of the grain size on the dielectric properties of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ceramics were studied by Buixaderas et al [79]. They reported smaller relative permittivity values in the cubic phase at small grain sizes (0.5 μm) compared to ceramics with larger grain size (10 μm). They also observed two additional dielectric relaxation regions in the MHz to GHz range; the one in the GHz range was attributed to the laminar ferroelastic domain-wall dynamics while that in the MHz range was attributed to 180° ferroelectric domain-wall dynamics.

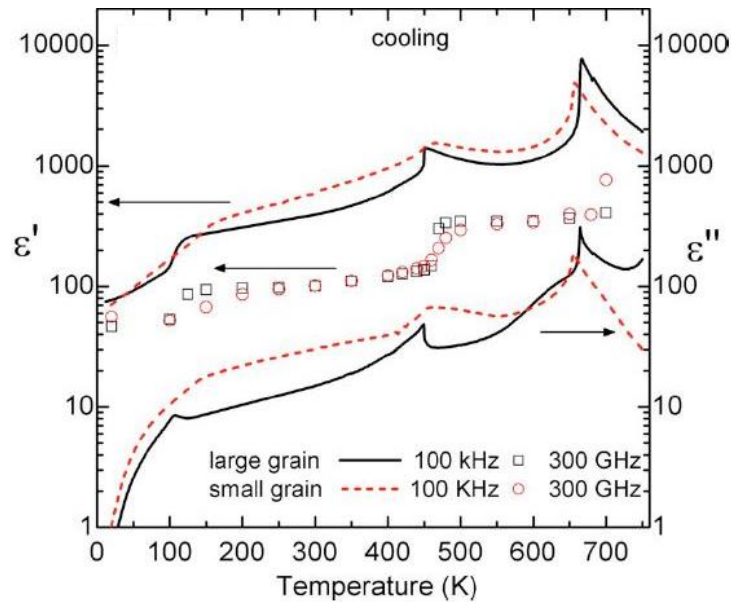


Figure 2.23 Dielectric measurements of KNN ceramics with different grain size (10 and 0.5 μm) on cooling (lines= relative permittivity and loss at 100 kHz; points=relative permittivity at 300 GHz) [79].

Rubio-Marcos et al. [80], studied stoichiometric (S) $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04})\text{O}_3$ and non-stoichiometric (NS) $\text{K}_{0.38}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04})\text{O}_{2.97}$ compositions synthesised via the mixed oxide and carbonate route. Calcined powders were cold isostatically pressed (CIP) at 200 MPa and then sintered between 1075 and 1175 $^{\circ}\text{C}$ for 2 and 8 h. The densification of non-stoichiometric (NS) compositions was assisted by a liquid phase sintering process. They reported an increase in the grain size of the stoichiometric samples from 0.64 to 0.89 μm when the sintering time increased from 2 to 8 h at a sintering temperature of 1125 $^{\circ}\text{C}$. The same trend was observed in the non-stoichiometric samples, with the grain size increasing from 1.44 to 1.6 μm when the sintering time increased from 2 to 8 h. Regarding the dielectric properties (shown in Figure 2.24), they reported a smaller dielectric constant for stoichiometric samples than for non-stoichiometric compositions. The stoichiometric samples also showed broader peaks in their ϵ_r -T curves. The stoichiometric sample sintered for 2 hours (2h S) had the smallest grain size reported (0.64 μm) and showed the lowest dielectric constant value and the broadest peak in the ϵ_r -T curve at about 200 $^{\circ}\text{C}$.

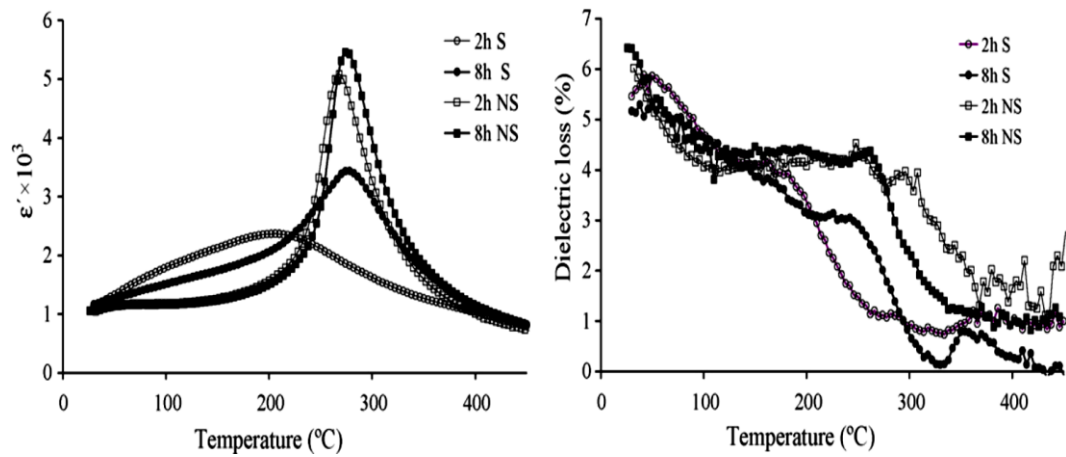


Figure 2.24 Temperature dependence of the dielectric constant and loss of unpoled stoichiometric (S) $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ and non-stoichiometric (NS) $(K_{0.38}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_{2.97}$ compositions sintered at 1125 °C for 2 and 8 h [80].

The relaxor ferroelectric-type behaviour of all the samples vanished in the NS samples as a consequence of the improved chemical homogeneity achieved by the grain growth induced by the liquid phase sintering process. The non-stoichiometric composition sintered for 8 h (8 h NS) exhibited the highest ferroelectric and piezoelectric properties of $P_r \approx 17 \mu C cm^{-2}$, $E_C \approx 20 kV cm^{-1}$ and $d_{33} = 195 pC/N$.

2.2.4.2 Modified KNN

The orthorhombic perovskite-type $(K_{0.5}Na_{0.5})NbO_3$ ceramics possess a relatively high Curie temperature ($T_C = 415 ^\circ C$) allowing them to be used over a wide temperature range. The addition of hexagonal pseudo-ilmenite-type $LiTaO_3$ ($T_C = 615 ^\circ C$) has been reported to enhance KNN piezoelectric response [81], not only because of the formation of an MPB but because of the hybridization of covalence onto ionic bonding. Saito et al [81] reported a d_{33} of 416 pC/N and a dielectric constant of 1570 in their chemically modified and textured KNN ceramics using reactive templated grain growth in the $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.1}Sb_{0.06})O_3$ composition.

Matsubara et al [82] studied the effect of Ta substitution in the Nb position in the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ solid solution with a small addition of 0.38 mol% $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ as a sintering aid. They reported soft piezoelectric characteristic in all the samples prepared and a shift of the T_C towards lower temperatures as the Ta content increases, as shown in Figure 2.25. They reported an increased electrostrictive effect with Ta additions, which combined with the piezoelectric effects led to a maximum strain of 0.11% (at $4 kV mm^{-1}$) and to a maximum d_{33} of 270 pm V^{-1} when $x=0.3$.

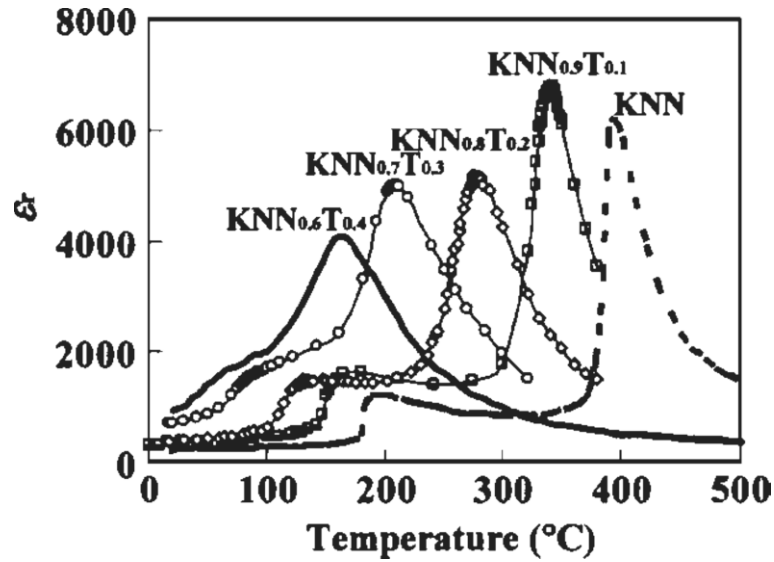


Figure 2.25 Dielectric constant versus temperature curve of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramics with 0.38 mol% $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ [82].

Hagh et al [83] explored the piezoelectric properties of the $K_{0.5}Na_{0.5}NbO_3$ – $LiTaO_3$ – $LiSbO_3$ (KNN–LT–LS) system using different processing conditions. The optimised piezoelectric response, with $d_{33} \geq 300 \text{ pC N}^{-1}$, was achieved when ceramics were sintered at 1150 °C for 1 h with a high flow rate of oxygen ($180 \text{ cm}^3 \text{ min}^{-1}$). They attributed this improved response to a reduced number of oxygen vacancies, which facilitated domain switching, leading to higher remanent polarization with a lower coercive field. The same group investigated the effect of the addition of Ba^{2+} in the KNN–LT–LS system [84]; they reported a decrease in the grain size from 3 to 0.5 μm with increasing Ba^{2+} additions. The optimum Ba^{2+} concentration of 1 mol% yielded a d_{33} of 210 pC/N.

Following Saito et al's [81] report, Wang et al [85] studied the piezoelectric properties of alkali niobate-based ceramics synthesised via the conventional solid-state reaction. The composition $(1-x)(K_{1-y}Na_y)(Nb_{1-z}Sb_z)O_3-xBi_{0.5}(Na_{1-w}K_w)_{0.5}ZrO_3$, with $0 \leq x \leq 0.05$, $0.40 \leq y \leq 0.68$, $0 \leq z \leq 0.08$, and $0 \leq w \leq 1$ was studied [85] with x , y , z , and w values being optimised to promote R–T phase boundary; a d_{33} value of 490 pC N^{-1} was obtained for a composition lying on the R–T phase boundary. These results proved that modified-KNN ceramics can offer a lead-free alternative to PZT for piezoelectric applications.

2.3 Overview of glass-ceramics

2.3.1 History and definition of glass

Glass-ceramics are classified as ceramic materials. They are polycrystalline materials that are formed by controlling the crystallisation of an amorphous glass. These materials are an important type of electroceramic and were successfully developed during the 1940 and 1950s. During this period, S. D. Stookey (Corning, USA) successfully used glass-ceramics as electrical insulators in electronics technology [7, 15]. The fundamental patent of Stookey was based on the concept that the TiO_2 works as a nucleating agent in a glass system. Additionally, ZrO_2 was used by Tasiro and Wada [7], in 1963 as a nucleating agent. Another discovery was made in the 1950s by Hummel, who discovered the crystal arrangement of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ system [86].

Figure 2.26 shows three types of an atomic structure with different atomic arrangements. A crystalline solid is one which has a long-range order in its atomic structure; an amorphous solid is one in which there is no long-range order in its atomic structure. Crystalline solids have two subdivisions, single crystal and polycrystalline. A single crystal has a periodic atomic arrangement. In this case, there are no grain boundaries. A polycrystalline solid contains many grain boundaries in the structure due to the differences in the orientations of the grains (that have a short-range order) [18].

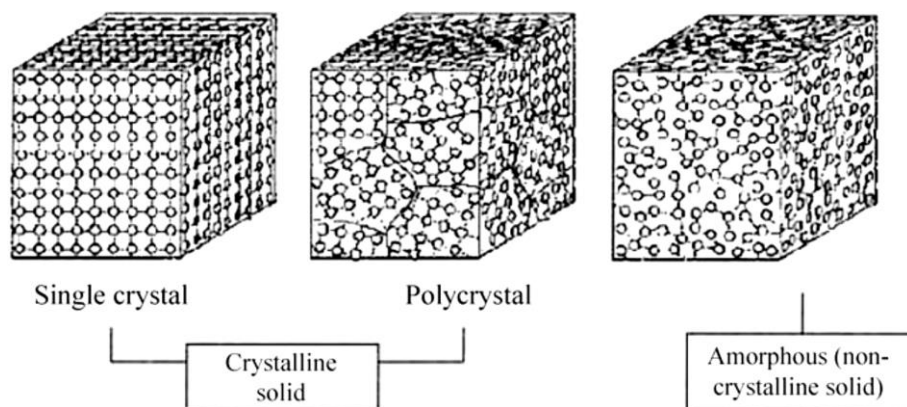


Figure 2.26 The structure of ceramics [18].

It is difficult to specifically define a glass since the behaviour of a glass alters with changes in temperature. There are two points at which a glass can be defined; the first is at high temperature, when the glass is a liquid, while the second is at a lower temperature when the glass is considered as a supercooled liquid. Although there are important structural differences between glasses and polycrystalline ceramics, their mechanical and functional properties at room temperature can be similar.

The traditional definition of glass is that it is a supercooled liquid. According to the American Society for Testing and Materials (ASTM), the definition of glass is that it is an inorganic product of fusion which has cooled to a solid state without being crystallized. However, there are alternate definitions for glass, one being that glass is a type of amorphous solid material that lacks long-range order (not a random arrangement) in its atomic structure. Another definition, also put forward by ASTM, is that a glass is a liquid that has lost its ability to flow [2, 7].

2.3.2 Heat treatment of glasses and glass-ceramics

The heat treatment of glass leads to the occurrence of many transitions. Differential scanning calorimetry (DSC) is a form of thermal analysis that depends upon the change in a material's physical properties [86]. In DSC, there is a difference in temperature (ΔT) that is seen between the sample and the reference. Here ΔT represents differences in heat flow as ΔQ . The two quantities, ΔT and ΔQ , are functions of thermal resistance (R), as shown in equation 2-12.

$$\Delta Q = \frac{\Delta T}{R} \quad 2-12$$

In the first step of the glass transition, some of the physical properties change for amorphous materials. This change occurs in the heat capacity, which can be measured by DSC as an endothermic change in the sample. The transitions in glass due to the effects of temperature occur in the range of temperature which is known as the glass transition temperature (T_g). Therefore, below T_g , materials display a rigid glassy structure. When the temperature is increased above T_g , these materials display a flexible structure.

Another transition which occurs due to changing temperature is crystallisation. In this case, the amorphous materials are transformed into a crystalline structure. With an increase in temperature, the next conversion is melting. At this point, the crystalline structure converts to a viscous amorphous structure. The melting point is dependent upon the chemical impurity of the materials. After the melting stage, a reaction inside the material causes an increase in the density of the material [7, 86].

2.3.3 Crystallisation of glass-ceramics

Generally, since 1960, there has been much research undertaken regarding glass systems in the field of glass-ceramics. Glass-ceramics are very important in many fields of application. They have demonstrated many desirable thermal, optical, biological,

chemical, and electrical properties. Some of these properties provide advantages to glass-ceramics over more traditional materials.

A glass-ceramic is a polycrystalline material formed by controlling the crystallization of glass. Therefore, in order to make glass-ceramics from glass, the main manufacturing process needs to be a thermal one. Figure 2.27 shows the steps of glass transforming into glass-ceramic. These steps begin at a low temperature with the formation of nuclei, then at higher temperatures crystallisation occurs by growth of the nuclei; this continues to produce the polycrystalline a glass-ceramic microstructure [7, 18].

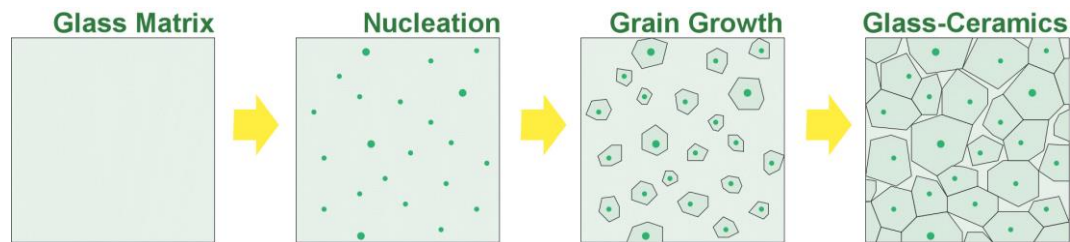


Figure 2.27 Schematic representation of glass-ceramic processing [7].

Microstructural control is said to be easier when the temperature required for crystallisation lies between but is significantly different from both the glass transition temperature and that of matrix devitrification. In such a case, the desired crystalline phase can be induced to form without devitrification of the glass matrix. The crystallite size generally increases with increasing temperature, as shown by the micrographs in Figure 2.28 [87].

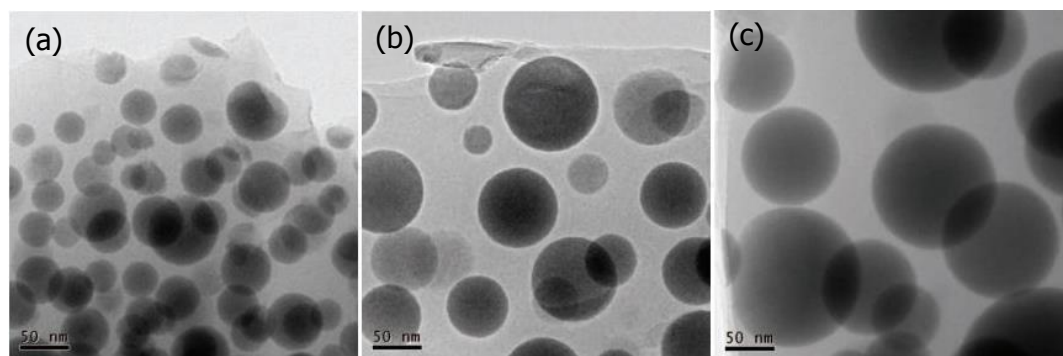


Figure 2.28 TEM micrographs showing nanoscale crystallites precipitated from a glass matrix of $\text{SiO}_2/\text{Lu}_2\text{Si}_2\text{O}_7$ heat-treated at 1100 °C (a), 1200°C (b) and 1300 °C (c) [87].

Figure 2.29 depicts the stages of glass transformation during cooling the glass. The glass transition temperature (T_g) occurs when the supercooled melt is changing into a glassy state, which is dependent upon the rate of cooling. In the case of slow cooling, the glass formed has a tendency to be more stable than that of fast cooling. This is due to the atomic arrangement of slowly cooled glass being closer to that characteristic

of the equilibrium liquid than the more rapidly cooled glass. At T_g , the slope of the thermal expansion curve reduces and becomes close to that of the crystalline solid. This region marks the transformation of glass to a supercooled liquid. At a temperature below T_g , the glass is considered to become a solid [2, 88].

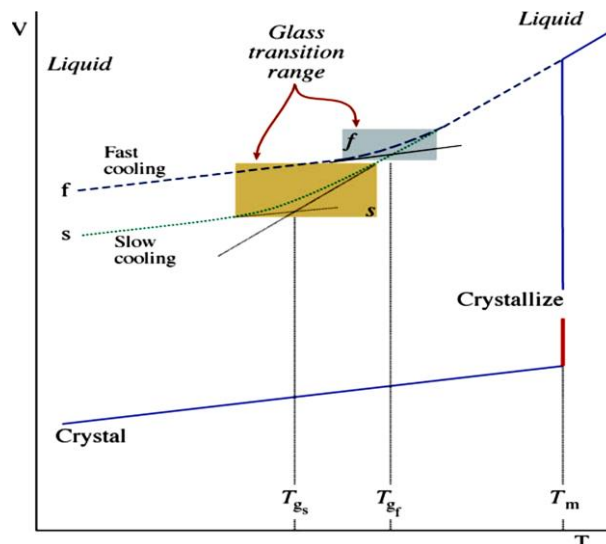


Figure 2.29. Thermal expansion curves illustrating changes in glass transition temperature as a function of the cooling rate [2].

In Figure 2.30, the typical thermal preparation of glass-ceramic can be seen. In this case, the raw materials, Li_2CO_3 and SiO_2 , are used to create lithium disilicate. There are two main stages in obtaining glass-ceramics: glass formation and glass crystallisation. In each stage, there are many steps which depend upon both temperature and time. The first stage begins by melting the components and then quickly cooling them. The nucleation and crystal growth occurs in the second stage. During this stage, controlled crystallisation of the glass produces nanoscale crystals [7].

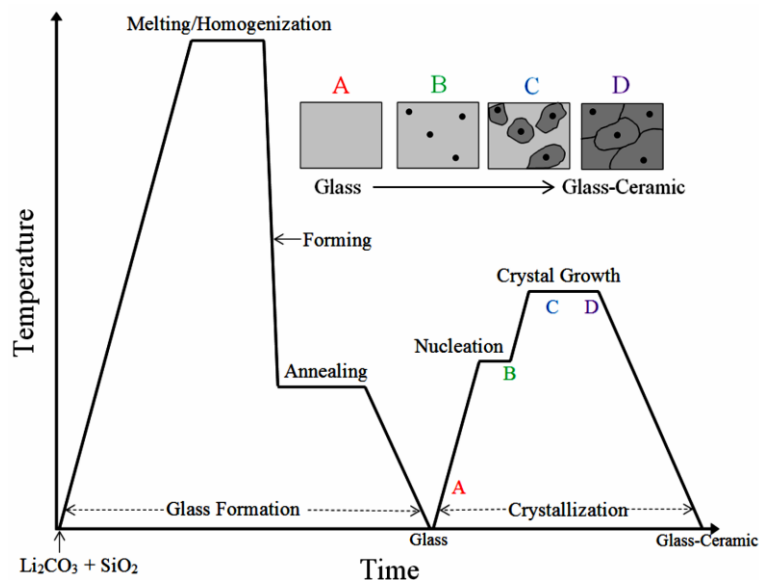


Figure 2.30 Schematic of glass processing in the formation of a glass ceramic [88].

2.3.4 Chemical compositions of glass-ceramic systems

2.3.4.1 Alumina-silica systems

Silicates are salts of silicic acid, H_4SiO_4 . Most of the silicates contain SiO_2 , while in the case of SiO_2 or quartz glass, only SiO_2 is present. For all other types of glass, additional oxides, such as: Li_2O , BaO , B_2O_3 , Na_2O , K_2O , MgO , CaO , or Al_2O_3 are employed as network formers or modifiers. Alkaline and alkaline earth oxides are important in glass due to their effects on the network. Therefore these additives work as effective network modifiers [89].

The alumina-silica system, $\text{Al}_2\text{O}_3\text{-SiO}_2$, is amongst the most important binary oxides and ceramic systems. Figure 2.31 shows the phase diagram of the binary $\text{Al}_2\text{O}_3\text{-SiO}_2$ system. The low solid solubility for SiO_2 in Al_2O_3 , and vice versa, can be seen in this diagram. At a high temperature below 1890 °C, part of the Al_2O_3 component is transformed to a molten state, while the other part remains solid. This also occurs with SiO_2 at a temperature below 1600 °C. The effect of the SiO_2 ratio in reducing the melting point of $\text{Al}_2\text{O}_3\text{-SiO}_2$, can be seen [90].

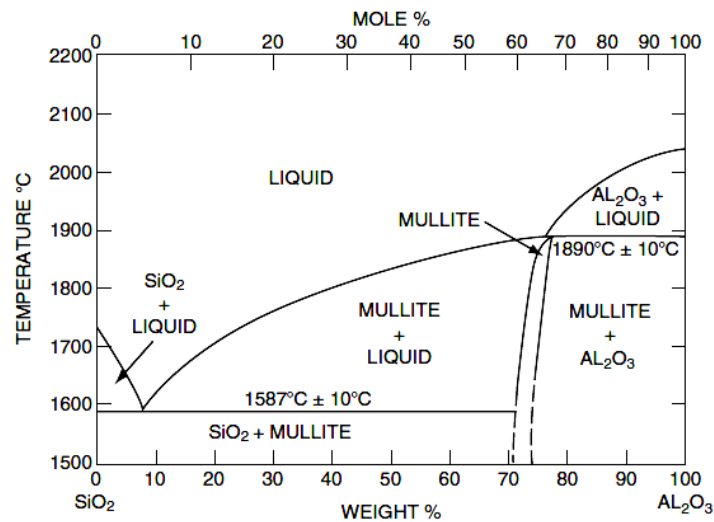


Figure 2.31 Phase diagram of the binary alumina-silica system [90].

Figure 2.32 shows the silica structure as a network. In Figure 2.32-A the basic units for silica are represented; these are Si⁴⁺ with O²⁻. The network of pure silica, also known as quartz, is presented in Figure 2.32-B, while Figure 2.32-C shows the structure of this 2D network with the addition of some alkaline additives as modifiers [89].

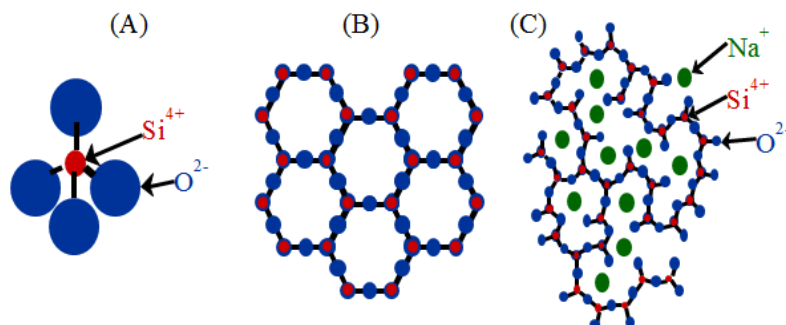


Figure 2.32 Silica network structure: (A) silica tetrahedron, (B) pure silica quartz, (C) and a soda lime silicate [89].

2.3.4.2 Alkaline and alkaline earth silicates

Glass-ceramics can be modified by a formulation process. Alkaline and alkaline earth oxides are modifiers of glass networks and act to decrease the connectivity of the glass network, effecting changes in the properties of the glass. There are many oxides that are used to modify glass-ceramics, such as: Ba, Li, B, Ca, Na, etc [89]. These glass-ceramic systems contain binary and ternary systems. Both types of systems contain oxides, such as: BaO, B₂O₃, MgO, CaO, PbO, ZnO, Al₂O₃, SiO₂, and SrO [7].

Some of the oxides contained within the glass are popular as sintering aids for ceramics. This is because of the high stability of their structures and the low glass

transition temperatures, in addition to their thermal and electrical properties. The systems of PbO-containing glasses (e.g. $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{PbO-B}_2\text{O}_3\text{-ZnO}$) are important due to the aforementioned reason [91, 92].

Other glass systems include $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{BaO-CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$, $\text{CdO-Bi}_2\text{O}_3\text{-PbO-B}_2\text{O}_3$, and $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ which have all been used to reduce the sintering temperature [5, 93]. The structure of PbO is not easy to crystallise, even with a high percentage of it within the glass, because PbO_4 is formed within the glass system. Recently, many glass systems have been developed as alternative lead-free materials. In this research, BaO, ZnO, and Bi_2O_3 are used instead of PbO [93].

Most glasses containing a high proportion of PbO are undesirable due to the toxicity of lead oxide causing environmental problems during or after production. Therefore, most researchers focus on decreasing the PbO content or replacing it with other oxides. This issue was addressed by Bobkova and Khot'ko [94], who were studied the $\text{ZnO-SrO-B}_2\text{O}_3$ system. They found that the optimum glass was produced when it contained a high ZnO and low B_2O_3 content. In addition, two ternary systems, $\text{B}_2\text{O}_3\text{-CaO-SiO}_2$ and $\text{B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$, have been studied by Vartanyan et al [95]. They found that these two systems successfully produced lead-free materials for low-temperature simultaneously fired ceramics (LSCs).

Glass manufacturing processes can be generally complex due to the materials which undergo different changes during the melting and cooling. The ternary systems of $\text{B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$, $\text{B}_2\text{O}_3\text{-CaO-SiO}_2$, and $\text{B}_2\text{O}_3\text{-ZnO-SiO}_2\text{-BaO}$ were developed at low melting points below 1000°C then used as sintering aids with ceramics at low sintering temperatures [94, 95]. Consequently, these systems ($\text{BaO-B}_2\text{O}_3\text{-SiO}_2$) and ($\text{BaO-B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$) possess their own particular thermal physical properties, where achieved a coefficient of thermal expansion ($11\text{-}17 \text{ ppm } ^\circ\text{C}^{-1}$) and low permittivity (≈ 7) [96].

$\text{B}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-SiO}_2\text{-ZnO}$ (BBSZ) is commonly used as an appropriate additive to reduce the sintering temperature of many dielectric materials and make them suitable for LTCC applications [97, 98]. Therefore in order to improve the electromagnetic properties of Ni-Cu-Zn ferrite (NCZF) and BaTiO_3 , the BBSZ glass was chosen as a melting agent [99].

Glass-ceramics based on the CaO-MgO-SiO_2 system has been studied with the additives B_2O_3 , P_2O_5 , Na_2O , and CaF_2 . The results showed that these systems required high melting points and the final crystallisation of the glass-ceramic occurred with temperatures of 900°C , producing high levels of density [100].

2.3.4.3 Barium borate system

The binary system of BaO-B₂O₃ is used in a wide range of glass ceramic production, oxide cathodes and the coloured materials in paints. In addition, these systems are used as sintering aids for low temperature co-fired ceramic applications due to the low softening temperature of the B₂O₃ [101]. Figure 2.33 shows the phase diagram for the binary system of BaO-B₂O₃ [102].

The procedures of melting and cooling the BaO-B₂O₃ systems lead to glass formation. In the phase diagram, it can be seen that the lowest melting point with high stability for these systems occurs with approximately 60 to 80 % B₂O₃. In practise, the optimum ratio also depends upon the rate of cooling of the glass [102].

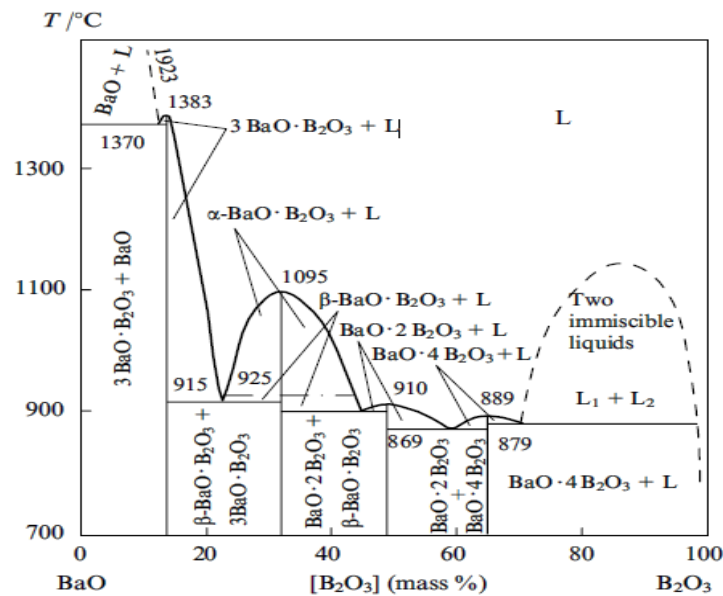


Figure 2.33 Phase diagram of the BaO-B₂O₃ system [102].

The binary system of BaO-B₂O₃ was modified by SiO₂ or Al₂O₃ as a network modifier. Therefore, it was expected that the mineral phase with odd physical characteristic would be obtained. Therefore, glass ceramics are prepared with low sintering temperatures [96]. It should be noted that the melting point of B₂O₃ is around 450 °C, which is much lower than SiO₂, which has a melting point of around 1710 °C. However, the crystalline glass of B₂O₃ is much more difficult to produce than that of SiO₂ [102].

SiO₂ added to borate glasses generally leads to an improvement in the density of the glass and an increase in its T_g and chemical durability [103]. The effect of the Al₂O₃ on the characteristics of BaO-B₂O₃-SiO₂ was reported by Lim et al [104]. It was found that the crystallisation temperature, sintering temperature, and glass transition temperature

increased with increased amounts of Al_2O_3 in the glass systems. The ternary glass system $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ was studied by Lim et al [93, 101]. The SiO_2 ratio was fixed at 10% and the effects of the amount of $\text{BaO/B}_2\text{O}_3$ on the thermal and physical properties of the glass system were studied. Increasing B_2O_3 content gave rise to a clear increase in the dielectric properties.

The electrical conductivity of solid silicates shows a complex dependence on glass formation processes, devitrification, and temperature. Here, a slight change in the composition of the glass can lead to marked differences in the electrical conductivity values. In spite of the fact that most studies are about the binary systems, however, there is a scarcity of experimental data on the electrical conductivity of the glasses. Accordingly, the study of the influence of the metal oxide on the electrical conductivity is important for the multicomponent silicate glasses for electrical purposes [105, 106].

It was reported that the electrical conductivity is decreased by the presence of the K^+ ions in the alumina-silica glasses while the glass transition temperature increased [105]. Wang et al. noted that the addition of Na_2CO_3 into $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (BST) ceramics caused a decrease in the room temperature dielectric constant of BST, while the highest Na^+ and K^+ content produced an increase in the energy storage density [107].

2.3.5 Applications of glass-ceramics

Glass-ceramics are amongst the most important hosts for transition metal ions [108]. There are several benefits of adding glass to ceramics, such as improving their dielectric properties and reducing both the sintering temperature and the porosity [6]. In glass-ceramics, the ferroelectric and dielectric properties are highly dependent on the characteristics of the glass matrix as well as the crystal volume fraction and crystal size [109].

Glass-ceramics are crucial in the development of more efficiently produced and controlled energy. They are thought to be efficient cathodes or solid electrolyte materials when used in lithium batteries. Dielectric glass ceramics are also of interest due to their uses in high-power microwave systems, distributed power systems, power electronics, and pulsed power.

To decrease the thickness of the dielectric layers in a capacitor and reduce the weight of portable pulsed power systems, it may be necessary to have high dielectric breakdown strength in the materials. In any case, improved control of the porosity,

along with enhanced energy storage capabilities, are important aspects of improving the performance of glass-ceramics [110].

The significance of glass-ceramics in many applications lies in the possibility of utilizing key properties such as transparency, strength, resistance to abrasion, and the controlled coefficient of thermal expansion. All these properties can be manipulated by the controlling the composition, extent of crystallisation, crystal morphology, crystal size, and aspect ratio of the materials [100].

Glass-ceramics are used in a range of applications across different fields such as telecommunication, radar, and navigation. With respect to the use of high-density electron device packages, the materials which are used in LTCC applications need to have good dielectric properties and a large coefficient of thermal expansion (CTE). These characteristics are important in order to achieve thermal matching between the components of the package [96, 111].

2.4 Ferroelectric glass-ceramic systems

The following sections summarise the results of previous research on the use of glass additives as sintering aids for ferroelectric ceramics, producing glass-ceramic composites, and on the heat treatment of amorphous glasses to produce glass-ceramics containing nanocrystalline ferroelectric phases. The emphasis of the present research is on lead-free ferroelectric materials and therefore previous work on lead titanate and PZT-based glass-ceramics is not included here.

2.4.1 Barium titanate (pure and modified)

BaTiO₃-based ceramics have been widely used in a number of electronics and electrical industries, due to their excellent dielectric properties [112]. Glass additives have been used during the sintering process of ceramic materials to form a liquid phase to improve the sintering behaviour of well-known ferroelectric ceramics such as BaTiO₃, PZT and KNN. During this process, the reactive liquid formed by the glass additives wets the solid particles and facilitates their rearrangement. This rearrangement of particles gives more effective packing and higher densities, desirable for ferroelectric applications. Furthermore, the capillary pressure developed at each inter-particle space provides an additional driving force for particle rearrangement and re-shaping during sintering, inducing densification.

2.4.1.1 Sintering aids of BaTiO₃

The use of solid state reaction for the preparation of BaTiO₃ ceramics has advantages where the products have good crystallinity and low cost, as well as a high level of accuracy of stoichiometric control [50]. However, many ferroelectric materials have high sintering temperatures (>1200 °C), making them unsuitable for certain applications, such as LTCC. In this case, it is necessary to include some additives to reduce the sintering temperature. There have been many studies aimed at lowering the sintering temperature of BaTiO₃. The typical additives used include ZnO, CuO, LiF, and CdO. Amongst these additives, LiF proved to be a very effective sintering aid. The effect of LiF in BaTiO₃ was investigated and the results indicate that the sintering point is reduced to approximately 900 °C [113, 114].

The use of glass additives in BaTiO₃ was also shown to improve densification behaviour and reduce the required sintering temperature. Jeon et al. [115] studied the effects of BaO-B₂O₃-SiO₂ (BBS) glass in BaTiO₃ ceramics. It was found that the sintering temperature required to reach a high density (≈ 93 %) could be reduced to ≈1000 °C.

The influence of glasses on the sintering behavior and properties of ceramics is dependent upon the glass additive content as well as the chemical reaction between the glass and ceramic phases. Three different glass additives for BaTiO₃ were studied by Hsianga; these were BaO-B₂O₃-SiO₂ (BBS), PbO-B₂O₃-SiO₂ (PBS), and ZnO-B₂O₃-SiO₂ (ZBS). It was reported that the glasses containing PbO and BaO led to degradation of the dielectric properties and densification of the ceramic. In addition, adding both BBS and PBS caused the formation of a large number of secondary phases [5].

Lin et al [116] added a manganese oxide-silica glass to pure BaTiO₃ and reported the effect of the liquid phase on the dielectric and ferroelectric properties of the material. The addition of the Mn-Si-O glass enabled densification of the nanocrystalline powder at temperatures in the range 1175-1300 °C. At high glass concentrations, they observed the formation of Ba₂TiSi₂O₈ and a Mn solid solution in BaTiO₃ grains growing at the grain boundaries and inhibiting grain growth. Figure 2.34 shows the influence of glass content on the structural and dielectric parameters [116]. It can be observed, that the ceramics with grain sizes in the range of 0.7-1 μm have the higher relative permittivity. Meanwhile, for the glass doped samples, the higher tetragonality of BaTiO₃ induced through the liquid phase sintering led to larger dielectric permittivity. However, the dielectric loss was also affected by the Mn solid solution in BaTiO₃ and the Ba₂TiSi₂O₈ phases.

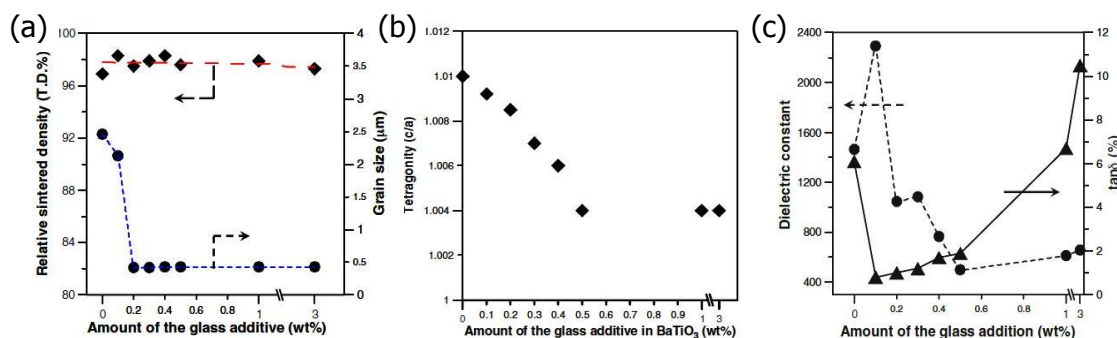


Figure 2.34 Effect of glass addition on the (a) grain size (b) tetragonality and (c) dielectric constant and loss of die-pressed BaTiO₃ [116].

More recently, Chen et al [117] studied the addition of 50-90% of B₂O₃-Bi₂O₃-SiO₂-ZnO (BBSZ) glass on the dielectric and ferroelectric properties of BaTiO₃. By this means, the sintering temperature was reduced to 400-450 °C. The second phase of Bi₂₄Si₂O₄₀ was observed when samples were sintered at 450 °C and the BBSZ concentration was higher than 60 wt%. Once the solubility limit of BBSZ on BaTiO₃ was exceeded (BBSZ > 60 wt%) and the formation of the Bi₂₄Si₂O₄₀ and glass phases took place, some pores of about 1-2 μm appeared due to the capillary pressure, rearranging the particles and affecting the packing; this reduction in density led to a lower relative permittivity for the 60 wt% modified samples. When the amount of liquid increased (up to 70 wt%), the porosity decreased and relative permittivity values of 132 and 207 were achieved at 100 kHz and 100 MHz, respectively. The dielectric loss remained at the same level as that of the pure glass at 100 kHz (0.006). At higher BBSZ concentration (80 and 90 wt%), the overall dielectric properties of the samples decreased due to the lower relative permittivity of the glass phase.

Choi et al. [118] reported that the addition of 1 to 7 wt% of BBS into BaTiO₃ (prepared using flame spray pyrolysis) reduced the sintering temperature at 1000 °C, yielding an improvement in relative permittivity in comparison with pure BaTiO₃ sintered at 1300 °C. It was also found that the glass additives improved the density of the material with an increase in the grain size by several microns.

Wang et al. [26] found that the sintering temperature of BaTiO₃ ceramics could be reduced to about 1100°C using a glass with the composition 27.68BaCO₃-6.92SrCO₃-29TiO₂-22SiO₂-12Al₂O₃-2.4BaF₂ (mol %). The effect of this additive was a reduction in the average grain size. It was also found that the energy storage density of the ceramics increased gradually with increasing glass concentration; the highest energy density value of 0.32 J cm⁻³ was obtained for the sample with 7 mol% of the glass.

The influence of glass additives on modified barium titanate ceramics was reported by Puli et al [35], who studied the dielectric and ferroelectric properties of glass-modified BCZT, specifically the composition $0.85(\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)-0.15(\text{Ba}_{0.7}\text{ZCa}_{0.3}\text{TiO}_3)$. The addition of 15 wt% ($0.1\text{BaO}+0.4\text{B}_2\text{O}_3+0.5\text{ZnO}$) and ($0.3\text{BaO}+0.6\text{B}_2\text{O}_3+0.1\text{ZnO}$) glass powders yielded dielectric breakdown field strengths of 260 and 280 kV cm⁻¹, with recoverable energy density values of about 1.12 and 0.50 J cm⁻³, respectively. The resulting samples were composites comprising a mixture of two phases, BCZT and the glass phase. They attributed the high breakdown strength to the presence of alkali free glass composition, and the low loss dielectric to the low dielectric loss of BZT–BCT ceramic composition.

The effect of up to 9 wt% of CaO–B₂O₃–SiO₂ (CBS) glass additions on the microstructure and electrical properties of Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃ (BCZT) was studied by Lai et al [119]. Samples were sintered at 1300 °C for 4 hours in air; in the CBS-free sample, they observed the coexistence of orthorhombic and tetragonal BCZT phases with a small amount of CaTiO₃ secondary phase by means of XRD. The addition of the CBS glass induced a phase transformation to pseudo-cubic, a shift of the reflections towards lower 2θ values and the coexistence of the orthorhombic and tetragonal phases disappeared. These phase transformations were accompanied by the appearance of another secondary phase, reported to be Ba₂TiSi₂O₈. The density of the BCZT samples increased with CBS content, reaching a maximum when the addition of CBS was 2 wt%, and then slowly decreasing at higher CBS concentrations. Regarding the electrical properties, the sample with 2 wt% CBS exhibited the best ferroelectric properties, a dielectric constant of 8874 (at 106 Hz), a Curie temperature of 116 °C, P_r of about 3.18 μC cm⁻², and d₃₃ of 159 pC N⁻¹ due to the improved density achieved by the addition of CBS.

2.4.1.2 Barium titanate glass-ceramics

The pioneering work of Stookey in 1949 [120] on photosensitive glasses led to the discovery of methods for heterogeneous nucleation, where crystal growth takes place from many nuclei dispersed in the glass matrix after the glass has been formed [121]. Later on, Herczog [122] studied the properties and composition of glasses suitable for crystallization of BaTiO₃ from glasses. Perovskite BaTiO₃ with a minor amount of BaAl₂Si₂O₈ was obtained by heat treating glasses of compositions corresponding to (x)(BaTiO₃)+(100-x)(BaAl₂Si₂O₈). The grain size was controlled in the range 0.01 to 1 μm by varying the heating rate and the final heat treatment temperature. When the

volume content of BaTiO_3 in the glass-ceramic increased from 30-60 % and the grain size was about 1 μm , the dielectric constant increased from 100 to 1200. For grain sizes less than or equal to 0.2 μm , the relative permittivity was further decreased and found to be independent of temperature; this was attributed to the presence of surface defects in the fine grains. The highest relative permittivity of 1300 at room temperature was achieved at average grain sizes of about 1 μm , as can be observed in Figure 2.35; the breakdown strength and electrical resistivity of this ceramic were also reported to be high.

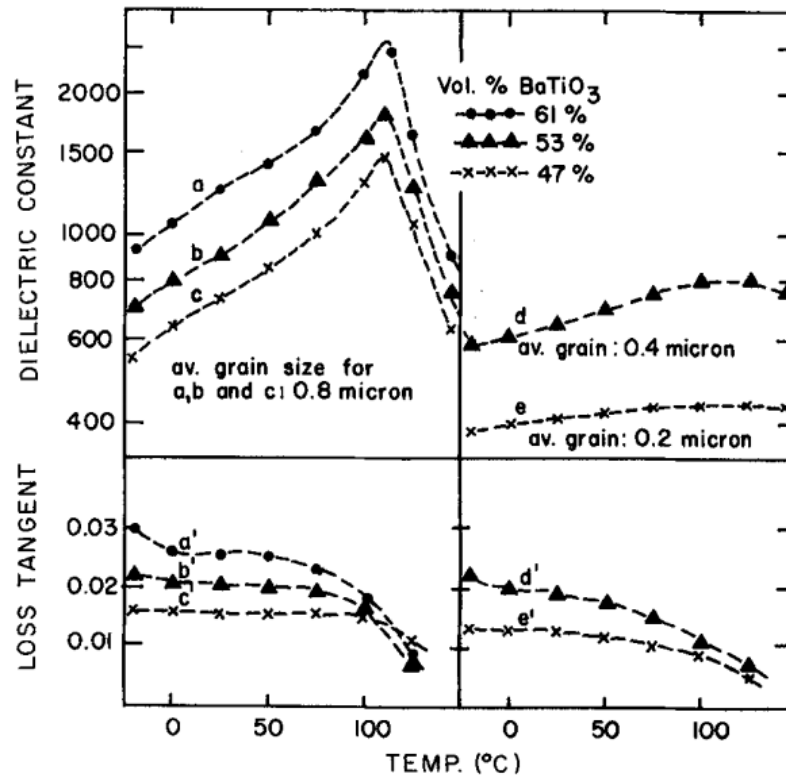


Figure 2.35 Variation of dielectric constant and loss tangent with the temperature at 1 kHz [122].

Nano-sized BaTiO_3 (20-80 nm) was produced by McCauley et al. [123] following the same approach as Herczog [122] and using different heat treatments and compositions. They observed intrinsic size effects at crystal sizes lower than 80 nm and predicted a critical size of 17 nm, at which BaTiO_3 cannot support a ferroelectric transition.

Takahashi et al. [124] reported the glass-ceramic of $0.65(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3\text{-}0.27\text{SiO}_2\text{-}0.08\text{Al}_2\text{O}_3$ (BSTS). The heating temperature of glass-ceramics was 1000 $^\circ\text{C}$ with a small amount of Sn or Zr; also the relative permittivity also decreased with the addition of

both of the Sn and Zr. The ϵ_r -T relationship showed a broadening and shift of the Curie point towards room temperature, as shown in Figure 2.36.

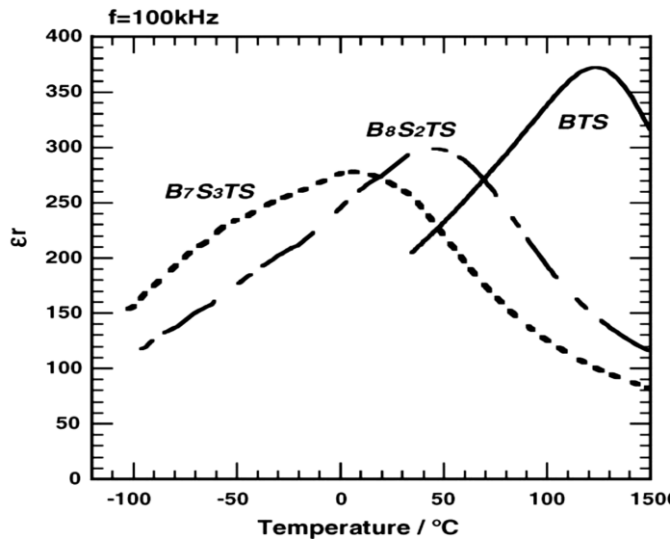


Figure 2.36 The ϵ_r -T relationship for BSTS bulk glass-ceramic derived from SnO₂-containing glasses [124].

2.4.2 Potassium sodium niobate (pure and modified)

KNN is one of the most promising candidates for energy storage properties, yet at present much research has focused on the development of, for example, (BaO,SrO)-TiO₂ [125, 126], (BaO,SrO)-Nb₂O₅ [127] and (BaO,Na₂O)-Nb₂O₅ [128] glass-ceramics. Therefore, the study of KNN glass-ceramics still needs more exploration and in-depth research [129].

2.4.2.1 Sintering aids of KNN

KNN ceramics prepared by solid state reaction usually require reaction temperatures around 800 °C or, sometimes, the double calculation in order to obtain a homogenous powder; sintering temperatures are usually in the range 1100 °C to 1200 °C [130]. The three starting materials used in KNN are Nb₂O₅, with a high melting point of 1520 °C, and two alkali metal carbonates, K₂CO₃ and Na₂CO₃, with melting points of 891 °C and 851 °C, respectively. Therefore, the alkali metal carbonates/oxides become volatile during the calcination, making it difficult to achieve a chemically homogeneous material. Excess alkali carbonate is used in order to compensate the losses during calcination and to obtain a single phase perovskite product [131].

The studies reported in [131, 132] indicated that a 5 mol% excess of K₂CO₃ and Na₂CO₃ in the raw materials leads to increased stability during calcination at 800 °C. The other effect of this excess an increase in particle size, which is probably due to the

liquid phase which forms during the calcination [131]. 3% and 1% excess alkali carbonate were used to improve the density of KNN and, at the same time, reduce the sintering temperature to 1000 °C [133, 134].

Sintering temperatures for KNN ceramics are usually >1000 °C. This needs to be lowered in order to decrease the alkali evaporation during the periods of high temperature, as well as to make it suitable for many desired applications [69]. If lithium additives are added to KNN, the sintering temperature reduces to lower than 1000 °C, there is a shift in T_C to a higher temperature, and there is an increase in the dielectric constant [135].

Barium borosilicate-based frit ($\text{BaO-B}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-K}_2\text{O-CuO-CaO}$) (abbreviated as BBS) was one glassy additive used previously as a sintering aid to KNN. It has been shown to reduce the sintering temperature to 1000 °C. In addition, the additive led to an increase in the mechanical properties and a decrease in the dielectric loss, whilst the T_C remained high at 400 °C; samples with 1.5 wt% glass frit showed optimal properties as follows: $\epsilon_r=410$, $\tan\delta=0.57$ and $d_{33}=108 \text{ pC N}^{-1}$, Figure 2.37 [136].

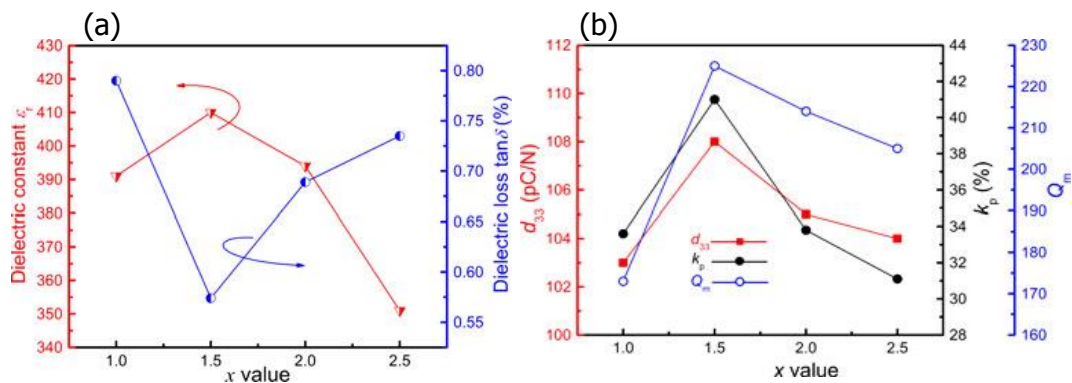


Figure 2.37 (a) ϵ_r and $\tan\delta$ (b) d_{33} , k_p and Q_m of KNN + x wt% BBS ceramics as a function of the x value [136].

2.4.2.2 KNN glass-ceramics

Many studies have been conducted on sintering of KNN, but there are currently few reports of true glass-ceramics.

Some previous studies have reported the formation of KNN in a glass-ceramic form [137]. Vernacolota et al. [138] reported that glass-ceramics containing KN and KNN phases can be obtained using silicate glasses prepared with alkali metal and niobium additions. The effects of substituting K by Na on thermal and crystallisation behaviour of KNN-SiO₂ glass-ceramics were reported by Aronne et al [139]. Kioka et al. [132] and

Kongputhon et al. [140] studied the control of the crystallisation behaviour in KNN-SiO₂, by varying the K:Na ratio, as a means of modifying the dielectric properties. Alumina-silicate glasses have also been used to fabricate glass-ceramics containing ferroelectric KNN and their dielectric properties reported by Yongsiri et al. [141]. The influence of CeO₂ as a nucleation agent in borosilicate glasses containing KNN have been reported for energy storage capacitor application by Hanyu et al. [129].

On the basis of their results, Yongsiri et al. [141] suggested that KNN glass-ceramics could be favourable for use in electro-optical applications. The microstructure, crystallite sizes, and crystal quantity of the KNN glass-ceramics were studied as a function of the heat treatment conditions. The heat treated glass-ceramics were found to contain a KAlSiO₂ phase at heat treatment temperatures between 600 and 675 °C, while the perovskite KNN phase was observed at a higher temperature of 700 °C, Figure 2.38. The glass-ceramic containing 23.75 mol% of SiO₂ exhibited a relative permittivity value of ≈ 260 and loss tangent ≈ 0.02 at 10 kHz.

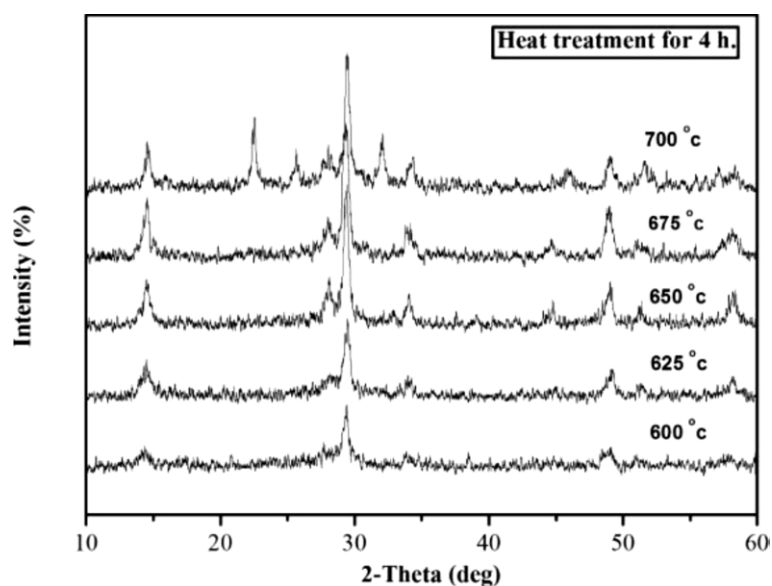


Figure 2.38 XRD patterns of the glass-ceramic sample with 5 mol% alumina and 23.75 mol% SiO₂ subjected to different heat treatment temperatures [141].

The use of a two-stage *incorporation* method, which involved the separate preparation of KNN and glass powders prior to melting, was also studied by Yongsiri et al. [77]. The calcined KNN powder was mixed with 25 mol% of SiO₂ then melted at 1300 °C using the conventional melt-quenching technique. The glass was heat treated at temperatures from 525 to 575 °C for crystallisation. Increasing heat treatment temperatures were found to improve the crystal size and crystallinity, which in turn plays an important role in controlling the properties of the glass ceramics, including

physical, optical, and dielectric properties. It is clear from the SEM results (Figure 2.39.) that the crystallisation of the KNN phase occurred at temperatures lower than the observed crystallisation temperature of 648 °C from the DTA results. Furthermore, the amorphous XRD patterns were observed in the glass-ceramic samples heat treated at temperatures lower than 550 °C. The highest relative permittivity value was 474 at a heat treatment temperature of 550 °C, while the transparency decreased with increased temperatures.

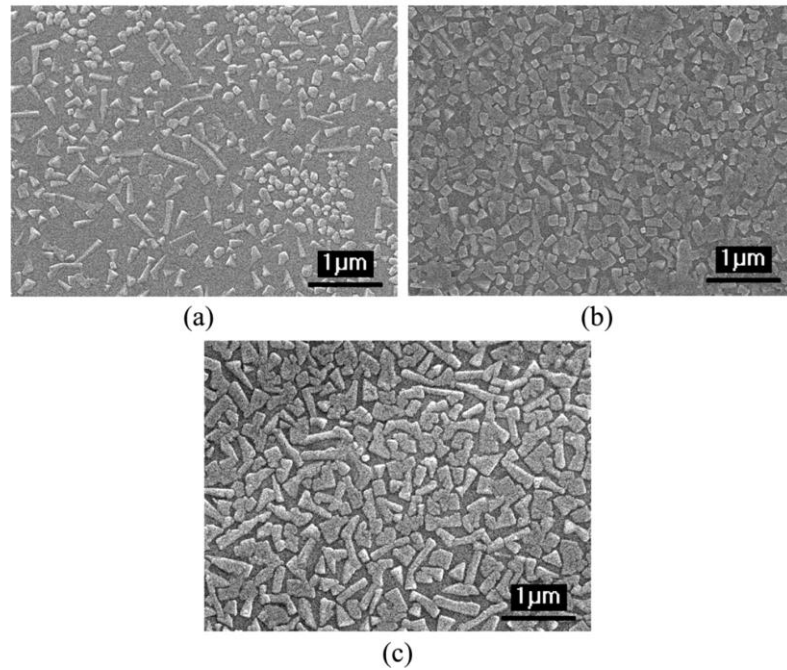


Figure 2.39 SEM micrographs for glass-ceramic samples heated at different temperatures. (a) 525 °C, (b) at 550 °C, (c) 575 °C [77] .

2.5 Glass-ceramic dielectrics

The potential applications of glass-ceramics in energy storage capacitors was investigated by Du et al. [142]. Here, the $\text{Na}_2\text{O-PbO-Nb}_2\text{O}_5\text{-SiO}_2$ glass-ceramics system achieved a highest relative permittivity of >600 after heated the sample at 850 °C. The results given by Gorzkowski et al. [143] shown that the interfacial polarization due to the difference in the dielectric and conductivity of glass phase and ceramic phase large hysteresis loss, led to low energy density (Max. 0.9 J cm^{-3}) and breakdown strength (Max. 800 kV cm^{-1}) of the BST glass-ceramics that expected much higher energy density ($\approx 3.5 \text{ J cm}^{-3}$ in case assuming is it ideal linear dielectric behavior) [143].

As the energy crisis intensifies, the search for novel, high performance and environmentally friendly energy storage devices have attracted wide attention. For a

material to possess high energy density capabilities, a high relative permittivity and dielectric breakdown strength are needed; this is a challenging task since theoretical and experimental studies on crystalline materials usually show a contrary relationship between these properties [144]. Compromises between relative permittivity and dielectric breakdown strength have encouraged the search for more efficient materials such as polymers and glasses. Recently, a high relative permittivity and a high dielectric breakdown strength were found in fluoropolymers, with energy density values up 25 J cm^{-3} being reported [145]. A high dielectric breakdown of $\approx 12 \text{ MV cm}^{-1}$ (1.2 MV mm^{-1}) was also reported [146] in a low relative permittivity ($\epsilon_r \approx 6$) alkali-free glass, showing the possibility to reach an energy density of 35 J cm^{-3} . These results are very promising since the relationships between relative permittivity and dielectric breakdown strength in inorganic glasses are not well established.

Xue et al. [38] studied the effect of glass concentrations on the energy storage capabilities of niobate glass ceramics $(100-x)(40\text{BaO}-10\text{Na}_2\text{O}-50\text{Nb}_2\text{O}_5)-x(63\text{SiO}_2-12\text{BaO}-16\text{B}_2\text{O}_3-9\text{Al}_2\text{O}_3)$ prepared via controlled-crystallization. They achieved dielectric breakdown strength of about 130 kV mm^{-1} and a charge–discharge efficiency of 92.5 %, with a relative permittivity of about 50 (see Figure 2.40 below).

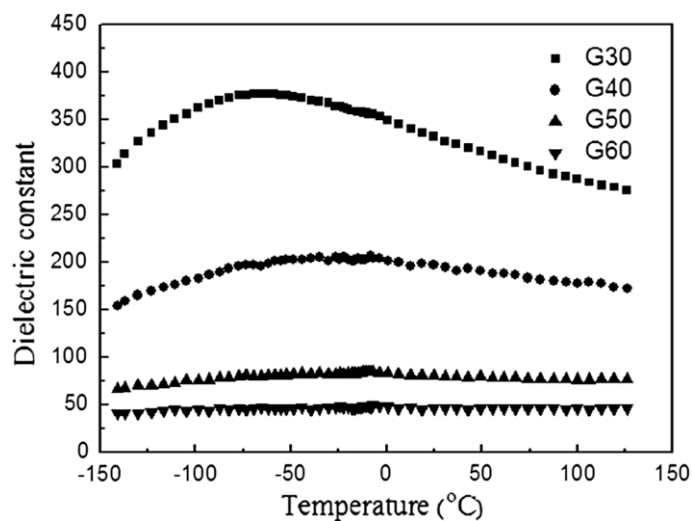


Figure 2.40 Relative permittivity versus temperature curves of niobate glass-ceramics prepared via the controlled-crystallisation route, samples were annealed at 1100°C . When the glass content was 30 % to 60 %, the samples were labelled G30 to G60, respectively [127].

2.6 Dielectrics in LTCC

In the 1980s, LTCC circuits were introduced to increase the central computing speed of processors. This was achieved by improving the multi-layer ceramic substrate with a high density. Before that, HTCC circuits were used with alumina insulators and some

compatible conductors [147]. The general groups of materials employed in LTCC and HTCC circuits are shown in Table 2.1.

Table 2.1 Typical material combinations in LTCC and HTCC [147].

	Ceramics		Conductor	
	Material	Firing temperature/°C	Material	Melting point °C
LTCC	(a) Glass/ceramics composite	900 to 1000	Cu	1083
	(b) Crystallized glass		Au	1063
	(c) Crystallised glass/ceramic composite		Ag	960
	(d) Liquid-phase sintered ceramics		Ag-Pd	960 to 1555
			Ag-Pt	960 to 1186
HTCC	(e) Alumina ceramics	1600 to 1800	Mo	2610
			W	3410
			Mo-Mn	1246 to 1500

Densification with a low sintering temperature is important in LTCC. In addition, there should be chemical compatibility between the materials of LTCC and the electrode [147]. Generally, dielectrics with high relative permittivity are typically used for layers of capacitors or resonating structures. The materials which have low relative permittivity in the range of 4 to 12 are used for substrate layers [18].

Recently, there have been many studies to develop microwave dielectric ceramics with low sintering temperatures [148]. Many of these ceramics have high sintering temperatures. Therefore, several ferroelectric ceramic materials with low sintering temperatures and good dielectric properties have been studied for LTCC applications [149]. In some applications, the sintering temperature must be below 900°C; this is a key point for LTCC. Three different compositions from ZnO-B₂O₃-Li₂O in the proportion of 3.5 wt% were added to BaTiO₃ to reduce the sintering temperature to 900°C. Other borosilicate glass powders, such as ZnO-B₂O₃, CdO-B₂O₃, CaO-B₂O₃, Bi₂O₃-B₂O₃, and CaO-Al₂O₃-B₂O₃ compositions have also been used with BaTiO₃ in order to decrease the sintering temperature [13].

The (Ca, Nd)TiO₃ system with H₂BO₃-CuO-Li₂CO₃ additives showed excellent dielectric properties and a low sintering temperature of ~900 °C for LTCC applications [150]. Several types of glass, BBS, PBS, and ZBS, were added to BaTiO₃; the sintering temperature decreased to 900°C with high relative density and a high dielectric constant [5]. Li₂TiO₃ ceramics doped with Li₂O-MgO-B₂O₃ were also found suitable for LTCC applications, decreasing the sintering temperature to 850 °C with retention of good microwave dielectric properties [149].

3. Principles of characterization techniques

This chapter explains the basic principles and different experimental techniques used in this thesis. The techniques of characterisation include X-ray diffraction (XRD), density measurement, high-resolution synchrotron X-ray powder diffraction (SXPd), and scanning electron microscopy (SEM).

3.1 Density measurement

The volume (v) of the sample was measured by measuring the diameter (r) and thickness (t), as well as the sample mass (m) to calculate the bulk density (ρ) for all disc samples, according to the following formula:

$$\rho_m = \frac{m}{v} \quad 3-1$$

The relative density (ρ_r) is defined as the ratio of measured density to the theoretical density in order to give a percentage of sample densification, where the formula is:

$$\rho_r = \frac{\rho_m}{\rho_t} \quad 3-2$$

The theoretical density of the pure crystalline ceramic phase was calculated first using the nominal composition together with the phase fractions and crystallographic parameters determined from the full-pattern XRD analysis using Topas v5.0. In contrast, the density of the glass phase was measured by immersion in water using the Archimedes method. Subsequently, the theoretical density of the ceramic-glass composite was calculated according to the following equation:

$$\frac{1}{\rho_t} = \frac{1-x}{\rho_1} + \frac{x}{\rho_2} \quad 3-3$$

Here ρ_t is the total density of glass-ceramic, ρ_1 and ρ_2 are the density of the ceramic and glass, respectively, and x is the %wt of the glass content.

3.2 X-ray diffraction

X-rays are electromagnetic waves that have wavelengths that are much shorter than those of visible light, in the order of 0.1 nm. XRD methods use the concept of wave interferences between the periodic electronic potential geometry of crystals and x-rays. Depending upon their phase difference, two waves of light travelling in the same direction are able to either cancel out or reinforce each other.

When two waves of light have a phase difference of $n\lambda$, with n being an integer, the waves are referred to as being 'in phase' and it leads to constructive interference. When the two waves of light have a phase difference of $n\lambda/2$, the waves are referred to as being 'completely out of phase' and it leads to completely destructive interference.

As shown in Figure 3.1, x-ray beams incident on a crystalline solid are diffracted by the crystallographic planes. Beams 1 and 2, two in-phase incident waves, are deflected by A and B, two crystal planes. The reflected waves are resultantly not in phase unless the following relationship is valid [151, 152].

$$n\lambda = 2d \sin\theta$$

3-4

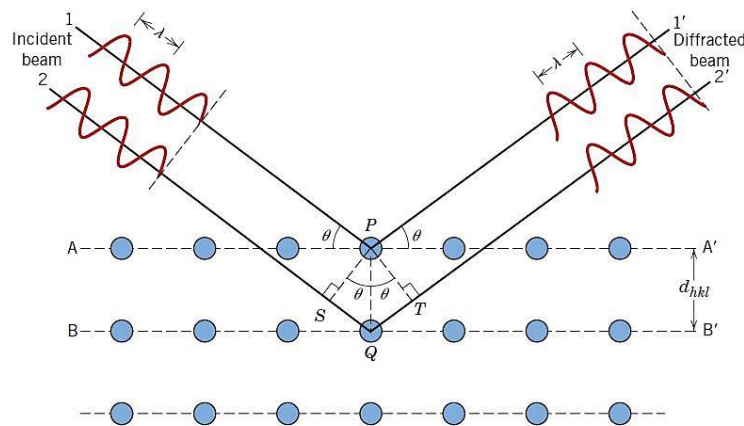


Figure 3.1 X-ray diffraction by crystal planes [152].

Bragg's law, shown in Equation 3-4 is the simple law of diffraction. It can be obtained by calculating the path difference that exists between the two beams in Figure 3.1. This difference is dependent upon the distance between the parallel crystal planes (d) and upon the incident angle (θ). Therefore, this functions as a basic equation linking the interatomic spacing and x-ray wavelength to the diffracted beam's angle.

Bragg's law may not be satisfied if the interference is nonconstructive and this will yield a diffracted beam with a very low intensity. The distance between two parallel and adjacent planes of atoms, also referred to as the interplanar spacing, is a function of the lattice parameter(s) and Miller indices (h , k , and l). Crystal structures, for example, display cubic symmetry in which the lattice parameter (unit cell edge length) is ' a '. The other six crystal systems mentioned in Table 3.1 harbour relationships similar to, but more complex than, those in Equation 3-5.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

3-5

Table 3.1 Lattice spacings in different types of crystals [152].

• Cubic:
$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
• Tetragonal:
$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
• Hexagonal:
$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
• Rhombohedral:
$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$
• Orthorhombic:
$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
• Monoclinic:
$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \csc^2 \beta$
• Triclinic:
$\frac{1}{d^2} = \frac{\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma + \frac{2kl}{bc} \cos \alpha + \frac{2hl}{ac} \cos \beta + \frac{2hk}{ab} \cos \gamma}{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$

3.3 Synchrotron x-ray diffraction

SXPD employs the same basic principles as XRD. SXPD, however, produces much higher-intensity x-rays, allowing for greater resolution and making Rietveld Refinement more accurate. As shown in Figure 3.2, there are several different aspects of the Diamond synchrotron.

A beam of electrons that passes through a linear accelerator is emitted through an electron gun in an electric field and a high vacuum. This beam proceeds to enter a booster ring, where it is accelerated by a source of radio frequency voltage. The required forces are provided by electromagnets and this allows the beam to repeatedly orbit the ring until it is at a high enough speed (approaching the speed of light). The beam is then released into the main synchrotron storage ring where it circularly orbits and its path is, again, bent by high field electromagnets.

The beam is accelerated as its direction changes and so it tangentially releases high energy photons in the form of x-rays. This process allows for many beamline stations

to be used simultaneously for experimentation, each having a high-energy x-ray beam. The x-ray beam's high intensity is able to be filtered to very small wavelengths, allowing for deeper penetration in samples when compared with laboratory XRD [153].

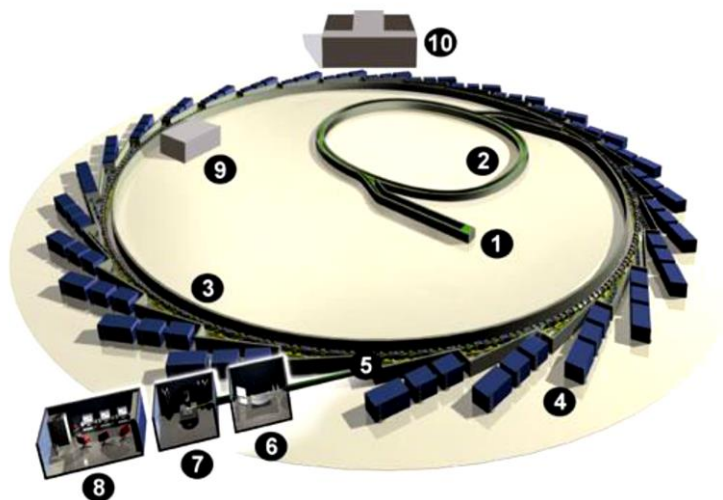


Figure 3.2 Schematic diagram of the Diamond synchrotron (UK) with its main components highlighted. (1) Electron gun and linear accelerator; (2) booster synchrotron; (3) storage ring; (4) beamlines; (5) front end; (6) optics hutch; (7) experimental hutch; (8) control cabin; (9) radiofrequency (RF) cabin; (10) Diamond house [153].

The UK's national synchrotron facility is the Diamond light source. It is able to produce intense, high-energy x-rays to help further scientific research in a number of fields, including material science, engineering, and proteins. The diamond synchrotron has used electrons travelling with an energy of 3GeV since it became operational (in 2007). It currently has nearly 22 beamlines and is aiming to increase this to 32 by 2017 [44].

3.3.1 Beamline I11-Diamond light source, UK

SXPD patterns with a high-resolution were obtained using the diamond light source's beamline I11. This beamline can be used for a range of materials, including alloys, ceramics, superconductors, and metal-organic frameworks. It can also carry out a detailed structural analysis of complex materials by using a combination of controlled temperatures, high count rates, and a very high resolution. This latter point is critically important in the present research regarding the development of crystalline phases during heat treatment and temperature-induced phase transformations [154].

3.4 Scanning Electron Microscopy

SEM with energy dispersive X-ray spectroscopy (EDX) is most often used for surface analytical purposes. A scanning (primary) electron beam produces high-resolution

images of surface topography with excellent field depths. As shown in Figure 3.3, a sample is imaged after being scanned by a high-energy electron beam in a raster scan pattern. This method is often used to illustrate a sample's morphology, surface topography, crystallographic information, and composition.

SEM makes use of the fact that accelerated electrons carry a relatively large amount of kinetic energy. Backscattered x-rays and electrons, as well as low energy secondary electrons, are created through a primary electron bombardment. The backscattered electrons' intensity correlates with the atomic numbers of the sample's elements. Therefore, qualitative information regarding the sample's elemental composition can be obtained.

EDX (or EDS) analysis of the x-rays that are emitted from a sample allows for the measurement of quantitative elemental data. EDX analysis can be limited to an analytical volume as small as 1 cubic micron. SEM with EDX provides a non-destructive, relatively rapid, and inexpensive approach to surface analysis. Often, these methods are employed to analyse a surface prior to the use of other, more specialised and more surface-sensitive, techniques [155, 156].

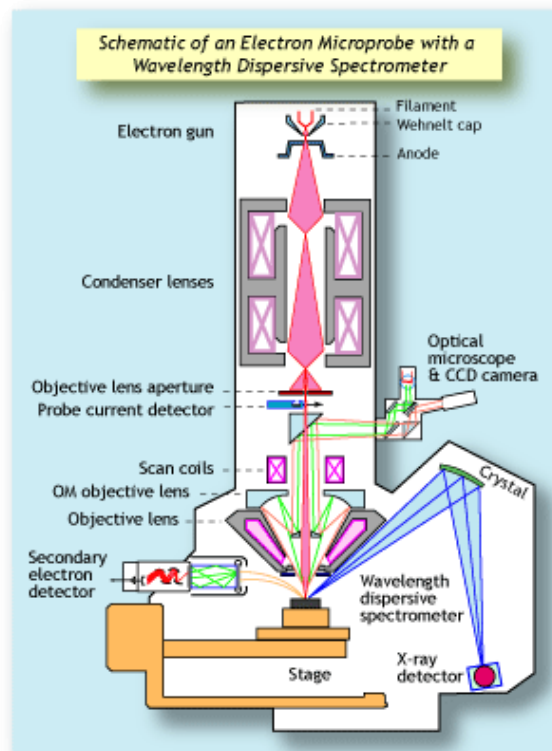


Figure 3.3 Schematic illustration of how SEM and EDS/EDX work [157].

4. Experimental Procedures

4.1 Overview of Processing Methods

The procedures used for processing the sintered ceramics and recrystallized glass-ceramics are summarised in Figure 4.1 below. Further details of the experimental methods and processing parameters are provided in the following sections 4.2 and 4.5.

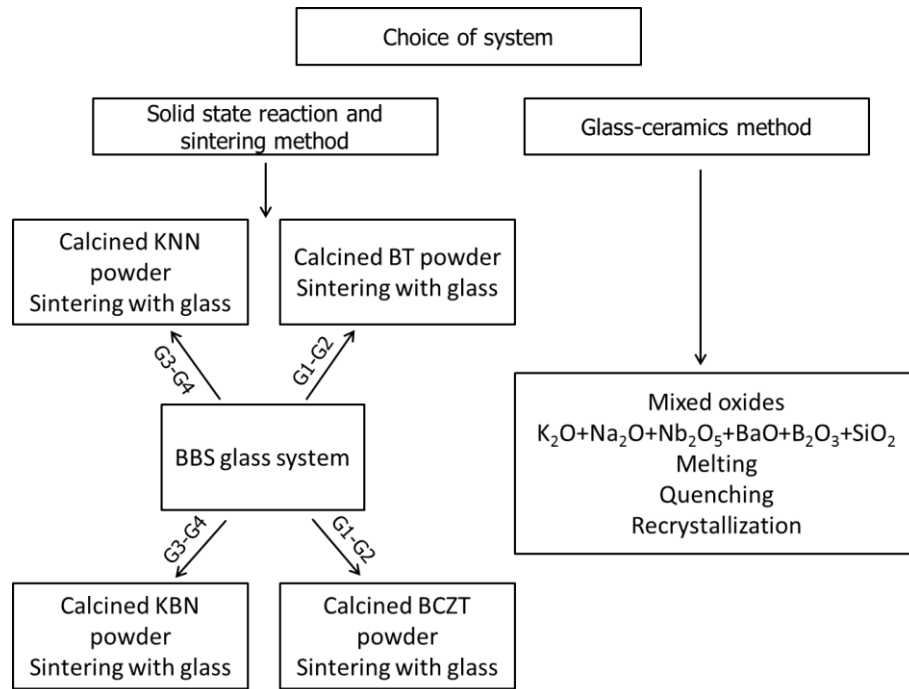


Figure 4.1 Overview of processing methods.

4.2 Preparation of ceramics

Ferroelectric ceramics are prepared conventionally by solid state reaction between the constituent oxides and carbonates. In this work, the two systems investigated are barium titanate (BaTiO₃) (BT) and potassium sodium niobate (K_xNa_{1-x}NbO₃) (KNN). These two systems were modified with Ca and Zr into BT, while Bi, Sb and Zr were added into KNN.

4.2.1 K_{0.5}Na_{0.5}NbO₃

The first system investigated is potassium sodium niobate (K_xNa_{1-x}NbO₃) (KNN). The KNN solid solution system between ferroelectric KNbO₃ and antiferroelectric NaNbO₃ forms several morphotropic phase boundaries (MPB), one of which exists between two orthorhombic phases near the composition x=0.5. Previous results, [131] indicate that the addition of excess alkali carbonate (Na₂CO₃ and K₂CO₃) could reduce the sintering temperature and improve the piezoelectric and dielectric properties. For this reason,

5 mol% excess of each of the Na_2CO_3 and K_2CO_3 were added to the starting mixture of KNN.

The raw materials for preparation of KNN ceramics were mixed by ball milling in propan-2-ol, in the proportion 1 g:1.2 cm^3 , with zirconia balls for 18 hours using polypropylene bottles. However, it is well known that carbonate powders are moisture sensitive [131]. Therefore, in this experiment, the starting materials for KNN which are Na_2CO_3 (Aldrich Co. 99.5 % purity), K_2CO_3 (Fluka Co. 99 % purity) and Nb_2O_5 (Treibacher Industrie AG 99.9 % purity), have been dried overnight in an oven at 90 °C for 48 hours before weighing in order to avoid non-stoichiometry of the calcined powders.

The precursors were dried and then calcined at different temperatures between 700 and 900 °C (alumina crucible with lid) using a Vecstar Furnace (VTF-SP 1500) zirconia milling balls and calcined for 10 hours at 900 °C to finish the reaction process. The calcined powders were studied by X-Ray Diffraction, XRD, to identify the phase formation and optimum calcination conditions for preparation of KNN powder. This powder was imaged using scanning electron microscopy, SEM, in order to gain information on the particle size and morphology for the various calcination conditions, and the influence of non-stoichiometry in the starting mixture.

The calcined powders were remixed by ball milling for another 6 hours to break down large agglomerates [158], and then the mixtures were dried overnight in an oven at 90 °C. Next, it was dried and pressed into disks of diameter 10 mm and thickness about 2 mm by applying a pressure of 100 MPa. The pellets of KNN were sintered at 1110, 1150 and 1200 °C for 3 hours, (alumina crucible with lid) using the Vecstar Furnace (VTF-SP 1500) for the sintering of all samples.

In parallel, the same procedure was followed to prepare modified KNN ceramics with high piezoelectric performance, using a single KNN-based system modified with Sb, Bi and Zr. The composition $0.96(\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3)-0.04(\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$ (KBN) was prepared using a calcination temperature of 850 °C for 6 hours followed by sintering at 1170 °C.

4.2.2 BaTiO₃

Barium titanate, BT, ceramics were also fabricated using the solid state reaction method. BaCO_3 (Fluka Co. 99% purity) and TiO_2 (Huntsman A-HR 99% purity) were used as raw materials in this reaction following the same procedure as above in KNN

ceramics preparation (section 4.2.1), although the milling process was carried out for 24 hours, the calcination temperature was 900 °C and the sintering temperature was in the range 1200 °C to 1300 °C.

Furthermore, calcium and zirconium-modified BT ceramics of $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (BCZT) were prepared following the same route of preparation of BT ceramic, using a double calcination process at 1000 °C for 6 hours. Then, the powder was sintered at temperatures in the range between 1300 and 1400 °C.

4.3 Preparation of glass systems

Several different types of glasses were prepared by conventional melting and quenching. The glass oxides powders were mixed, dried and melted using alumina crucibles at a temperature in the range from 900 to 1140 °C for a holding time between 30 and 90 min, then air quenched onto a steel plate to form glass. Here, the Carbolite rapid heating Furnace (Newtronic, micro 96-1500) has been used for the melting and preparation of all the glass samples. The glass oxides and glasses were studied by XRD to identify the best conditions to glass forming. Four types of glasses, denoted G1 to G4 were produced as sintering aids, as presented in Table 4.1.

Table 4.1 Chemical composition of glasses.

Glass	glass composition (mol %)							
	BaO	B ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O	CuO	Bi ₂ O ₃	ZnO
G1	54.61	19.48	25.91	-	-	-	-	-
G2	20	40	20	10	10	-	-	-
G3	20	40	20	8	5	7	-	-
G4	-	27	6	-	-	-	35	32

4.3.1 BaO-B₂O₃-SiO₂ (G1)

The barium borosilicate, BBS, glass system of composition 54.61-BaO-19.48-B₂O₃-25.91-SiO₂ (mol %) was prepared, where the BaCO₃ (Fluka Co. 99% purity), H₃BO₃ (Fisons Co. 99.5% purity) and SiO₂ (Alfa Aesar Co. 99.5% purity) were used as raw materials. This composition was identified by A. Shukla due to its low ternary eutectic melting point [159]. The raw materials were mixed then milled for 24 hours in propan-2-ol using zirconia balls in plastic bottles. Next, the precursors were dried at 90 °C for

24 hours. The mixed-dried powder was melted using an alumina crucible at a temperature in the range between 1040 °C to 1140 °C for 45 to 60 min and air quenched onto a stainless steel plate having a thickness of 2 mm.

4.3.2 BaO-B₂O₃-SiO₂-K₂O-Na₂O (G2)

Potassium and sodium-modified barium borosilicate glass composition 20BaO-40B₂O₃-20SiO₂-10K₂O-10Na₂O (mol%) was prepared in a similar manner to that described above (section 4.3.1), using a temperature of 1050 °C for 30 min. The composition reported by Li et al. [136] was used as the basis for this work, with a slight change in the ratio of the constituent oxides to form glasses G2 and G3.

4.3.3 BaO-B₂O₃-SiO₂-K₂O-Na₂O-CuO (G3)

To lower the melting point of the glass, potassium-sodium and copper-modified barium borosilicate glass of composition 20BaO-40B₂O₃-20SiO₂-8K₂O-5Na₂O-7CuO (mol%) was prepared in a similar process to that described above (section 4.3.1), using a melting temperature of 1000 °C and heating time of 30 min.

4.3.4 Bi₂O₃-B₂O₃-ZnO-SiO₂ (G4)

As an alternative strategy to lower the melting temperature of the glass, bismuth borosilicate glass was prepared as a sintering aid for ceramics. BBSZ of 35Bi₂O₃-27B₂O₃-32ZnO-6SiO₂ (mol %) were prepared by the melt-quenched method. This composition of glass has been used previously by Chen et al for sintering BT at low temperatures [117]. The raw materials were mixed and dried then milled using the same methods described above (section 4.3.1) and using a temperature of 900 °C for 1 hour.

4.4 Sintering of ceramics with BBS glass systems

The glass systems described above (G1-G4) were employed as sintering aids for pure and modified BT and KNN powders. The compositions used are abbreviated as (BT-x wt% G_y), (BC-x wt% G_y), (KNN-x wt% G_y) and (KBN-x wt% G_y), where x= 2 to 15 wt% proportions and y=1 to 4.

4.4.1 KNN-x wt% glasses

Glass systems of G3 and G4 were mixed with KNN and KBN powders as sintering aids. The compositions used are abbreviated KNN-x(G3, G4) and KBN-x(G3, G4) where x=5, 10 and 15 wt% proportions. The mixed (calcined powder:glass) were milled 6 hours in

propan-2-ol using zirconia milling balls and then drying for 24 hours at 90 °C. The dry mixture was pressed into disks of diameter 10 mm and thickness of 2 mm by applying a pressure of 100 MPa. In order to prevent the loss of volatile elements of sodium and potassium, the pellets were embedded in powders of the same composition before the sintering procedure [158]. Then the pellets prepared were sintered at temperatures in the range 1050 to 1150 °C for 3 to 5 hours.

4.4.2 BT-x wt% glasses

Both ceramic systems BT and BC were mixed with glasses (G1 and G2) as sintering aids. The compositions used are abbreviated BT-x(G1, G2) and BCZT-x(G1, G2) with $x=2, 5, 10$ and 15 wt% proportions. The calcined powders and glass powders were mixed and milled for 6 hours in propan-2-ol. After drying for 24 hours, the mixture was pressed into disks of diameter 10 mm and thickness of 2 mm by applying a pressure of 100 MPa. The pellets prepared were sintered at temperatures in the range between 1100 and 1300 °C for 3 hours.

4.5 Melting and crystallization of KNN glass-ceramics

Potassium and sodium-modified barium borosilicate glass (BBSKN-G2) was combined with KNN by the conventional melt-quenching method and then heat treated to induce crystallisation, producing nanostructured glass-ceramics. The glass-ceramic samples were prepared by a conventional melt-quenching method using the low-melting-point barium borosilicate glass, $20\text{BaO}-40\text{B}_2\text{O}_3-20\text{SiO}_2-10\text{K}_2\text{O}-10\text{Na}_2\text{O}$, BBSKN, with KNN contents ranging from 50 to 80 mol%. The raw materials were dried overnight in an oven at 90 °C before weighing in order to avoid non-stoichiometry of the calcined powders.

The ceramic and glass powders were mixed and milled in propan-2-ol for 18 hours, then dried at 85 °C for 24 hours. The powder was heated, within an alumina crucible, up to 1250 °C for 60 min to melt. The resulting glass was air quenched onto a stainless steel plate having a thickness of 2 mm to form the amorphous glass phase. The amorphous nature of the quenched glasses was confirmed using XRD. Several KNN-BBSKN glass samples were subsequently heat-treated at temperatures between 550 and 850 °C for 4 hours. The occurrence of the crystallisation process and the nature of the resulting phases were examined using DSC, high-resolution synchrotron X-ray powder diffraction, SXPd, and SEM. In addition, the relative permittivity and high field ferroelectric properties have been tested.

4.6 Experimental Characterisation Techniques

4.6.1 Density measurement

Using Equation 3-1 and Equation 3-2, both the density and relative density of all ceramics and glasses were measured. The OHAUS Adventure Pro AV213 balance was used to measure the sample mass (m); the diameter (r) and the thickness (t) were measured using a digital micrometer.

The theoretical densities of the pure crystalline phases (BT, BC, KNN and KBN) were calculated first using the nominal composition together with the phase fractions and crystallographic parameters determined from the full-pattern XRD analysis using Topas v5.0 [160]. In contrast, the density of the glass phase was measured by immersion in water using the Archimedes method by the OHAUS Analytical Standard AS120 balance. Subsequently, the theoretical density of the ceramic-glass composite was calculated according to equation 3-3 described in section 3.1 above.

4.6.2 Thermal analysis

Thermal analysis was conducted in order to identify the glass transition (T_g) and crystallisation temperature (T_{cr}) for glass-ceramics. A NETZSCH STA 449C was employed to study the differential scanning calorimetry (DSC). Here, a small amount (40-80 mg) of glass (bulk/powder depending on the glass type) was placed in a small alumina crucible and another empty crucible was used as a control. The sample was heated up to a temperature of up to 900 °C with a heating rate of 10 °C min⁻¹.

4.6.3 X-ray diffraction procedure

4.6.3.1 Lab XRD

XRD was used to identify the phases present in the powders and sintered ceramics. The XRD (X'pert-PRO PANalytical) was used to identify the structural properties of the samples. A Cu-K alpha X-ray radiation tube was used during this operation, with a wavelength $\lambda=1.54060$ Å, a 40 mA current, and a 40 kV voltage. In addition, the diffraction scanning angles were scanned from 10° to 90° 2 θ by scanning in 0.05° steps with a scan step time of 299.72 sec.

To achieve a flat and smooth surface, all the ceramic pellet samples were polished using a SiC paper followed by annealing at 500 °C for 30 min to remove any stresses occurred during the polishing, which may have otherwise led to a change in the XRD

patterns. The lab XRD, as described above, was employed in structural studies of pure and glass-modified BT, KNN and KBN.

4.6.3.2 High-resolution synchrotron SXP

In-situ high-resolution SXP was carried out on beamline I11, Diamond light source, UK, to identify the occurrence of the crystallisation process and the nature of the resulting phases in KNN-based glass-ceramics. Furthermore, SXP was also used in case of pure and glass-modified BCZT to identify the phases present, with in-situ SXP in case of BCZT-5G1. The I11 beamline has a wavelength $\lambda=0.825925 \text{ \AA}$ and 15 keV with zero-point errors (z.p.) = 0.01508 [161]. The SXP patterns were recorded using a wide-angle position sensitive detector (PSD) spanning the 2θ range from 3° to 70° , with an angular resolution of 0.004° , using a collection time of 10 sec.

Glass and ceramic samples were prepared by crushing and grinding the sample to fine powders and were then loaded into quartz capillaries of 0.5 mm diameter. The sample preparation and the experimental apparatus within the I11 beamline hutch are displayed in Figure 4.2 and Figure 4.3, respectively.

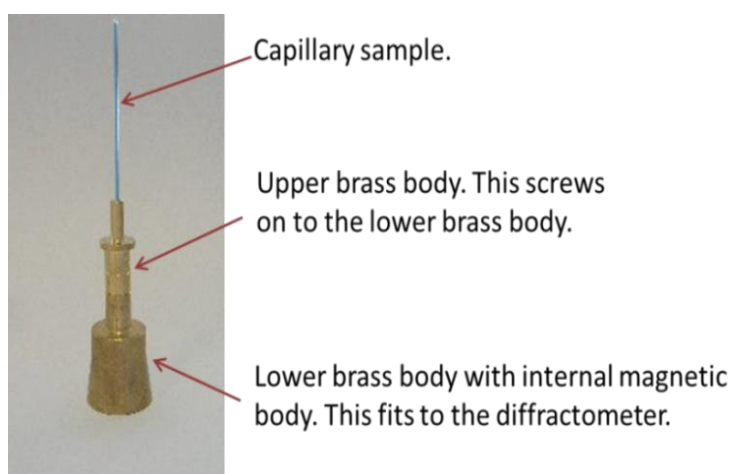


Figure 4.2 Capillary spinner [154].

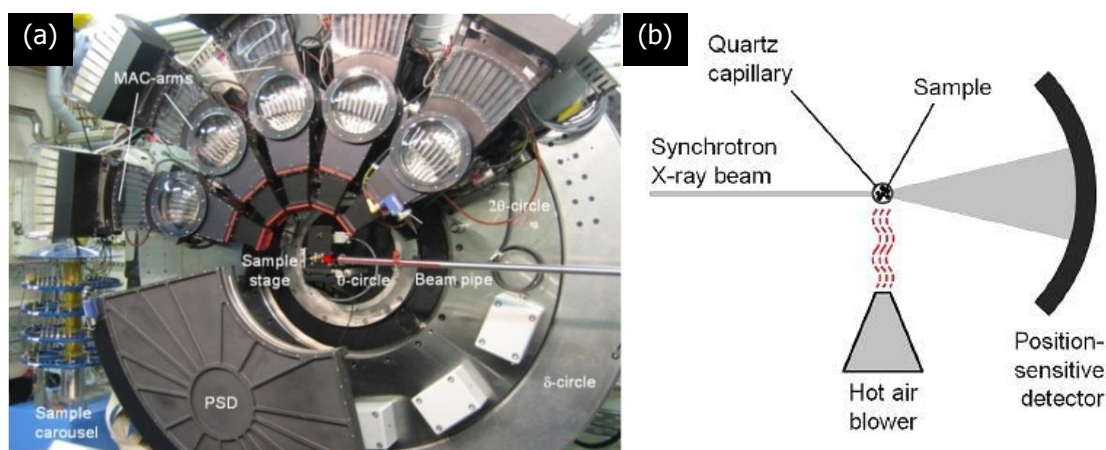


Figure 4.3 (a) The detector and sample arrangement within the diamond light source beamline I11 and (b) the schematic of the experimental setup [154]. The position sensitive detector (PSD) was employed for recording the SXP patterns.

The controlled temperature conditions on I11 for in-situ SXP were used. The Cryostar hot air blower was used to heat the sample from 25 to 850 °C with a heating rate of 10 °C min⁻¹ (or 5 °C min⁻¹ for the glass-modified BCZT heated up to 150 °C). Figure 4.4 shows one of the glass samples prepared for an in-situ SXP test and heated up to 850 °C; the area of the capillary exposed to the hot air blower is shown.

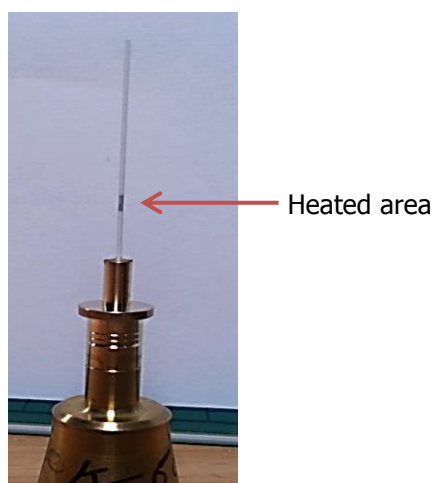


Figure 4.4 Glass-ceramic sample after heating up to 850 °C.

X'pert HighScore Plus software has been used to analyse the XRD results using pattern fitting by the international centre for diffraction data database (ICDD) and *Topas* v5.0 software [160] was then employed for full-pattern Rietveld refinement [162]. Furthermore, the lattice parameters and relative phase quantities were recorded from refinements of the XRD patterns in order to determine the crystallographic parameters.

The instrument parameters for XRD on beamline I11 were set up in *Topas* in order to perform Rietveld refinement. These instrument parameters, which are important in the

refinement of diffraction data, include peak profile parameters, error correcting parameters and background.

The Scherrer equation, published in 1918 [163], was used to provide a simple estimate of crystallite size from the breadths of a diffraction peak. The crystallite size, D , for the glass-ceramics was calculated by Topas according to this equation given below:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad 4-1$$

where K is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle (in degrees).

4.6.4 Scanning Electron Microscopy

A Quanta FEG 650 or Philips XL30 SEM was used to examine both the powders and ceramic discs. The ceramic discs were ground using 400 to 2400 grade SiC paper and then polished using the 6, 1, and ¼ micron diamond paste, followed by polishing with dilute OPS (Oxide Polishing Suspension) colloidal silica solution for 90 minutes. The sample was washed with soap and ethanol in between each stage, after which the ultrasonic bath was used for 10 min in ethanol. All samples were coated with carbon using a Quorum coater (Q150T). During the experiment, the accelerating voltages 10 kV to 20 kV used were and the working distance was approximately 10 mm.

For the grain size measurements, the linear intercept method was used in order to determine the grain size for ceramics [164]. Here, the number of lines is drawn across the microstructure image after setting the scale accurately and then the types of boundaries (e.g. grain boundary and/or pore boundary) are marked along these lines; also the correction factor for the grain shape was introduced.

Furthermore, from the SEM images the average grain size, $\bar{D}$, was calculated using the more accurate method devised for polycrystalline ceramics, which was proposed by Mendelson, as illustrated in equation below [165]:

$$\bar{D} = K \bar{L} \quad 4-2$$

where $\bar{L}$ is the average intercept length over a large number of grains as measured on the polished cross-section and K is the proportionality constant. The value of K depends on the grain shape, which in the case of an unknown shape and size distribution is taken to be equal to 1.126 [165].

4.6.5 Transmission Electron Microscopy

The TEM study was carried out using a Tecnai T20 operated at 200 keV in order to examine the microstructures of the glass-ceramics after heat treatment. The TEM sample was prepared using a small piece of the heat treated glass-ceramics sample. After crushing the sample using an agate mortar, CHCl_3 was used to disperse the crushed powder in order to form a suspension. Next, the suspension was dropped using a pipette on a Lacey carbon grid and then dried.

4.6.6 Electrical measurements

The ceramics and glass-ceramics, with surface area A , were ground to produce a flat and smooth surface, using SiC paper followed by annealing at 500 °C for 30 min to remove any stresses occurred during the polishing. Then, silver paint (C2000107P3, Gwent Electronic Materials, UK) was used to coat both pellet faces, followed by drying and then firing at 550 °C for 30 min. These samples were used to obtain dielectric and ferroelectric measurements.

4.6.6.1 Permittivity-temperature measurements

Pellets with approximately 1 ± 0.2 mm in thickness (t) and a surface area of ' A ' were placed between two electrode silver wires inside a furnace, as shown in Figure 4.5. An LCR meter (Hewlett Packard 4284A) with a Carbolite CWF 1200 Furnace was used to measure the capacitance (C) and loss tangent ($\tan\delta$) at frequencies of 1, 10, and 100 kHz with temperatures ranging from ≈ 25 °C to above the T_C with a heating rate of 2 °C min^{-1} . Then the real part of the permittivity (ϵ_r) was calculated using Equation 4-3.

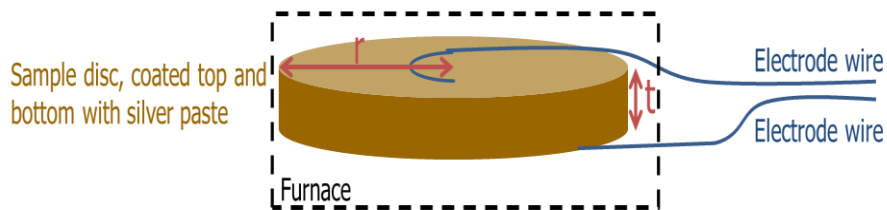


Figure 4.5 Representation of sample prepared to be clamped in between two silver plates, in preparation for the dielectric.

$$C = \frac{A\epsilon_0 \epsilon_r}{t} \quad 4-3$$

where r and t are the radius and thickness of the sample, respectively. Uncertainties were estimated based on the resolution of the LCR meter, the magnitude of stray capacitances and statistical variations in sample dimensions.

4.6.6.2 Nonlinear ferroelectric/dielectric properties and energy storage density

High field ferroelectric P-E hysteresis measurements ($>1\text{kV}$) were carried out for all pellets under silicone oil at room temperature ($24 \pm 2^\circ\text{C}$) using a function generator (Hewlett-Packard 33120A) and EHT Amplifier produced by Chevin Research Ltd. Four sinusoidal cycles were applied using the 'burst' mode of the function generator. A specially constructed current amplifier was also used to measure the induced current [166]. The applied voltage and current waveforms were recorded using a Measurement Computing USB-1608FS-Plus A/D card and they were analysed using the LabVIEW-based software [166]. The method involved the numerical integration of the current waveform over time to yield electric charge, leading to the calculation of the polarisation as surface charge density. The P_s , P_r and E_c values were determined by averaging the values obtained from several recorded P-E hysteresis loops.

For calculating ϵ_r' and ϵ_r'' from the P-E loops, we first determine the magnitude of the complex permittivity [167], $|\epsilon_r^*|$, given by:

$$|\epsilon_r^*| = \frac{P_0}{\epsilon_r E_0} \quad 4-4$$

where E_0 and P_0 represent the amplitude of the applied electric field and polarisation waveforms, respectively. Then, the hysteresis loss, U_H , which is the energy loss per cycle per unit volume was determined as the area enclosed within the hysteresis loop, as shown in Figure 4.6 below, which is given by:

$$U_H = \int_{-P_s}^{+P_s} E dP + \int_{+P_s}^{-P_s} E dP \quad 4-5$$

where $-P_s$ and $+P_s$ are polarisation values at the start and end of a complete cycle. For energy storage efficiency calculations, the energy loss for a half-cycle, U_{loss} , was calculated simply as $0.5 U_H$. The imaginary part of the relative permittivity, ϵ_r'' , was calculated from hysteresis loss, U_H , using the following relation:

$$U_H = \pi \epsilon_0 \epsilon_r'' E_0^2 \quad 4-6$$

Subsequently, the real part of the relative permittivity, ϵ_r' , was calculated as:

$$|\epsilon_r^*| = \sqrt{(\epsilon_r')^2 + (\epsilon_r'')^2} \quad 4-7$$

The stored (recoverable) energy density, U_{rec} , is a function of the relative permittivity and breakdown strength of the material. The U_{rec} values of the sintered ceramics and heat-treated glass-ceramics were calculated from high field P-E hysteresis loops in terms of the area between the P-E hysteresis curve and the polarisation axis, represented in Figure 4.6 below, given by the equation:

$$U_{rec} = \int_{+P_s}^{+P_r} E dP \quad 4-8$$

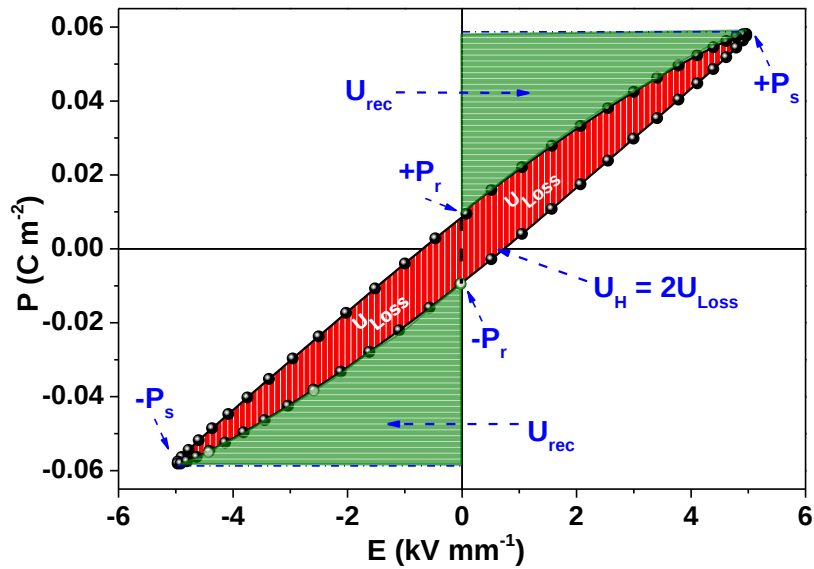


Figure 4.6 Typical P-E hysteresis loop for glass-modified KNN, illustrating the calculation of U_{rec} (green areas) and U_H (red area). Limits of integration are defined by the P_s and P_r values indicated on the figure. U_{rec} values were determined as an average of the results obtained from the positive and negative segments.

5. Results and discussion

5.1 Development of barium borosilicate glass systems

The ternary system of BaO-B₂O₃-SiO₂ was modified by CuO, Na₂O and K₂O as well as Bi₂O₃-ZnO in order to firstly, obtain a reduced melting temperature for the glass and subsequently to improve the physical characteristics of the sintered ceramics, such as the density and the dielectric properties. Secondly, the CuO and Bi₂O₃-ZnO were employed to produce glasses suitable for sintering KNN ceramics. Thus, the fabrication of glasses having low melting temperatures was required to improve the ceramic density by removing the microstructural defects and reducing the sintering temperature. Four types of glasses (G1-G4), presented in Table 4.1, were added into ceramic systems as sintering aids, as will be discussed in this section.

5.1.1 Physical appearance and density

The physical appearances of the BBS glass systems, G1 to G4, are summarised in Table 5.1. It is evident that both G1 and G2 are fully transparent, while G3 and G4 have black and yellow appearances due to the presence of CuO and Bi₂O₃ additives, respectively. The measured densities of the BBS glass systems also are shown in Table 5.1. It can be seen that the densities of G2 and G3 are lower than that of G1 due to the incorporation of K₂O, Na₂O and CuO additives, while G4 has the highest density due to the presence of Bi₂O₃ and ZnO, which is in general agreement with the results of Chen et al [117].

The preparation temperatures of glasses (determined experimentally) and the working point (determined experimentally and using DSC) are presented in Table 5.1. Here, the working point (T_w) is the temperature at which a glass is easily deformed, which is related to its viscosity [2]. Note that these temperatures decrease in the order G1 to G4.

Table 5.1 The physical properties of BBS glass systems.

physical appearances	Sample	Density g cm^{-3}	Preparation $T/^{\circ}\text{C}$	Working point $T/^{\circ}\text{C}$
	G1	4.117 ± 0.17	1140	860 ± 10
	G2	2.876 ± 0.12	1050	790 ± 10
	G3	3.121 ± 0.13	1000	680 ± 8
	G4	6.284 ± 0.21	900	600 ± 8

The theoretical density of the pure crystalline ceramics (BT, BCZT, KNN and KBN) phase prepared with different ceramic:glass ratios are shown in Figure 5.1 (a)-(d). These densities were calculated according to the method described in section 4.6.1. It is evident that the addition of either G1 or G2 glasses leads to a reduction in the theoretical density of BT/BCZT-based ceramics, due to the presence of the light metal oxides. A similar effect is shown for the influence of G3 on the densities of KNN and KBN in Figure 5.1 (c)-(d). However, the opposite trend occurs for the KNN/KBN-based ceramics combined with G4 due to the relatively high density of this glass.

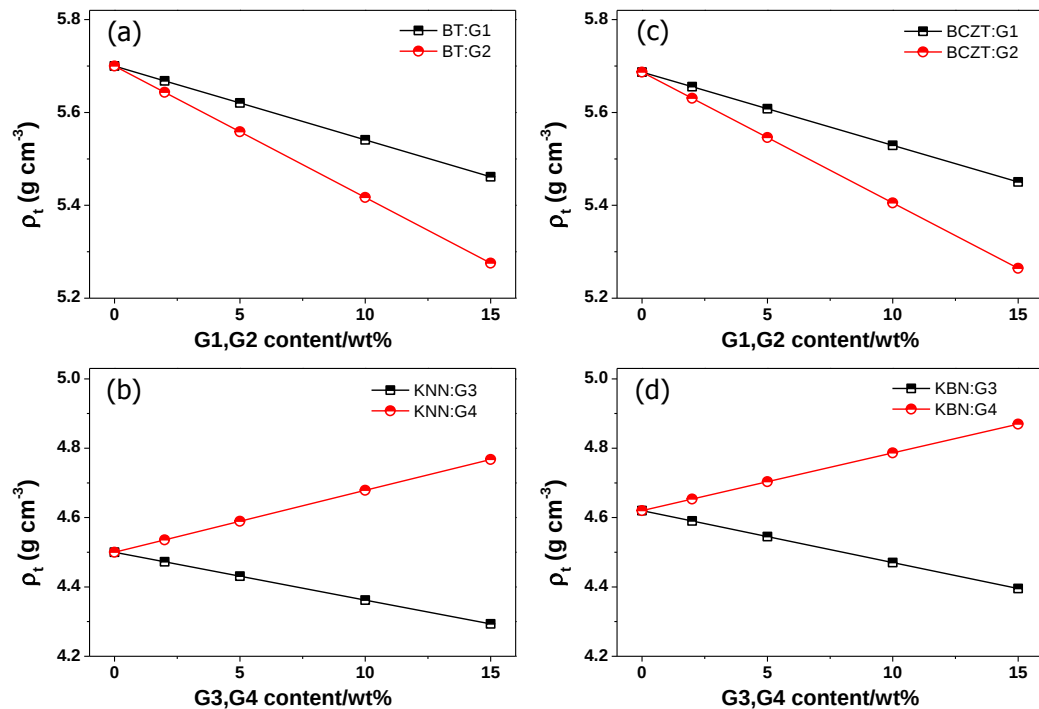


Figure 5.1 The theoretical density of ceramic:glass compositions, (a) BT:G1,G2, (b) BCZT:G1,G2, (c) KNN:G3,G4 and (d) KBN:G3,G4.

5.1.2 Lab XRD results

XRD results for BBS glass systems as a function of preparation temperature and glass modifier are presented in Figure 5.2 and Figure 5.3. In this case, the glasses were prepared by quenching in the air after melting at a temperature in the range 900 °C to 1140 °C with a holding time between 30 and 90 min.

XRD patterns obtained for G1 at temperatures ranging from 1040 °C to 1140 °C are illustrated in Figure 5.2 (a). For temperatures up to 1100 °C it can be seen there are still some diffraction peaks associated with the crystalline precursor oxides; this is also indicated by the opaque white appearance of the glass, as shown in Figure 5.2 (b). On increasing the temperature up to 1140 °C, these peaks are no longer present in the pattern, leaving broad bands that indicate an amorphous glassy state.

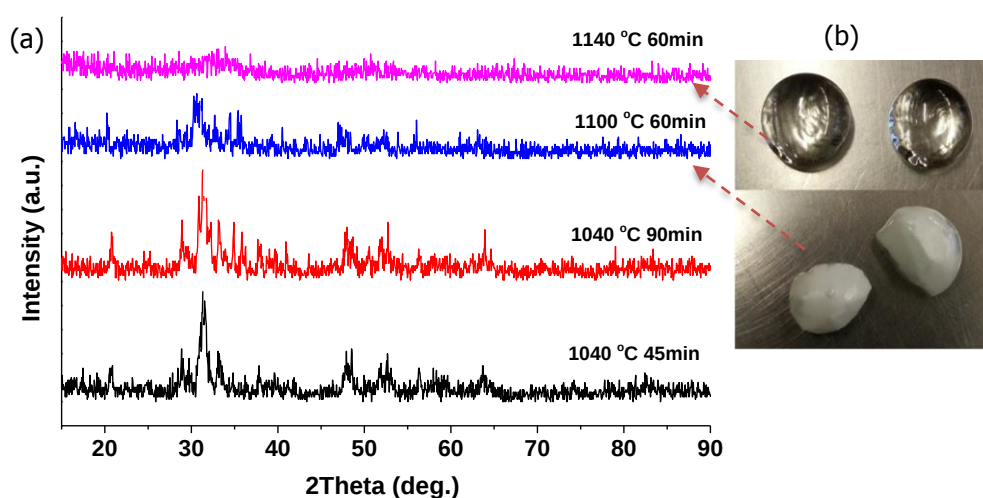


Figure 5.2 (a) XRD patterns of BBS glass system prepared at temperatures from 1040 to 1140 °C for different annealing times and (b) physical appearances after annealing at 1100 °C and 1140 °C for 60 min.

The XRD results of glasses G2, G3 and G4 are shown in Figure 5.3; these were prepared after annealing at 1050 °C for 60 min, 1000 °C for 30 min and 900 °C for 90 min, respectively. The results for each of these glasses indicate a fully amorphous state.

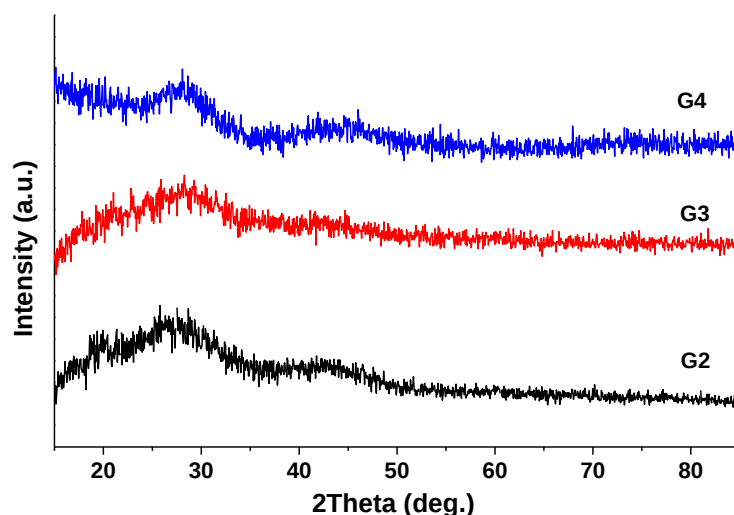


Figure 5.3 XRD patterns of G2, G3 and G4 glass system prepared at temperatures of 1050 °C/60 min, 1000 °C/30 min and 900 °C/90 min, respectively.

5.1.3 Dielectric properties

The electrical properties of G1-G4 are presented in Table 5.2. Uncertainties were estimated based on the likely stray capacitance (≈ 0.1 pF) and the resolution in phase angle measurement for the instrument. The relative permittivity of the glasses clearly decreased with the addition of K_2O , Na_2O and CuO for both G2 and G3, while it increased for G4 due to the presence of Bi_2O_3 .

It is well known that the high relative permittivity (from 8 to 11 as a function of BaO content, as reported by Lim et al. [101]) of glasses containing barium oxide can be attributed the high polarizability of the large Ba^{2+} cation [101, 103]. For this reason, the replacement of Ba^{2+} by K^+ and Na^+ , in the case of G2 or G3, leads to a reduction in relative permittivity. On the other hand, the high polarizability of Bi^{3+} and Zn^{2+} leads to a higher relative permittivity for G4 [99, 106].

Table 5.2 Dielectric properties of G1-G4 glasses. Numbers in parentheses represent estimated uncertainties in the last significant digit(s).

Sample	Dielectric properties at 100 kHz, 25 °C	
	ϵ_r	$\tan\delta$
G1	10.5(4)	0.013(1)
G2	7.4(4)	0.017(1)
G3	6.4(5)	0.020(1)
G4	24.3(4)	0.008(1)

5.1.4 Thermal analysis

Differential scanning calorimetry (DSC) results for glasses G1-G4 are presented in Figure 5.4. All the samples were heated up to 900 °C at a heating rate of 10 °C/min. These curves show significant differences in their characteristics, depending on composition. The T_g shifted to lower temperatures, from approximately 570 °C to 490 °C, as the K_2O , Na_2O and CuO additives increased in G2 and G3, respectively. The T_g for G4 was considerably lower at approximately 380 °C. The working points (T_w) of G1-G3 glasses shown in Table 5.1 are in general agreement with the DSC curves. The incorporation of these ions leads to modification and weakening of the glassy network causing reductions in both melting and crystallization onset temperatures [168, 169].

It is interesting to note that the glasses also showed additional peaks in the DSC curves that might be associated with recrystallisation. This could also have some influence on the microstructures of the sintered ceramics, which was observed in the case of the KNN ceramics prepared with glass additives 5.4.2 below.

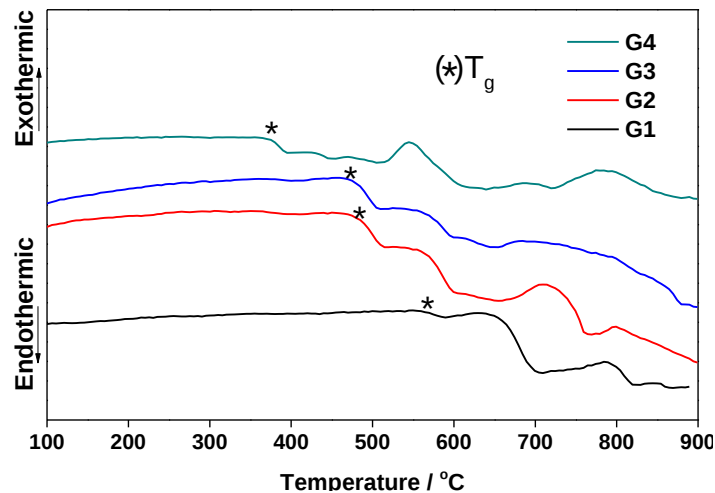


Figure 5.4 The DSC trace of G1-G4 glasses showing endothermic and exothermic peaks for heating cycle.

5.1.5 Summary

Different types of barium borosilicate (BBS)-based glass systems have been prepared successfully using conventional melting and quenching. The glass types G1 and G2 were prepared as sintering aids for BT/BCZT ceramics, while G3 and G4 were prepared for use with KNN/KBN ceramics. Variations in the ionic radii and polarizabilities of the elements present in each glass caused changes in the relative permittivity, which could play a role in determining the dielectric properties of the sintered ceramics.

5.2 Glass-modified BaTiO₃ ceramics

BaTiO₃ ceramics have been widely investigated due to their high relative permittivity and good thermal stability, leading to applications in multilayer ceramic capacitors, MLCCs, and low temperature co-fired ceramics, LTCCs. It is well known that the manufacture of MLCCs at low cost requires the use of base metal (e.g. Ni) internal electrodes, which demands the use of low sintering temperatures and reducing atmospheres [170]. Nevertheless, pure BT is generally sintered at temperatures above 1200 °C, which can restrict its use in MLCC and/or LTCC. Therefore, it is very important to reduce the sintering temperature of BT-based materials [13, 171].

In this chapter, BT ceramics are sintered at relatively low temperatures by using the G1 and G2 glasses. The influence of these additives on densification, microstructure and dielectric properties of BT will be discussed. The glasses were added to the calcined BT powder in varying proportions (1-x) BT-xG1, G2 with x=2, 5 and 10 wt%.

5.2.1 Relative density analysis

The densities of pure BT ceramics sintered at different temperatures are shown in Figure 5.5. The values of the relative density increased from approximately 61 to 93 % as the sintering temperature increased from 1100 to 1300 °C, similar to results obtained previously for pure BT [53].

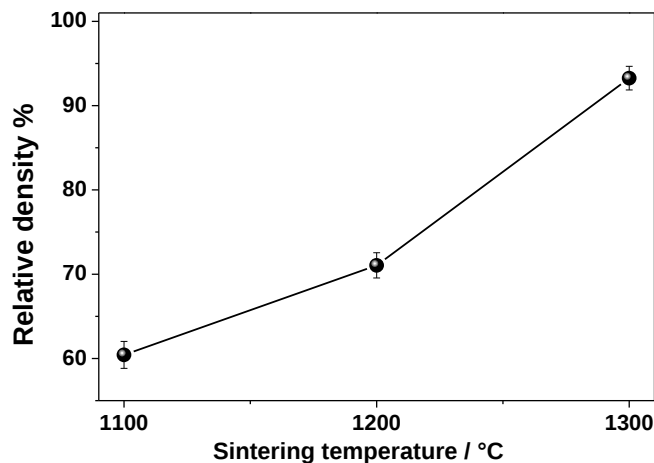


Figure 5.5 The relative density of BT ceramic sintered at temperatures from 1100 to 1300 °C.

The influence of glass content and sintering temperature on the relative densities of the BT-G1 and BT-G2 ceramics are shown in Figure 5.6 (a)-(b), respectively. Note that the figure insert shows the changes in theoretical density of the ceramic-glass composites with glass content, calculated using the method described in section 4.6.1 above.

It can be seen the theoretical density of the ceramic-glass composites decreased with increasing glass content. For a sintering temperature of 1100 °C, the relative density achieved was no more than 82 % for all samples. Then with increasing sintering temperature, the relative density increased to approximately 95 % for BT-2G1 sintered at 1100 °C and BT-5G2 sintered at 1200 °C, which are agreement with those results reported by Lin et al [116]. Generally, the relative density decreased slightly for high G1 contents above 2 wt%, while with G2 it increased from 2 to 5 wt% but decreased slightly at higher values. Higher sintering temperatures generally improved densification.

The reduction in density for the BT-G1 ceramics at glass levels of 5 wt% and above could be a result of compaction defects, if the glass phase acted to prevent particle rearrangement processes during pressing. Some evidence was found to support this interpretation from the microstructural examination presented in section 5.2.3 below.

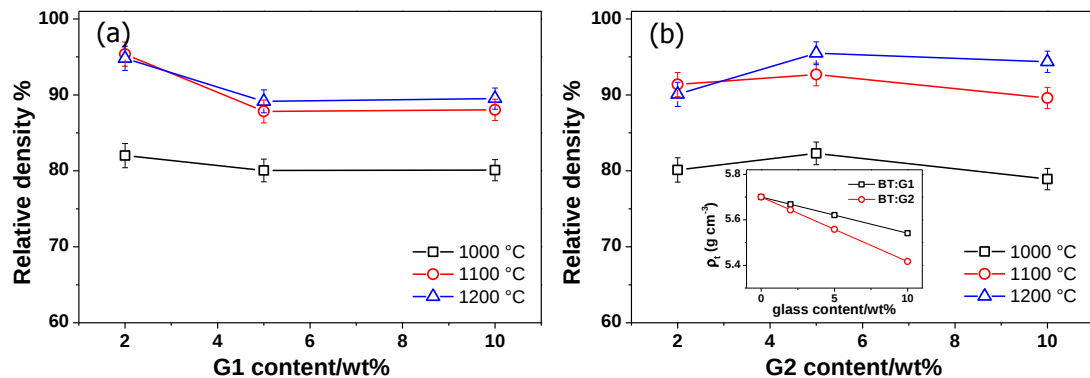


Figure 5.6 Influence of glass content on the relative density for (a) BT-xG1 and (b) BT-xG2 sintered at 1000-1200 °C, with x=2, 5 and 10 wt%. The inserted figure is theoretical density of BT-(G1, G2) ceramic-glass composite as a function of the BBS content.

5.2.2 Lab XRD results

The XRD patterns of pure BT powders calcined at temperatures from 700 to 900 °C are presented in Figure 5.7. Three phases, comprising TiO_2 , BaCO_3 , and BT, were detected at 700 °C, consistent with the precursor oxides. The BT crystal phase started to form at 800 °C while, at the same time, significant decreases in the intensities of the peaks associated with BaCO_3 and TiO_2 were observed. A pure perovskite BT phase was obtained at 900 °C and the intensity of the BT peaks gradually increased. No significant peak splitting was observed at this stage, suggesting that the powder was poorly crystalline and appeared to be a globally cubic. Similar observations concerning

particle size effects in BaTiO₃ have been made previously and are generally attributed to surface defects, which become more dominant at small particle sizes [172].

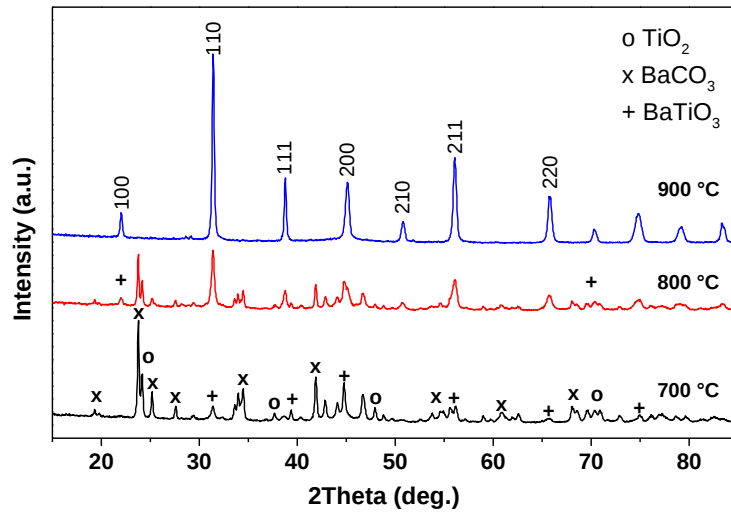


Figure 5.7 XRD patterns of BT powders calcined at 700, 800 and 900 °C. Precursor oxide phases are labelled as (o) TiO₂, (x) BaCO₃ and (+) BT, while the Miller indices indicate the formation of the pseudo-cubic perovskite phase at 900 °C.

The XRD patterns of BT after sintering at temperatures of 1200 and 1300 °C are shown in Figure 5.8. It can be seen, that the diffraction peaks corresponding to the perovskite phase are narrower, indicating improved crystallinity, and show evidence of splitting associated with the formation of the tetragonal phase. For example, the {200} peak at 1300 °C comprises both (002) and (200) peaks, corresponding to the tetragonal c- and a- axes, respectively.

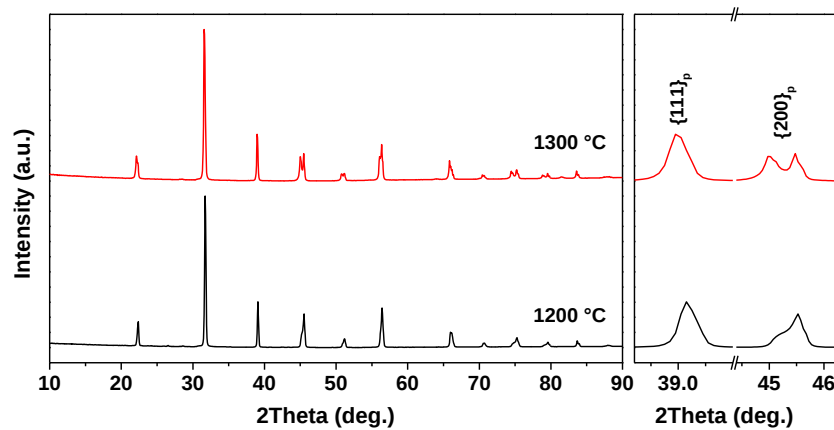


Figure 5.8 XRD patterns of pure BT ceramic sintered at temperatures of 1200 and 1300 °C.

The effect of the glasses G1 and G2 on the crystallinity of BT ceramics is illustrated by the results presented in Figure 5.9, which shows the XRD patterns obtained for BT-5G1 and BT-5G2 sintered at temperatures in the range from 1000 to 1200 °C. In this case,

all ceramics mainly present the tetragonal perovskite phase without any secondary phases. In addition, it is evident that narrowing of the diffraction peaks and clear peak splitting occurred at temperatures as low as 1000 °C, indicating the development of a highly crystalline BaTiO₃ phase. Similar results were obtained at higher glass contents up to 10 wt%, which confirms that the G1 and G2 glasses are stable and show good compatibility with BaTiO₃-based ceramics.

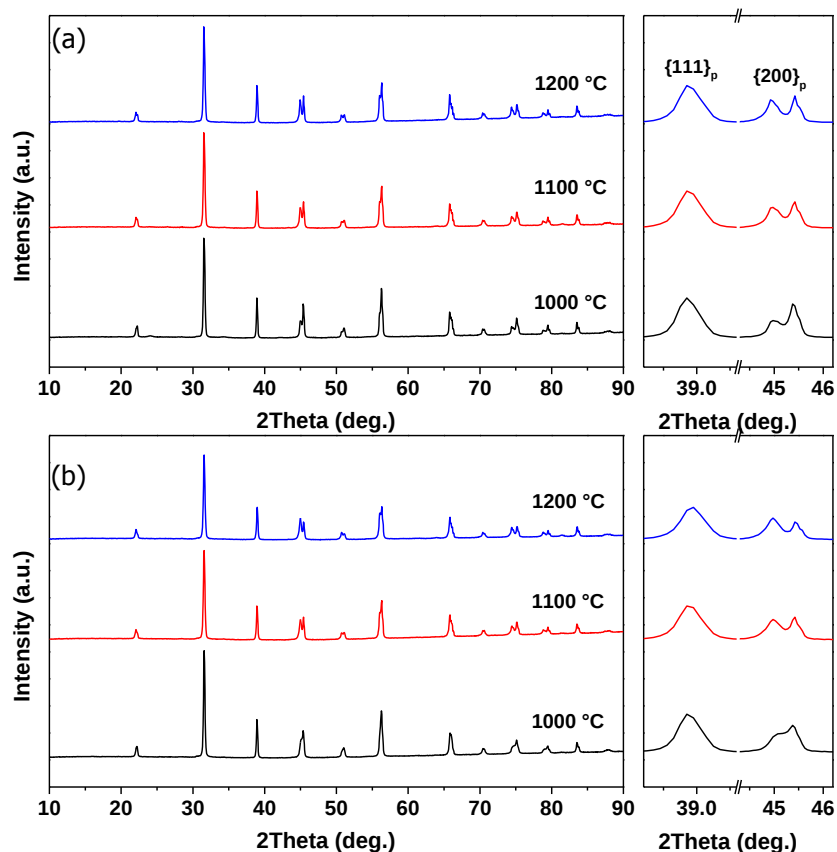


Figure 5.9 XRD patterns of (a) BT-5G1 and (b) BT-5G2 ceramics sintered at 1000-1200 °C.

The results of full-pattern fitting for pure BT sintered at 1300 °C, shown in Figure 5.10 (a), indicate that the pure BT comprised tetragonal phase [15]. The addition of 5 wt% G1 and G2 glasses, Figure 5.10 (b)-(c), yielded similar results and had little impact on the crystallographic parameters, as summarised in Table 5.3.

The presence of the single-phase tetragonal structure is in agreement with the dielectric property measurements, as described below in section 5.2.4 which indicate the occurrence of a single phase transition, from tetragonal to cubic, on heating above room temperature [15]. Furthermore, it is evident that the addition of the BBS glasses to BT did not significantly affect the structural parameters; the *c/a* ratio increased slightly from 1.008 to 1.009 with the addition of 5 wt% BBS glass. Therefore it is

unlikely that there was any inter diffusion of the components of the glass into the BaTiO₃ lattice, unlike the results reported by Hsianga et al who observed the formation of second phases when various glass systems were added to pure BT [5].

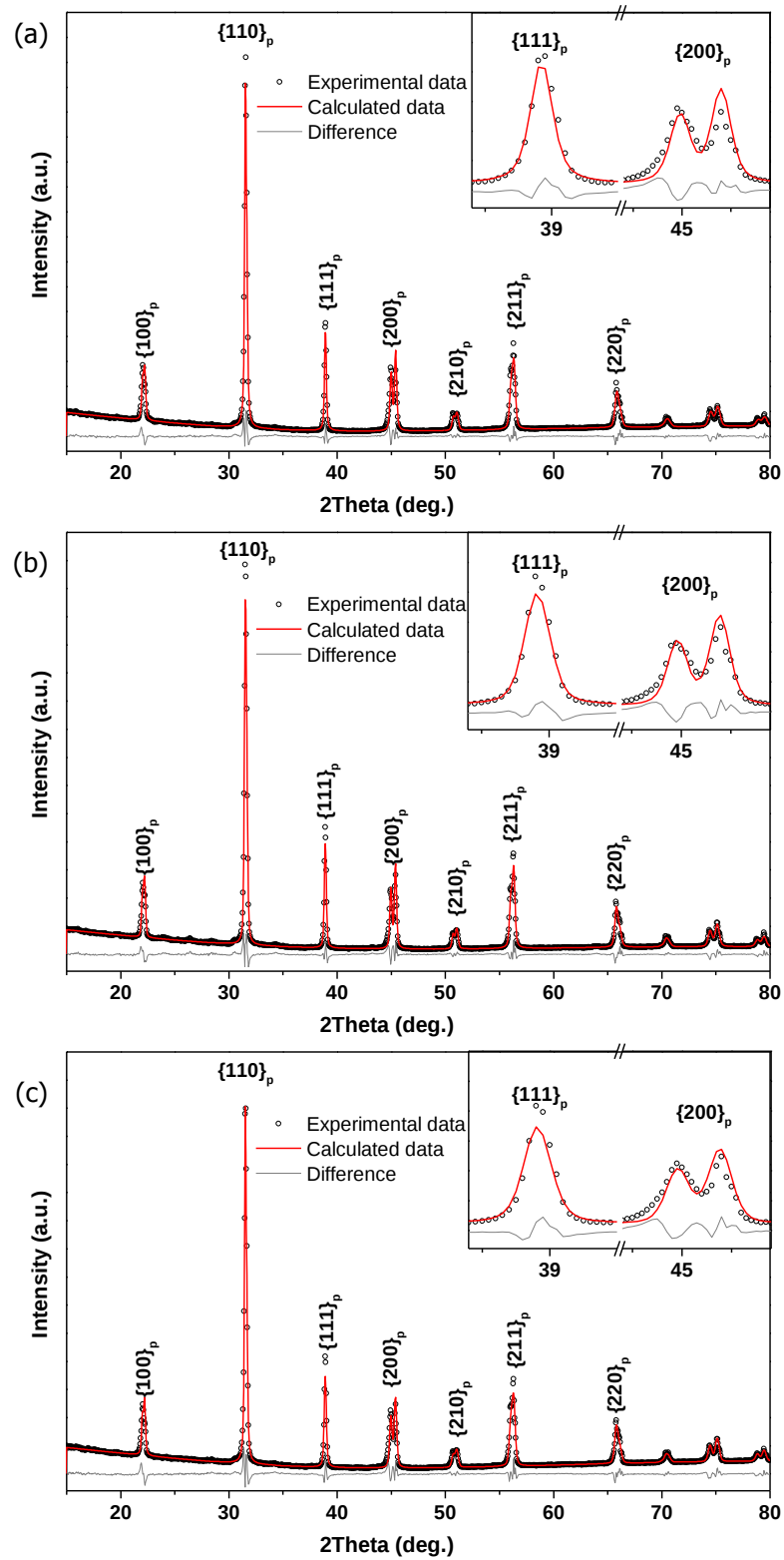


Figure 5.10 Comparison of experimental and calculated XRD peak profiles of (a) pure BT ceramic sintered at 1300 °C, (b) BT-5G1 ceramic and (c) BT-5G2 ceramic sintered at 1100 °C.

Table 5.3 Phase fractions, lattice parameters, χ^2 and R_{wp} of BT ceramics. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

Composition	Phase fraction (%)	Lattice parameter			χ^2	R_{wp}
		a (Å)	b (Å)	c (Å)		
Pure BT/1300°C	T = 100	$a_T = 3.9920(4)$	--	$c_T = 4.0273(3)$	4.69	8.08
BT-5G1/1100 °C	T = 100	$a_T = 3.9968(3)$	--	$c_T = 4.0329(1)$	4.56	8.63
BT-5G2/1100 °C	T = 100	$a_T = 3.9965(2)$	--	$c_T = 4.0325(3)$	4.73	8.48

5.2.3 Microstructure analysis

The microstructure analyses for BT-pure ceramics and BT sintered with glass are shown in this section in order to understand the influence of the glasses on microstructure and subsequently on the electrical properties.

The SEM micrographs obtained for pure BT ceramics sintered at 1200 and 1300 °C are presented in Figure 5.11. It is noticed that the ceramic sintered at 1200 °C has a fine grain size ($<1 \mu\text{m}$) and is highly porous, consistent with the low relative density ($\approx 70\%$). At the higher sintering temperature, the grain size has increased to around $6.4 \pm 1.8 \mu\text{m}$ and the density improved to $\approx 93\%$. The remaining pores are both inter- and intra-granular, with the inter-granular pores being larger (approximately 2 to $4 \mu\text{m}$).

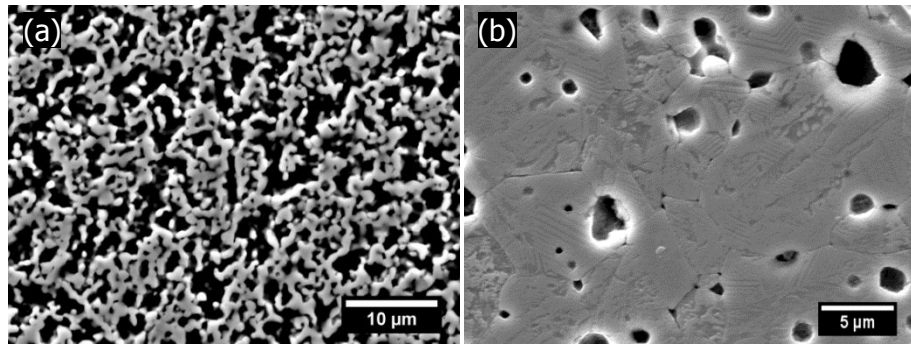


Figure 5.11 SEM micrographs for BT ceramics sintered at (a) 1200 °C and (b) 1300 °C.

The effects of the glass additives on the microstructures of the BT ceramics are illustrated by the SEM micrographs presented in Figure 5.12. There is generally an increase in the grain size with the addition of G1 glass additive; the average grain sizes were determined as approximately 8.1 ± 1.1 , 8.9 ± 2 and $10.3 \pm 2.6 \mu\text{m}$ for 2, 5 and 10 wt% G1, respectively. Also, the grain sizes are noticeably larger than those of pure BT sintered at the same temperature. The presence of the glassy phase between the BT grains is also clearly apparent in these micrographs; the identity of this phase is

confirmed in Figure 5.15 below. In contrast, the increase in G2 glass content led to a slight reduction in grain size, from $\approx 9.6 \pm 1.7$ to 6.1 ± 0.5 μm . Interestingly, the presence of a needle-like second phase was also observed in the G2-modified BT ceramics, which could be associated with the K_2O and Na_2O content in G2 [107].

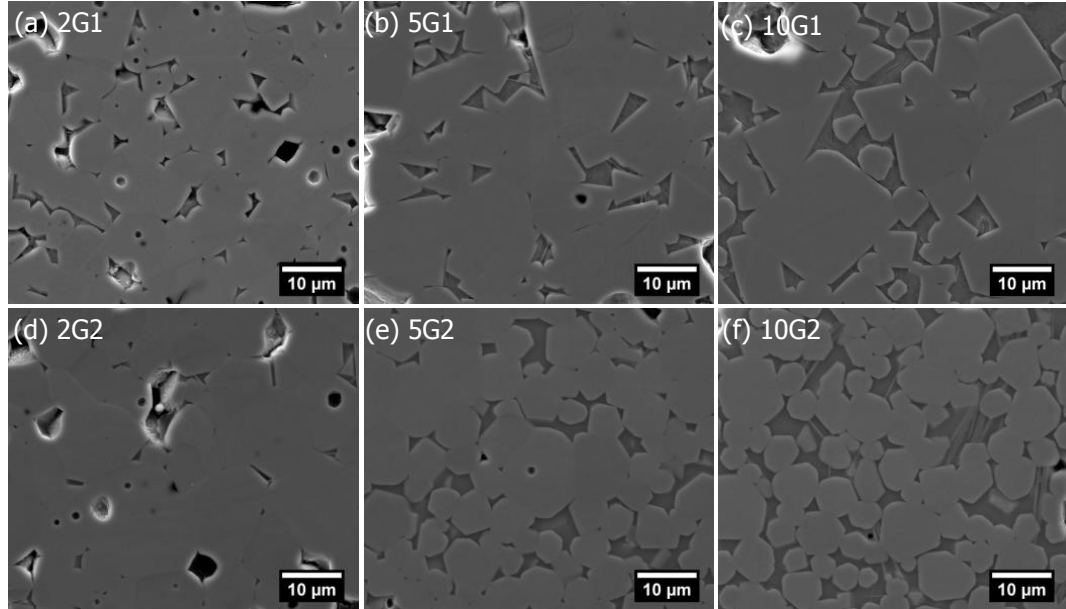


Figure 5.12 SEM micrographs for (a)-(c) BT-G1 and (d)-(f) BT-G2 ceramics sintered at 1200 °C.

The effect of the sintering temperature on microstructure for BT sintered with 5G1 and 5G2 is illustrated by the SEM micrographs shown in Figure 5.14. The reduction of porosity and increase in grain size as the sintering temperature increases from 1000 °C to 1200 °C is clearly evident. The densification process for G1 and G2 appears to be similar, although the final grain sizes are larger for G1. Furthermore, the final microstructures show that the grain-glass interfaces in BT-G1 are mostly flat whereas those in BT-G2 have a more rounded appearance. The rounded shapes of the grains are attributed to the presence of the liquid phase during sintering, which allows the surfaces to adopt an equilibrium state defined by the surface energies [173]. The re-entrant angle for the interface between grain boundary and liquid phase at equilibrium is given by:

$$\gamma_{SS} = 2\gamma_{SL} \cos \frac{\phi}{2} \quad 5-1$$

Here, γ_{SS} and γ_{SL} are the solid-solid and solid-liquid interface energies, respectively as illustrated in Figure 5.13 below.

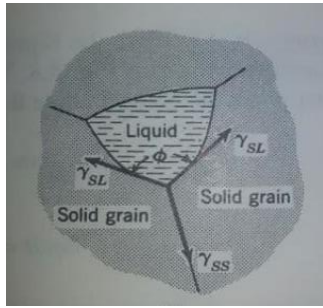


Figure 5.13 Dihedral angle at equilibrium where a grain boundary meets a surface [173].

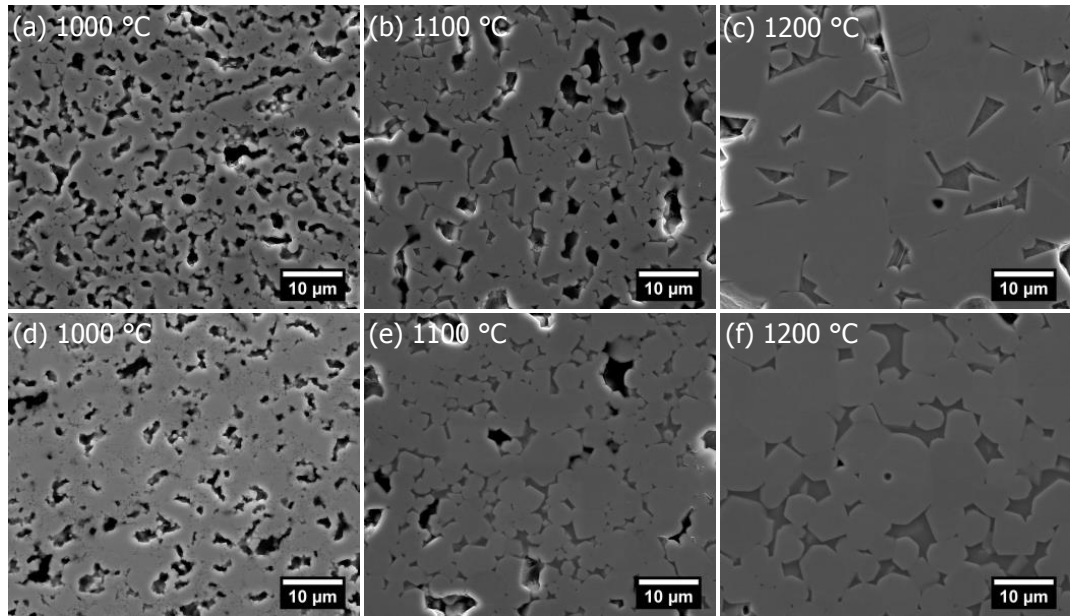


Figure 5.14 SEM micrographs for (a)-(c) BT-5G1 sintered at 1000-1200 °C and (d)-(f) BT-5G2 sintered at 1000-1200 °C.

Energy-dispersive X-ray spectroscopy (EDS) was used to create elemental maps of Ba, Ti and Si, to illustrate their spatial distributions, yielding the results shown in Figure 5.15. In both cases, for BT-G1 and BT-G2, the results confirm that the elements Ba and Ti are concentrated in the crystalline BT grains while Si is present in the glassy phase between the grains, as expected.

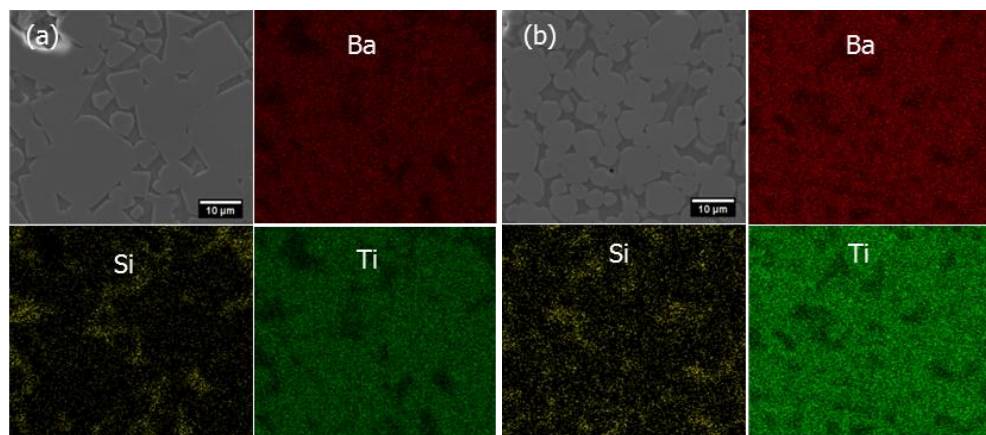


Figure 5.15 SEM micrographs and EDS mapping for (a) BT-5G1 and (b) BT-5G2 sintered at 1200 °C.

5.2.4 Temperature-dependence of dielectric properties

5.2.4.1 Dielectric properties of pure BT

The temperature-dependence of relative permittivity and loss tangent for BT ceramics sintered at 1200 and 1300 °C are shown in Figure 5.16. The tetragonal-cubic phase transformation at the Curie temperature, T_c , around 130 °C gives rise to a sharp peak in relative permittivity for the sample sintered at 1300 °C, with a value at room temperature around 1800, which is comparable with that reported in previous publications for relatively coarse-grained BaTiO_3 [174]. In contrast, a much lower relative permittivity (less than 500) and a broad peak were obtained for a sintering temperature of 1200 °C; this behaviour can be understood in terms of the poor densification, high porosity and fine particle size of the pure BT ceramic sintered at relatively low temperatures. The poorly crystalline nature of the ceramic sintered at 1200 °C also gives rise to a diffuse phase transformation in contrast to the sharp transition of the coarse-grained ceramic sintered at 1300 °C.

For both of the sintering temperatures, the increase in loss tangent below the Curie point is attributed to the appearance of ferroelectric domains with an associated domain wall loss mechanism [175]. An additional increase in loss at low temperatures is apparent for the low-temperature sintered ceramic; this could be caused by the presence of adsorbed atmospheric moisture within the continuously-connected internal porosity, which gradually evaporates on heating.

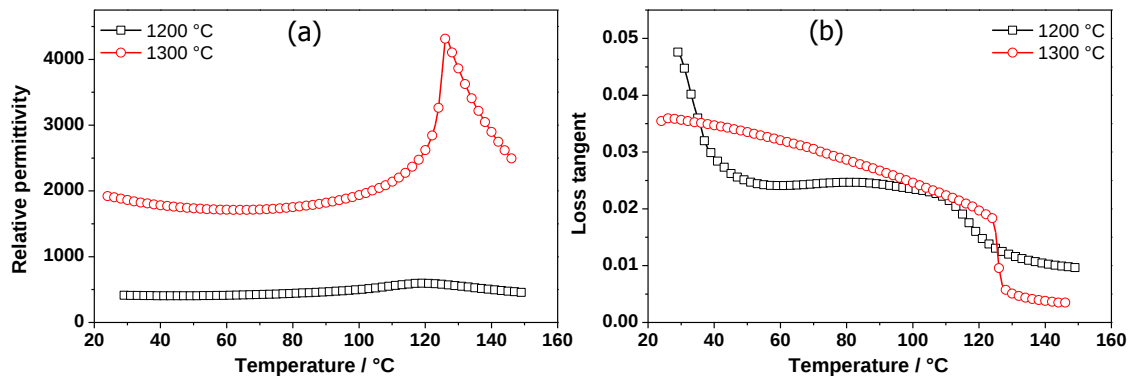


Figure 5.16 (a) Relative permittivity and (b) loss tangent as a function of temperature for BT sintered at 1200 and 1300 °C measured at a frequency of 100 kHz.

5.2.4.2 Temperature-dependence for glass-modified BT

The influence of the glass additives on the dielectric behaviour of BT ceramics is illustrated by the results presented in Figure 5.17 to Figure 5.19, which show the temperature-dependence of relative permittivity and loss for BT-G1 and BT-G2

ceramics prepared using various sintering temperatures (1000 to 1200 °C) and glass contents (2 to 15 wt%). Quantitative analysis of these results (and those for BCZT presented in section 5.3 below) is hindered by their dependence on the 3 main microstructural features of porosity, glass content and grain size, which are all inter-related and dependent on processing conditions.

In general, it is anticipated that the relative permittivity should increase as porosity reduces as a result of the low relative permittivity of the gas phase ($\epsilon_r \approx 1$). The presence of the glass phase enhances densification, thereby reducing porosity and increasing relative permittivity, but also causes a reduction in relative permittivity due to the low relative permittivity of the solidified glass ($\epsilon_r \approx 7.5$ to 10.5). The grain size effect is more complex since it is well-established that the room temperature relative permittivity of pure BaTiO₃ ceramics exhibits a peak value ≈ 5000 around a grain size of $0.7 \mu\text{m}$, as noted in section 2.2.1. The relative permittivity reduces at very fine grain sizes due to the presence of surface defects and also reduces at larger grain sizes as the beneficial effect of internal inter-granular stress is lost. Furthermore, the peak in relative permittivity at the Curie point tends to increase in magnitude and shows a sharper transition as the grain size increases above $1 \mu\text{m}$ due to improved crystallinity [176].

The influence of the G1 and G2 glasses on the dielectric properties of BT ceramics, over a range of measurement frequencies, is shown in Figure 5.17. The results obtained for BT-2G1 and BT-2G2 sintered at 1100 °C are similar to those for the unmodified BT ceramic sintered at 1300 °C, showing sharp transitions in both ϵ_r and $\tan\delta$ at the Curie point. The room temperature relative permittivity values are highest for BT-G1, consistent with the higher density and slightly reduced grain size in comparison with pure BT. The slightly lower room-temperature ϵ_r values and the increase in $\tan\delta$ at low temperatures for the BT-G2 ceramic at this sintering temperature are attributed mainly to the higher porosity/lower density.

For both BT-G1 and BT-G2, the recorded Curie temperatures are ≈ 10 °C lower than that of the unmodified BT ceramic. The origin of this effect is not completely clear since it could be caused by disordered grain surface layers, a slight reduction in tetragonal distortion or internal stress in the fine-grained glass modified ceramics [176]. The relative permittivity and Curie temperature values are relatively independent of frequency for both BT-G1 and BT-G2, in contrast to the case of BT ceramics modified with calcium borosilicate glass, which was said to develop a type of

dielectric relaxation behaviour [119]. These results indicate that the barium borosilicate glass used in the present investigation reacts to a lesser extent with the primary crystalline BT phase and therefore is generally more compatible than calcium-containing glasses.

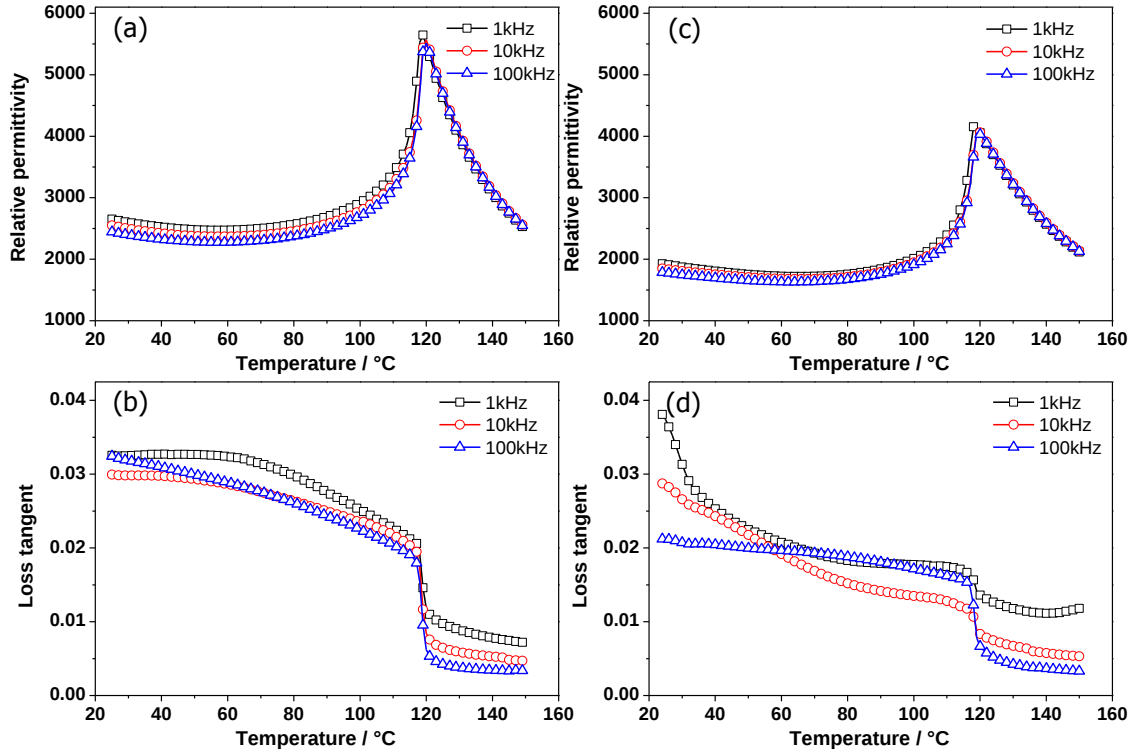


Figure 5.17 ϵ_r -T and $\tan\delta$ -T relationships for (a)-(b) BT-2G1 and (c)-(d) BT-2G2 sintered at 1100 °C, measured at frequencies of 1, 10 and 100 kHz.

5.2.4.3 Influence of sintering temperature for glass-modified BT

The influence of sintering temperature on the dielectric properties of BT-2G1 and BT-2G2 is shown in Figure 5.18. It was found that relative permittivity values generally increased with increasing sintering temperature, due to enhanced densification. However, an apparently anomalous result was obtained for BT-G1 sintered at 1200 °C, which exhibited a lower value than that sintered at 1100 °C. This result can be understood in terms of the dominant grain-size effect in barium titanate ceramics, since the densities of these two materials (5.372 and 5.405 g cm⁻³, respectively) were almost identical i.e. the grain size of BT-G1 (in the range 5 to 10 μm) is closer to the optimum value of 0.7 μm than that of BT-G2. Lower relative permittivity values and a more diffuse phase transition were evident for the materials sintered at 1000 °C, due to their relatively low densities, very fine grain sizes and poor crystallinity.

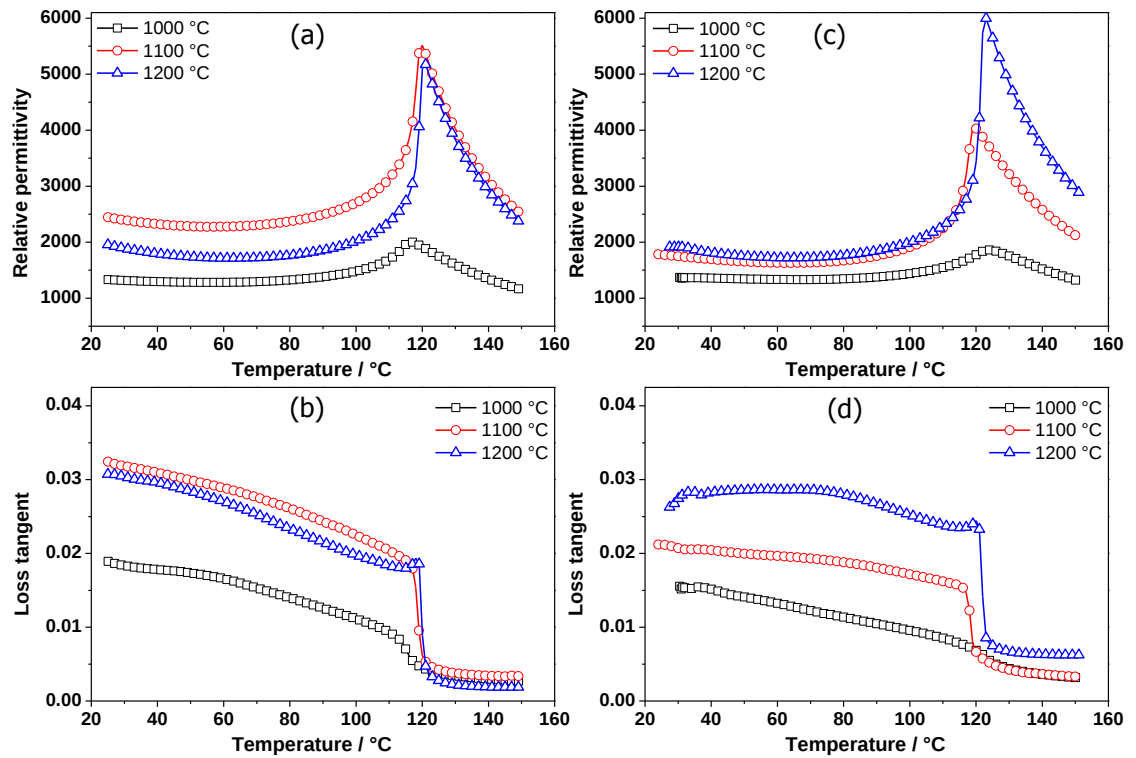


Figure 5.18 Relative permittivity and loss tangent as a function of the temperature for (a-b) BT-2G1 and (c-d) BT-2G2 sintered at 1000 °C-1200 °C measured at frequencies of 100 kHz, respectively.

5.2.4.4 Influence of glass content for glass-modified BT

Increasing glass content generally gave rise to reductions in relative permittivity for BT-G1 and BT-G2 ceramics sintered at 1100 °C, as shown by the results presented in Figure 5.19. The overall trends can be understood in terms of the influence of the low-relative permittivity glass phases since the relative densities of these materials were all in the range 90 to 95 %. An apparently anomalous result was obtained for BT-10G1, which displayed a high relative permittivity ≈ 4000 from room temperature up to the Curie point of 120 °C. This effect is attributed partially to the strong dependence of relative permittivity on grain size in BT ceramics, assuming that the grain size of the BT-10G1 ceramic (in the range 2 to 5 μm) is closer to the optimum level of 0.7 μm than those of the other glass-modified materials.

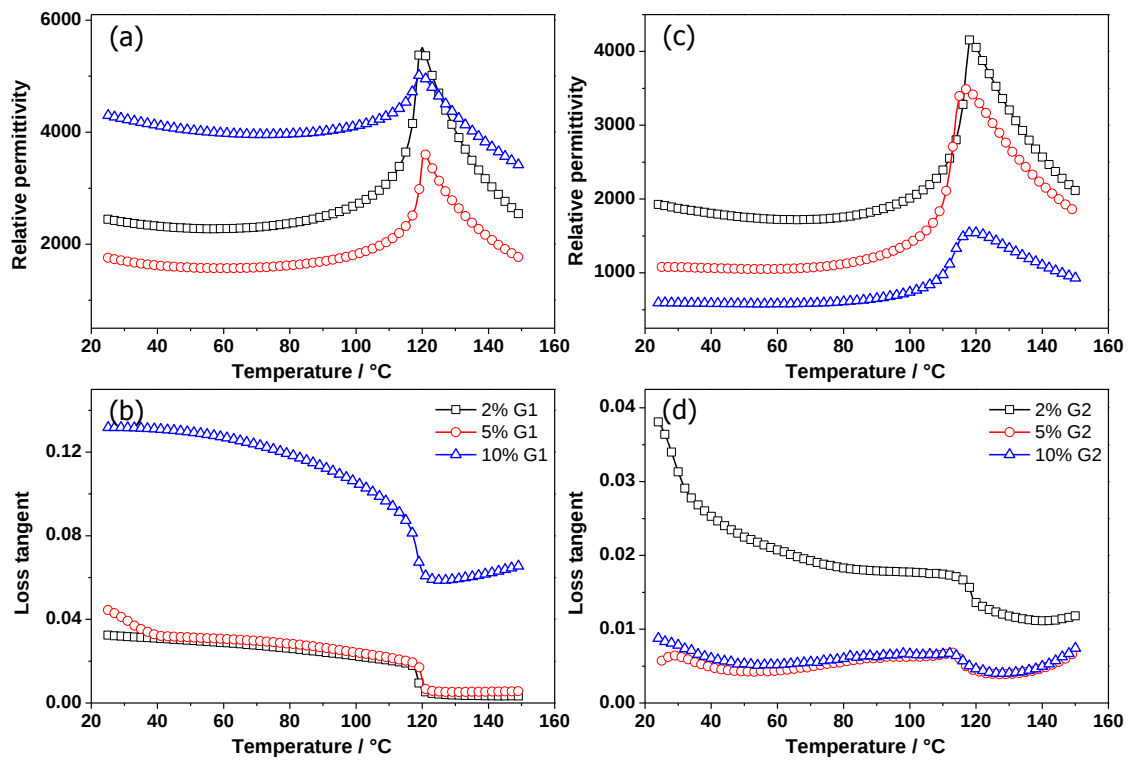


Figure 5.19 Relative permittivity and loss tangent as a function of the temperature for (a-b) BT-xG1 and (c-d) BT-xG2 (x=2, 5 and 10) sintered at 1100 °C measured at frequencies of 100 kHz, respectively.

It was also observed that the dielectric properties of the high relative permittivity BT-10G1 ceramic sintered at 1100 °C exhibited a strong frequency-dependent behaviour and a very high loss tangent (≈ 0.32) at room temperature, as shown in Figure 5.20. This could indicate that the high relative permittivity has its origin in an interfacial polarisation effect caused by a relatively high electrical conductivity. Supporting evidence for this proposal is also found in the loss tangent data, which shows an increase in $\tan\delta$ at low frequencies. It was reported by Hardtl that the conduction contributions to dielectric loss generally show an inverse frequency-dependence [175].

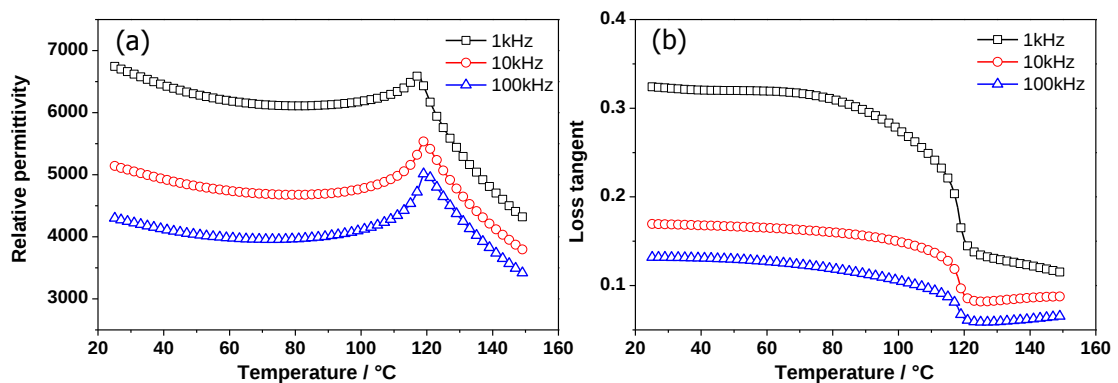


Figure 5.20 (a) ϵ_r -T and (b) $\tan\delta$ -T relationships for BT-10G1 sintered at 1100 °C, measured at frequencies of 1, 10 and 100 kHz.

5.2.5 Ferroelectric properties

The ferroelectric P-E hysteresis loops of the pure BT ceramics sintered at 1200°C and 1300°C are shown in Figure 5.21. The improved densification of the material sintered at the higher temperature gives rise to higher polarisation and lower coercive field values, as expected. The saturation and remanent polarisation values were measured as 0.131 C m⁻² and 0.043 C m⁻², respectively while the coercive field was 0.49 kV mm⁻¹ at a maximum electric field amplitude of 5 kV mm⁻¹, which are similar those reported in the literature for pure BT ceramics [177].

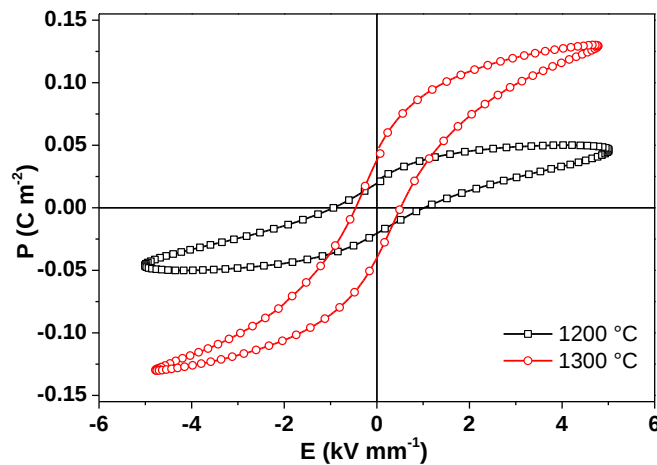


Figure 5.21 P-E hysteresis loops for BT sintered at 1200 and 1300 °C measured at an electric field amplitude of 5 kV mm⁻¹ and frequency 2 Hz.

The influence of the glass additives, G1 and G2, and sintering temperature on the ferroelectric properties of BT ceramics are illustrated by the results presented in Figure 5.22. In common with the dielectric properties reported above, the ferroelectric switching behaviour was generally enhanced by the increase in sintering temperature, yielding increased saturation and remanent polarisation values. The highest P_s and P_r values of 0.175 C m⁻² and 0.066 C m⁻², respectively, obtained for BT-2G1 sintered at 1100 °C, are comparable with those of the pure BT ceramic sintered at 1300 °C.

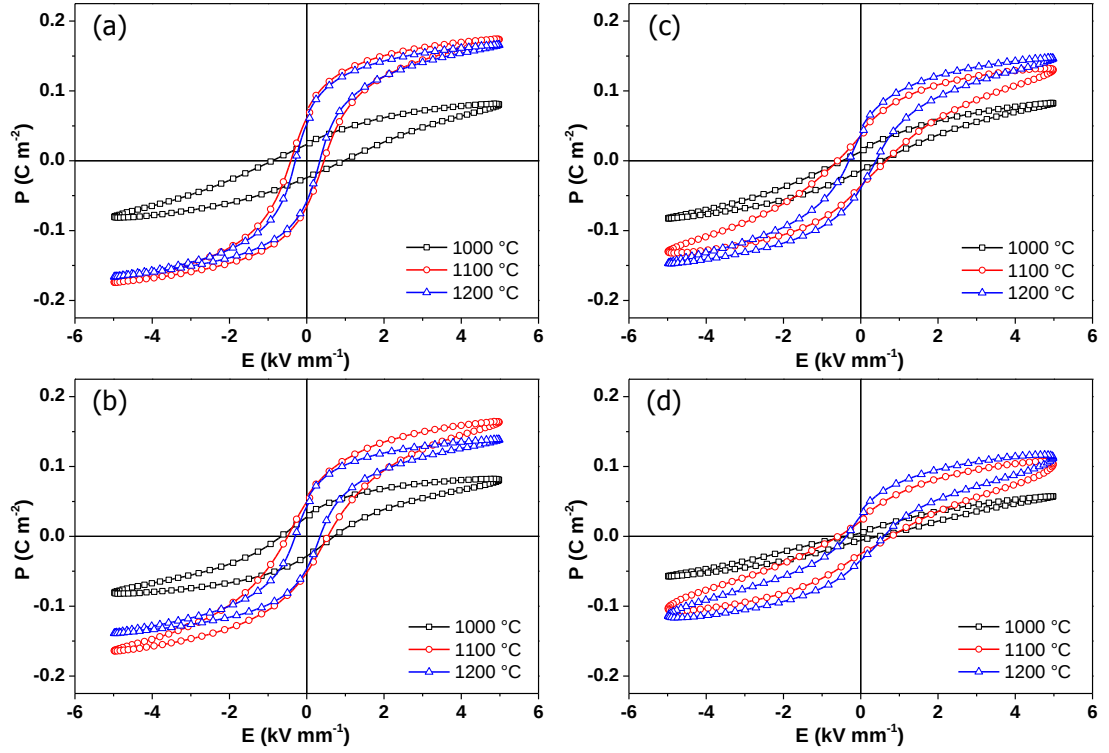


Figure 5.22 P-E hysteresis loops of (a-b) BT-2G1 and BT-5G1, (c-d) BT-2G2 and BT-5G2 sintered at 1000-1200 °C measured at a field of 5 kV mm⁻¹ and frequency 2 Hz.

The effect of glass content on the ferroelectric properties of BT ceramics is shown by the P-E loops presented in Figure 5.23. The increase in glass content generally led to a reduction in polarisation values, which was most pronounced in the case of G2. The latter observation can be correlated with the lower relative permittivity of G2 relative to that of G1 ($\epsilon_r \approx 7.5$ compared with 10.5). The degradation of ferroelectric properties with increasing glass concentration can be understood in terms of the presence of the low-relative permittivity glass phase between ferroelectric BT grains, which acts to partially 'shield' the grains from the externally-applied field, E_a . Assuming a simple series arrangement of the grain and grain boundary regions, the continuity of the dielectric displacement, D , across a grain boundary demands that

$$\epsilon_g E_g = \epsilon_b E_b \quad 5-2$$

where ϵ_g , ϵ_b are the effective relative permittivities and E_g , E_b the electric fields within the grain and grain boundary (or glass phase) regions, respectively. Therefore, the electric field in the boundary region is increased by the ratio ϵ_g/ϵ_b , while the electric field in the grain is reduced by the same ratio. The ratio of E_g to E_a is also affected by the relative thicknesses of the grain and boundary regions, t_g and t_b , as follows

$$\frac{E_g}{E_a} = \frac{\left(1 + \frac{\varepsilon_g t_b}{\varepsilon_b t_g}\right)}{\left(1 + \frac{t_b}{t_g}\right)} \quad 5-3$$

So that the shielding effect is not as drastic as it might seem at first sight. For example, a typical relative permittivity ratio could be 2000/10 (=200) while the thickness ratio would be in the order of 1/20. This yields an apparent reduction of the applied field by a factor of 10, which clearly could have a serious effect on the electric field within grains. However, this very rough estimation neglects the effects of inhomogeneity in microstructure and the associated grain-grain contacts (percolation effects), which can counteract the shielding effect.

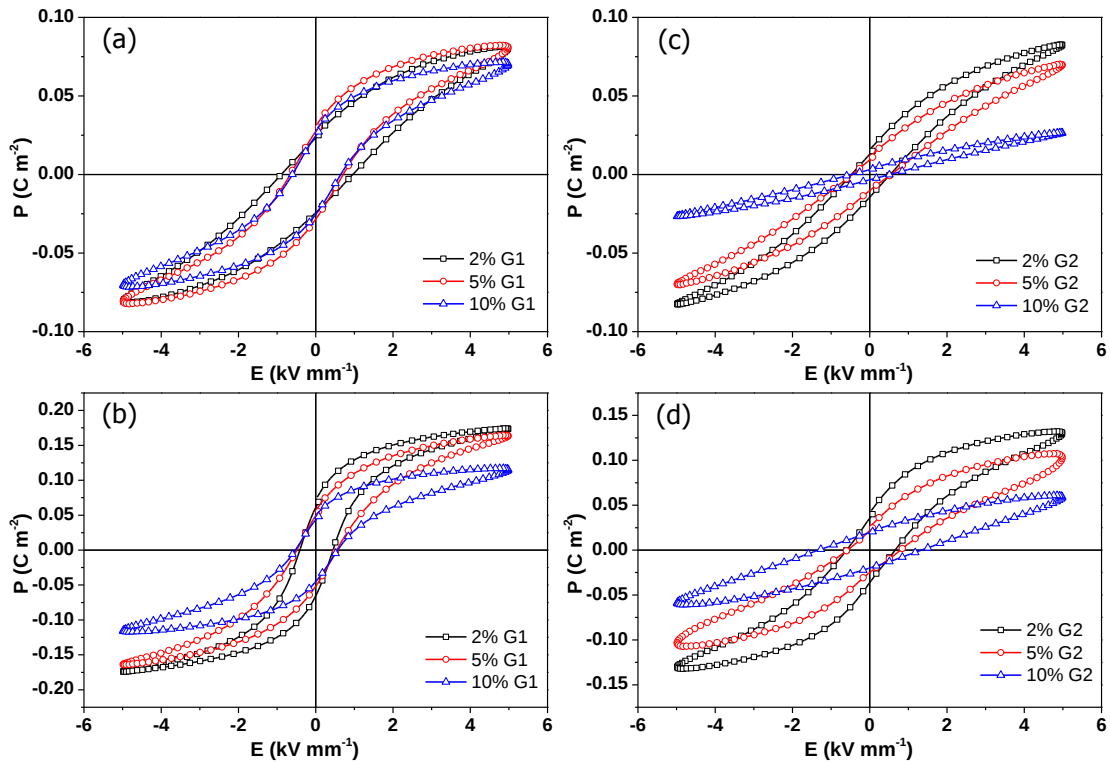


Figure 5.23 P-E hysteresis loops of (a-b) BT- G1 and (c-d) BT-x wt% G2 sintered at 1000 °C and 1100 °C, with an electric field amplitude of 5 kV mm⁻¹ and frequency 2 Hz.

Figure 5.24 shows the variations in P_r and P_s for BT sintered with G1 and G2 additives as a function of the glass content. The P_r and P_s values decreased gradually with increasing glass content but were generally enhanced at higher sintering temperatures. In common with the results for relative permittivity, the BT-G1 ceramics exhibited higher P_r and P_s values than those of BT-G2 as a result of the higher relative permittivity of the G1 glass in comparison with G2. Furthermore, the maximum values

of P_r and P_s were obtained for BT-G1 at a sintering temperature of 1100 °C. This could be associated with the finer grain size and higher relative permittivity obtained at this temperature, as shown in Figure 5.14 and Figure 5.18.

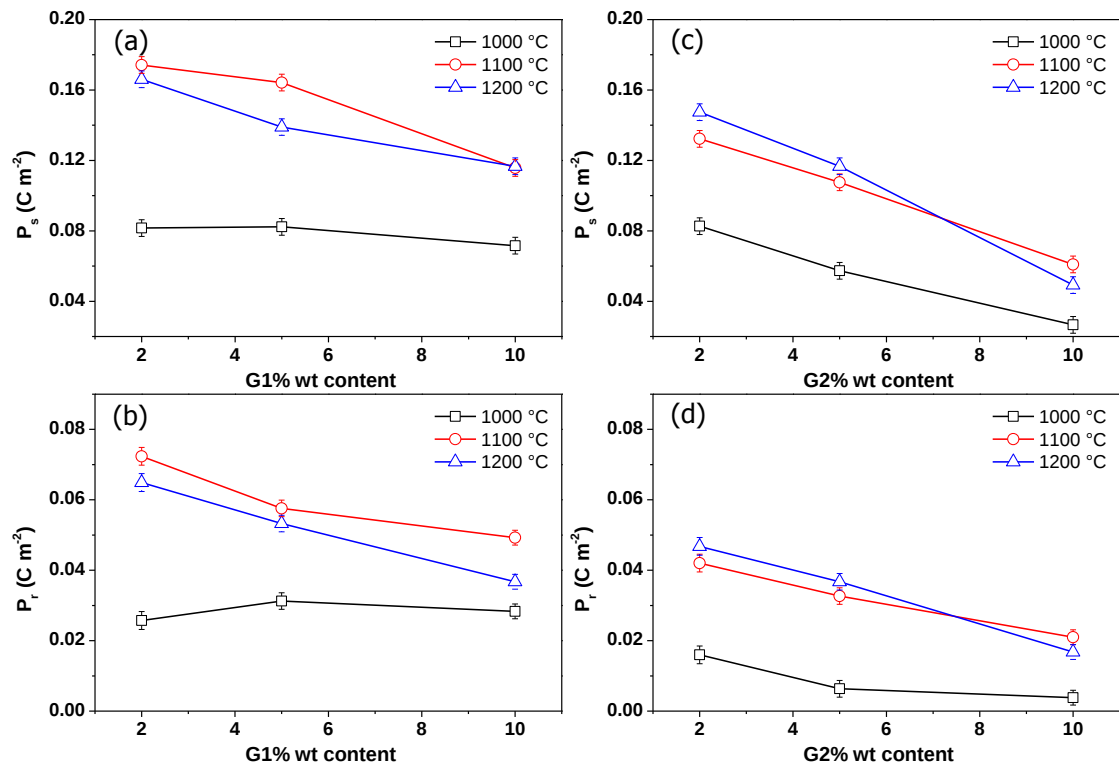


Figure 5.24 Influence of BBS content on P_s and P_r of (a)-(b) BT-G1 and (c)-(d) BT-G2 ceramics sintered at 1000-1200 °C as a function of glass content, measured at a maximum electric field of 5 kV mm⁻¹.

5.3 Pure and glass-modified BCZT ceramics

Recently, there has been significant attention on BCZT ceramics following reports of a high piezoelectric coefficient ($d_{33} \approx 500 \text{ pC N}^{-1}$ at room temperature), described by Liu and Ren [59]. Furthermore, BCZT is considered as an environment-friendly piezoceramic material due to the absence of lead in its composition. Nevertheless, the pure perovskite phase for BCZT is only obtained after heat treatment at high temperatures; calcination is typically performed at approximately 1350 °C and sintering around 1500 °C. The high preparation temperatures associated with BCZT can cause problems during processing and incompatibility with co-fired substrates and electrode materials, for example [60, 62].

In this chapter, the influence of G1 and G2 glasses on the microstructure and dielectric properties of BCZT will be discussed. The glasses were added to the calcined BCZT powder in varying proportions (1-x)BCZT-xG1, G2 with x=2, 5, 10 and 15 wt%, using a sintering temperature in the range 1100 to 1300 °C.

5.3.1 Relative density analysis

The influence of sintering temperature on the relative densities of the pure BCZT ceramics is shown in Figure 5.25. The densities were determined as 81, 84 and 91% for the ceramics sintered at 1300, 1350 and 1400 °C, respectively, confirming that high sintering temperatures are necessary to achieve significant densification of BCZT in the absence of sintering aids [60].

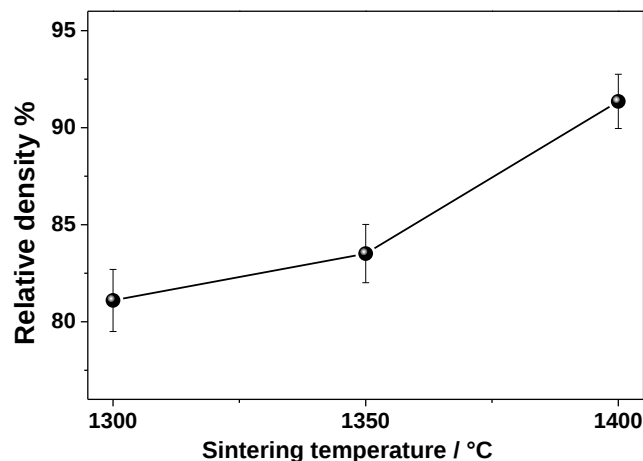


Figure 5.25 the relative density of pure BCZT ceramic sintered at temperatures from 1300 to 1400 °C.

The influence of glass content on the relative densities of the glass-modified BCZT ceramics, sintered at different temperatures, is shown in Figure 5.26. Here, the figure

insert illustrates the changes in theoretical density of the composite BCZT-glass materials as a function of the glass content, calculated according to the method described in section 4.6.1. The relative densities of the BCZT-G1 ceramics sintered at a temperature of 1100 °C were all in the region of 85 % or less, indicating poor densification at such low temperatures. Increasing the sintering temperature to 1200 °C resulted in an increase in relative density to values in the range 91 to 94 %, which suggests that the BBS liquid phase can be considered as an effective sintering aid for BCZT. However, reductions in density were observed at the higher sintering temperature of 1300 °C. The latter effect could be due to volatilisation of B_2O_3 at high temperatures, as reported by Lai [119]. The BCZT ceramics modified with G2 showed generally lower densities, suggesting that the incorporation of Na_2O and K_2O in the BBS glass did not enhance the densification of BCZT ceramics, despite the significant reduction in melting temperature.

For temperatures of 1200 °C and above, the relative density values were moderately independent of BBS content up to approximately 10 wt% BBS. However, significant reductions in density of the BCZT-G1 ceramics were observed for BBS contents beyond this level. The latter effect could be due to volatilisation of B_2O_3 at high temperatures, as reported by Lai [119]. Microstructural observations, described in section 5.3.3 below, indicate that the increased porosity in BCZT ceramics prepared with high BBS contents is predominantly in the form of ($\approx 10 \mu m$) pores associated with compaction defects. The use of improved processing procedures (e.g. the use of lubricants or cold isostatic pressing) could help to prevent the formation of such defects and hence yield further improvements in densification.

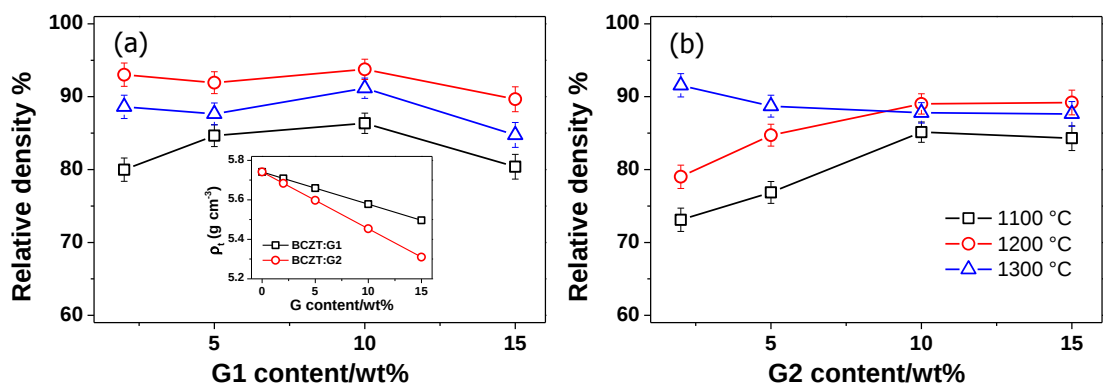


Figure 5.26 Influence of glass content on the relative density for (a) BCZT-xG1 and (b) BCZT-xG2 sintered at 1100-1300 °C, with x=2, 5, 10 and 15 wt%. The inserted figure is theoretical density of the BCZT-(G1, G2) ceramic-glass composite as a function of the BBS content.

5.3.2 Structural studies at room temperature

The XRD pattern of BCZT powder produced by double calcination at 1000 °C for 6 hours is shown in Figure 5.27. It can be seen, that the BCZT perovskite phase is present as the main phase, with a small amount of unreacted CaTiO_3 phase, as reported [178, 179], marked as *. This is due to the low calcination temperature which has been used.

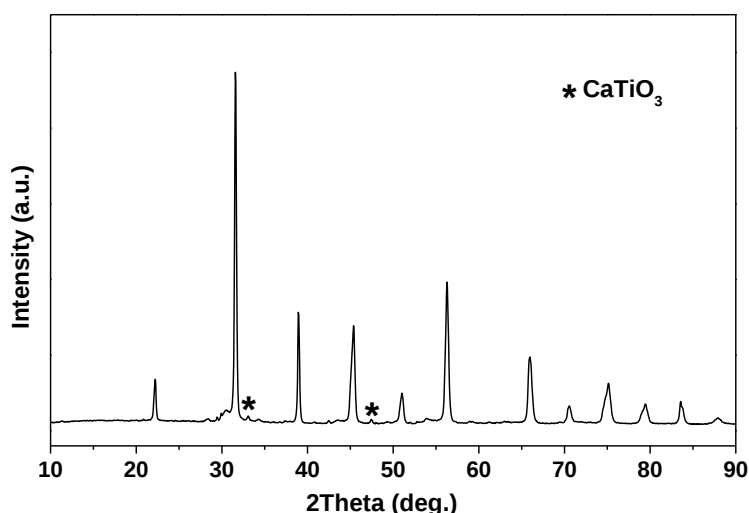


Figure 5.27 XRD pattern of BCZT powder calcined with double calcination at temperature 1000 °C.

SXPD patterns of the sintered pure BCZT ceramics are presented in Figure 5.28. These patterns are consistent with a perovskite phase, with no evidence to indicate the presence of any other crystalline second phases. Asymmetry in both $\{111\}_p$ and $\{200\}_p$ peak profiles suggests the presence of at least 2 different types of structurally-distorted perovskite phases; this observation is consistent with previous reports, which indicate that BCZT ceramics having the present composition are likely to contain coexisting orthorhombic (O) and tetragonal (T) phases at room temperature [62]. The individual peak profiles were generally narrower at the higher sintering temperature, indicating an improved crystallinity associated with the larger grain size (described in section 5.3.3 below).

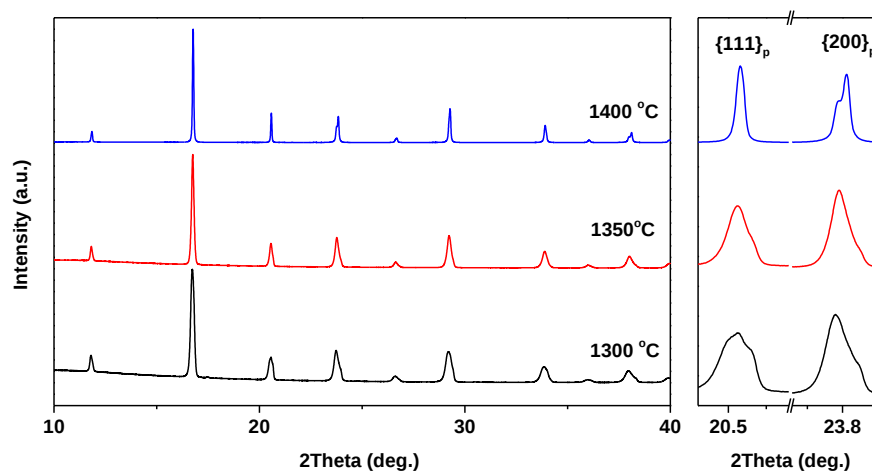


Figure 5.28 SXPD patterns of pure BCZT ceramics sintered at temperatures from 1300 to 1400 °C.

The incorporation of BBS into BCZT ceramics had a relatively little impact on the overall appearance of the SXPD patterns, as shown in Figure 5.29. It is evident that the presence of the glass phase did not cause any significant reactions with BC or lead to additional crystalline second phases. However, subtle changes in the individual peak profiles are apparent, which could indicate variations in the phase fractions of the coexisting perovskite-type phases. A general narrowing of the peak profiles of the BCZT-BBS (G1, G2) ceramics (relative to those of pure BCZT) was attributed to improved crystallinity.

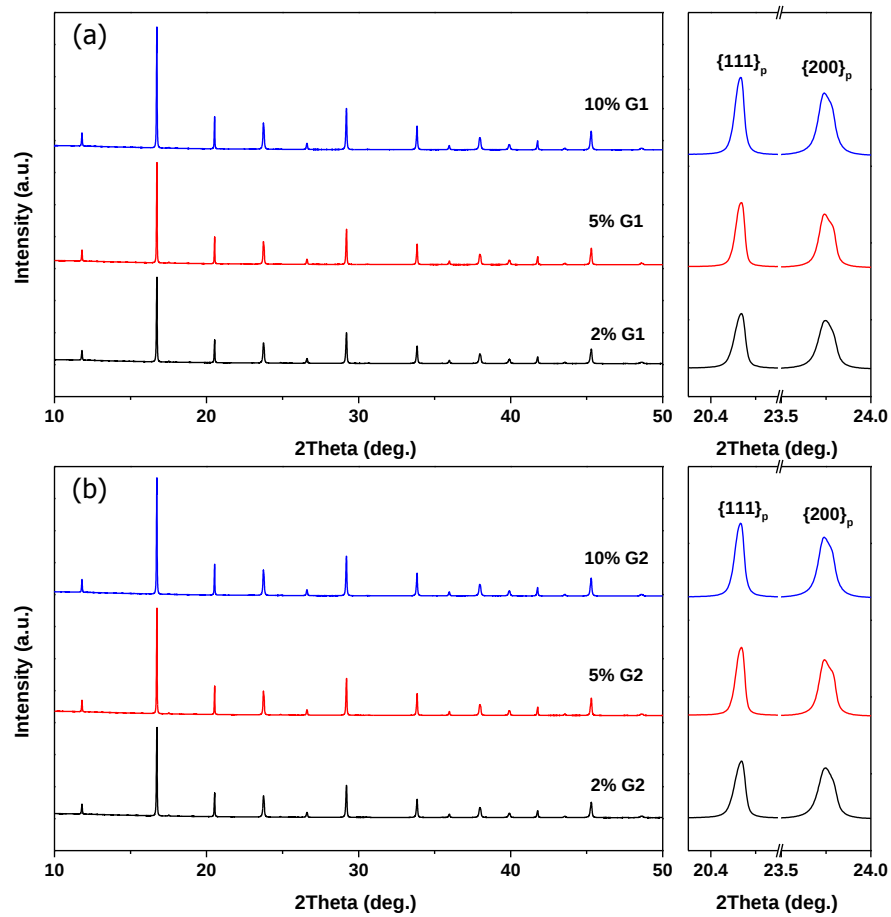


Figure 5.29 SXPD patterns of (a) BCZT-G1 and (b) BCZT-G2 ceramics with various glass contents, sintered at 1200 °C.

The results of full-pattern fitting for pure BCZT sintered at 1400 °C, shown in Figure 5.30 (a) and Table 5.4, indicate that the pure BCZT comprised coexisting orthorhombic (O) and tetragonal (T) phases with O and T phase fractions of approximately 19 and 81 %, respectively. The addition of 5 wt% BBS glasses, Figure 5.30 (b)-(c) and Table 5.4, favoured the formation of the orthorhombic (O) and rhombohedral (R) phases, yielding phase fractions of 78 and 83 % for the O phase for G1 and G2, respectively. The increase in the proportion of O phase and appearance of the R phase with increasing BBS content is consistent with the increase in the O-T phase transformation temperature, T_{O-T} , as described below in section 5.3.4. since this acts to stabilise the orthorhombic phase at room temperature.

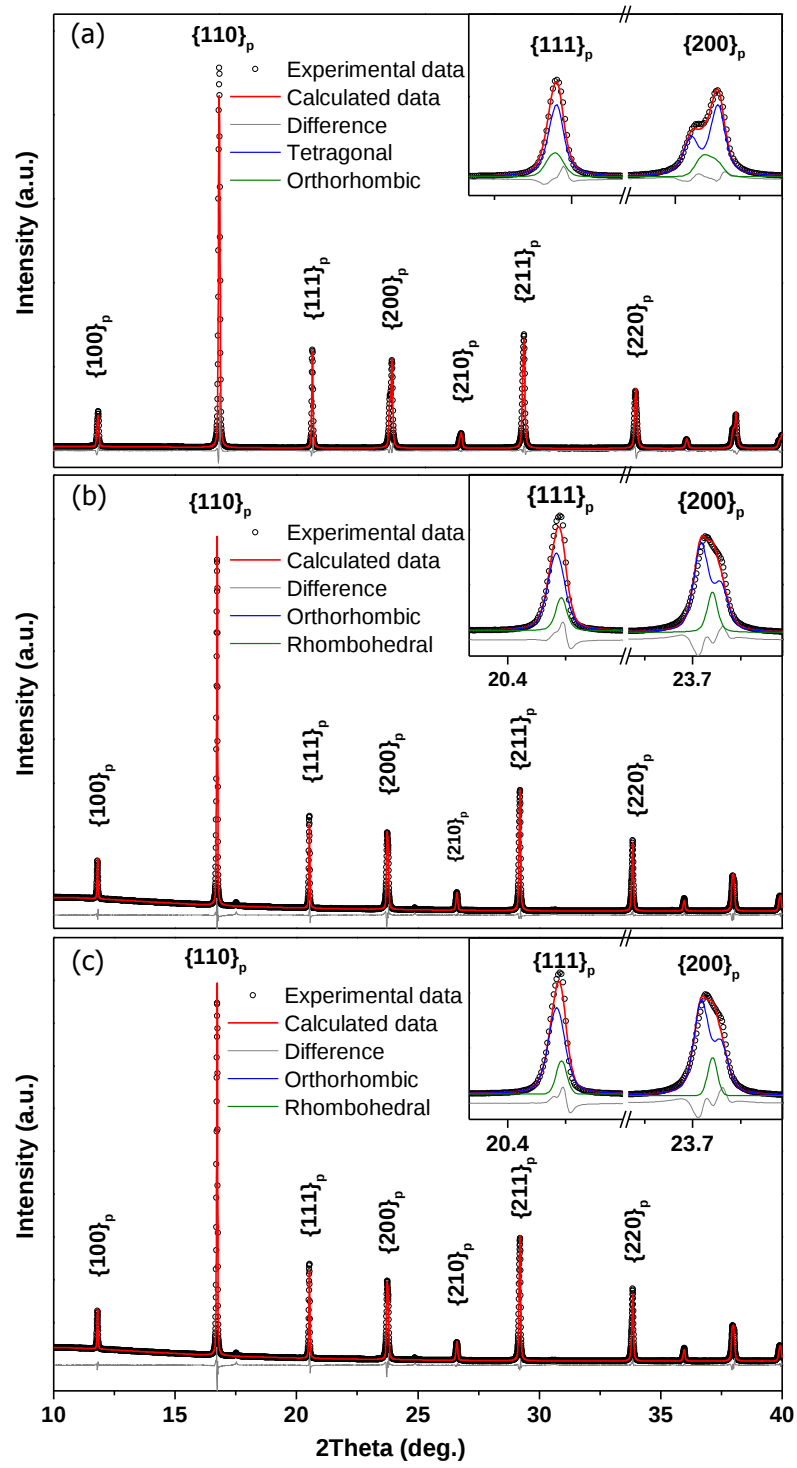


Figure 5.30 Comparison of experimental and calculated SXPD peak profiles of (a) pure BCZT ceramic sintered at 1400 °C, (b) BCZT-5G1 ceramic and (c) BCZT-5G2 ceramic sintered at 1200 °C.

Table 5.4 Coexisting phases, phase fractions, lattice parameters, χ^2 and R_{wp} of BCZT ceramics. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

Composition	Phase fraction (%)	Lattice parameter				χ^2	R_{wp}
		a (Å)	b (Å)	c (Å)	α (°)		
Pure BCZT/ 1400 °C	T = 81(2)	$a_T=3.9963(3)$	--	$c_T=4.0139(2)$	--	6.1	6.77
	O = 19(1)	$a_O=5.6642(2)$	$b_O=3.9972(3)$	$c_O=5.6673(1)$	--		
BCZT-5G1/ 1200 °C	O = 78(3)	$a_O=5.6771(5)$	$b_O=4.0057(1)$	$c_O=5.6819(4)$	89.98(1)	5.6	4.55
	R = 22(1)	$a_R=4.0101(3)$	--	--	--		
BCZT-5G2/ 1200 °C	O = 83(2)	$a_O=5.6776(4)$	$b_O=4.0059(2)$	$c_O=5.6816(1)$	89.97(1)	5.7	4.53
	R = 17(3)	$a_R=4.0102(2)$	--	--	--		

5.3.3 Microstructure analysis

The microstructure analyses for the pure and glass-modified BCZT ceramics are shown in this section to understand the effect of the glass content on microstructure and subsequently on the electrical properties. The SEM micrographs of the pure BCZT ceramics are shown in Figure 5.31. Poor densification and a very fine grain size are apparent for the pure BCZT ceramic sintered at 1300 °C, consistent with the low relative density of 81 % reported in section 5.3.1. Increasing the sintering temperature for pure BCZT led to a reduction of porosity and a dramatic increase in grain size, yielding final grain sizes approximately 12.2 ± 4.1 μm for a sintering temperature of 1400 °C.

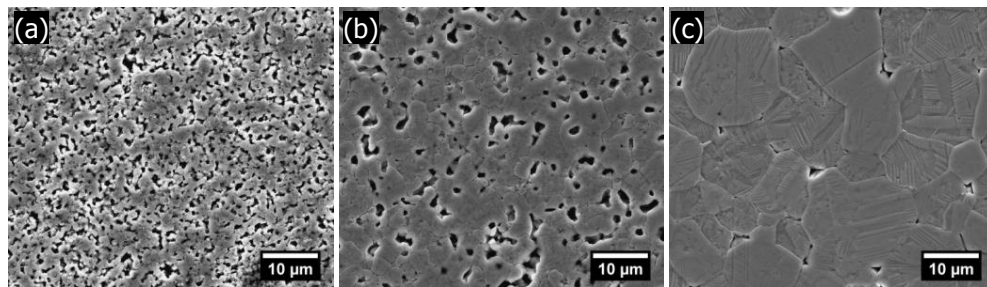


Figure 5.31 SEM micrographs of BCZT ceramic sintered at (a) 1300 °C, (b) 1350 °C and (c) 1400 °C.

In contrast, significant reductions in porosity and limited grain growth are already apparent at a sintering temperature of only 1200 °C for the BBS-modified BCZT ceramics, shown in Figure 5.32. At a given sintering temperature, the effect of adding

BBS glass was to enhance densification and grain growth. On the other hand, the ultimate grain sizes of the BCZT-G1 and BCZT-G2 ceramics were somewhat lower than those of pure BCZT due to the different ranges of sintering temperatures employed in the present study. For example, the final grain size for the BCZT-10G1 ceramic, sintered at 1200 °C, was approximately $2.9 \pm 0.2 \mu\text{m}$, lower than that of pure BCZT sintered at 1400 °C, given as $12.2 \pm 4.1 \mu\text{m}$ in Figure 5.31 above.

The presence of the glassy phase between the grains became more clearly apparent with increasing glass content and sintering temperature, as illustrated in Figure 5.32 to Figure 5.34. It was also observed that some needle-like grains were present within the glass phase for BCZT-G2 ceramics; this could be due to the K_2O and Na_2O content in G2 [107]. These second phases were not apparent in the XRD patterns, indicating that they represent a relatively small phase fraction.

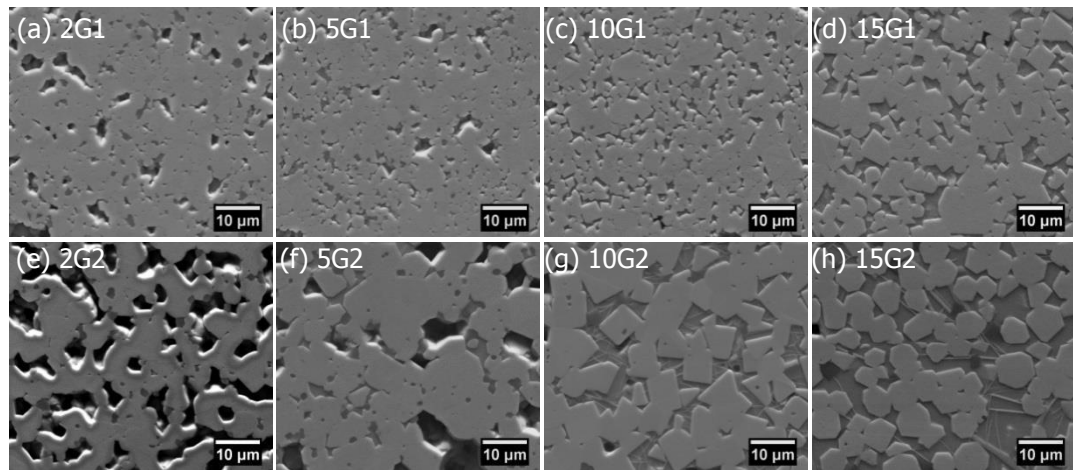


Figure 5.32 SEM micrographs of (a)-(d) BCZT-xG1 and (e)-(h) BCZT-xG2 sintered at 1200 °C.

SEM micrographs illustrating the effect of the sintering temperature on microstructure for BCZT modified with 10G1 and 10G2 are shown in Figure 5.33. It is apparent that the ceramics sintered at the lowest temperature of 1100 °C are porous (relative density $\approx 85 \%$) and have a very fine grain size. Improvements in density (up to 95%) and increased grain size were obtained by increasing the sintering temperature up to 1300 °C. Furthermore, the needle-like second phase particles become evident for BCZT-G2 at a sintering temperature of 1200 °C, similar to the results reported by Wang et al. [107].

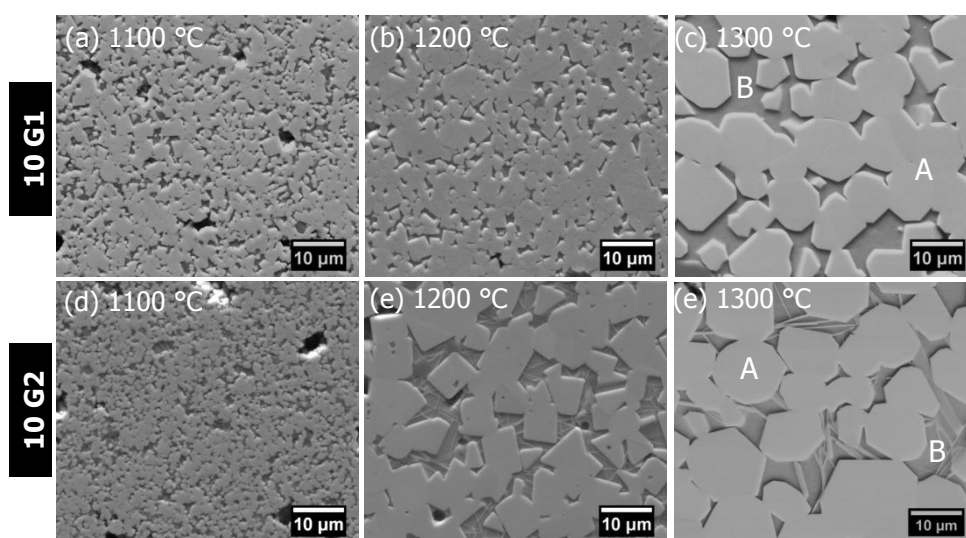


Figure 5.33 SEM micrographs of BCZT-10G1 sintered at (a) 1100 °C, (b) 1200 °C, (c) 1300 °C and BCZT-10G2 sintered at (e) 1100 °C, (f) 1200 °C, (g) 1300 °C. The ceramic and glass phases are labelled as 'A' and 'B', respectively.

EDS mapping was employed to determine the distribution of BCZT and BBS phases in the BCZT-2G1 and BCZT-10G1 ceramics, as illustrated by the results shown in Figure 5.34. It is evident that the heavier metallic elements, represented by Ba and Ti, are distributed uniformly throughout the crystalline BCZT grains while the lighter elements, represented by Si, are concentrated in the glassy BBS phase, which occurs as a continuously connected matrix between the grains.

However, it can be seen the ceramic grains surrounded by glassy phase, also, it can be clearly seen the increase in the distribution of Si element between the two samples as expected due to increase in glass content.

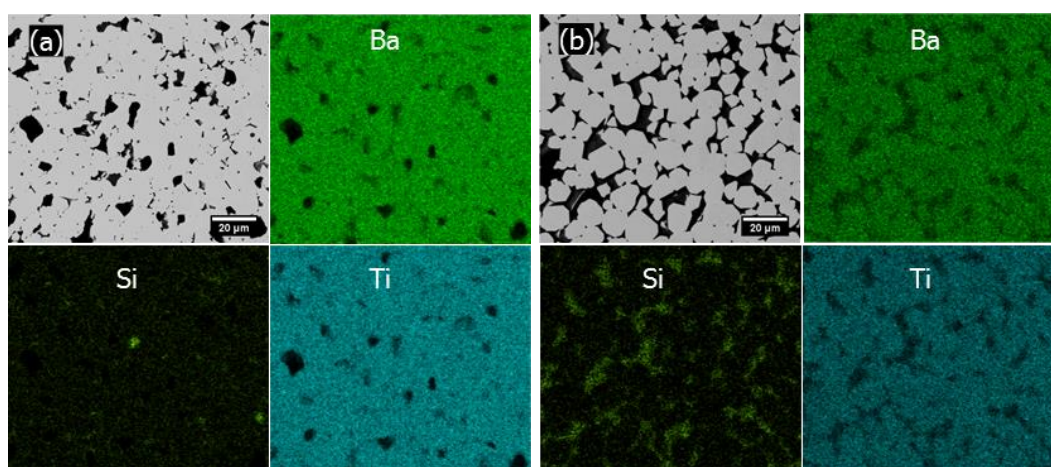


Figure 5.34 SEM micrographs and EDS mapping of (a) BCZT-2G1 and (b) BCZT-10G1 sintered at 1300 °C.

5.3.4 Temperature dependence of dielectric properties

5.3.4.1 Dielectric properties of pure BCZT

The temperature-dependence of relative permittivity and loss for pure BCZT ceramics are shown in Figure 5.35. In the case of the ceramic sintered at 1400 °C, a high relative permittivity in the region of 3800 was obtained at room temperature, consistent with the high relative density and large grain size of this material [180, 181]. Furthermore, a relatively sharp peak in relative permittivity was apparent at a temperature of 85 °C. On the basis of previous results and the XRD data presented in section 5.3.2 above, it is apparent that this peak is associated with the ferroelectric Curie point, T_C , and corresponds to a structural transformation from tetragonal (T) to cubic (C). Although, the ϵ_r -T curve does not exhibit any obvious anomalies in the region below T_C , small variations in $\tan \delta$ in the temperature range from 30 to 40 °C could be associated with the lower-temperature O to T transition.

In contrast, the relative permittivity values for the pure BCZT ceramics sintered at 1300 and 1350 °C were significantly lower and did not show such a strong peak at the Curie point. These changes in the ϵ_r -T relationships are attributed to the combination of low density/high porosity and poor crystallinity of these materials.

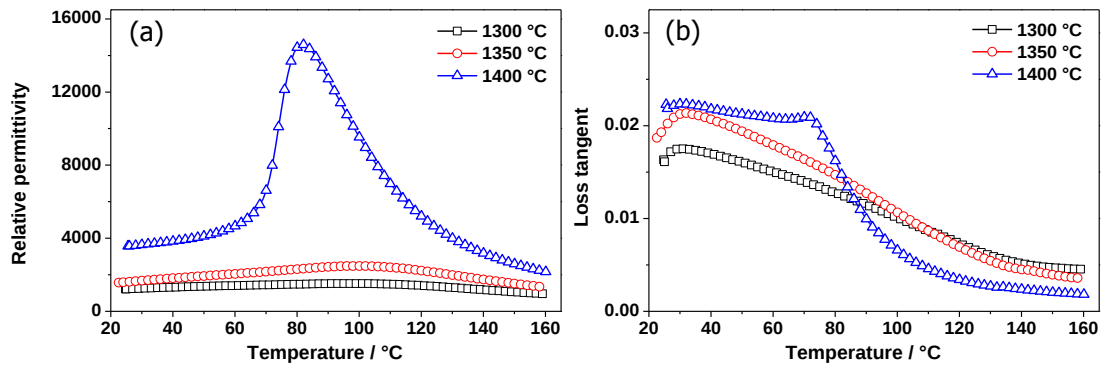


Figure 5.35 Influence of sintering temperature on (a) relative permittivity and (b) loss tangent for pure BCZT, measured at a frequency of 100 kHz.

5.3.4.2 Influence of frequency for glass-modified BCZT

Figure 5.36 shows the influence of temperature on the relative permittivity and loss ($\tan \delta$) for BCZT-2G1 and BCZT-2G2 ceramics sintered at 1300 °C, at various measurement frequencies from 1 to 100 kHz. These results suggest the occurrence of two phase transitions in the glass-modified BCZT ceramics, indicated by the lower temperature shoulder and the main peak in the ϵ_r -T relationship. The anomalies in the

relative permittivity curves correspond to the orthorhombic-tetragonal transformation (T_{O-T}) at approximately 50 °C and the tetragonal-cubic (T_{T-C}) transformation at the Curie temperature of approximately 85 °C. The same transformations are indicated by peaks in the $\tan \delta$ -T curves. Furthermore, it is evident that the dielectric properties are not affected significantly by measurement frequency, unlike the results presented by Lai for BCZT ceramics modified by the CaO-Bi₂O₃-SiO₂ glass [119].

The appearance of the O-T transformation in the region above room temperature indicates that the presence of the glass leads to subtle changes in the chemical composition of the crystalline perovskite phase. According to the phase diagram of the BCT-BZT system, shown in Figure 2.19. in section 2.2.1.2, even a slight change of the BCT/BZT ratio can lead to significant modification of the phase transformation temperatures [64, 182]. More specifically, reduction of the Ca/Zr ratio in the perovskite phase could be the origin of the observed increase in T_{O-T} , from below room temperature to $\approx$ 50 °C. One possible mechanism to achieve this could be the selective dissolution of CaTiO₃ into the liquid phase during sintering. The absence of crystalline second phases in the sintered glass-modified BCZT ceramics suggests that the small amount of additional CaTiO₃ is incorporated within the glass phase during cooling. This proposal is reasonable given that CaO and TiO₂ are well-known as modifiers for silicate glasses [183, 184].

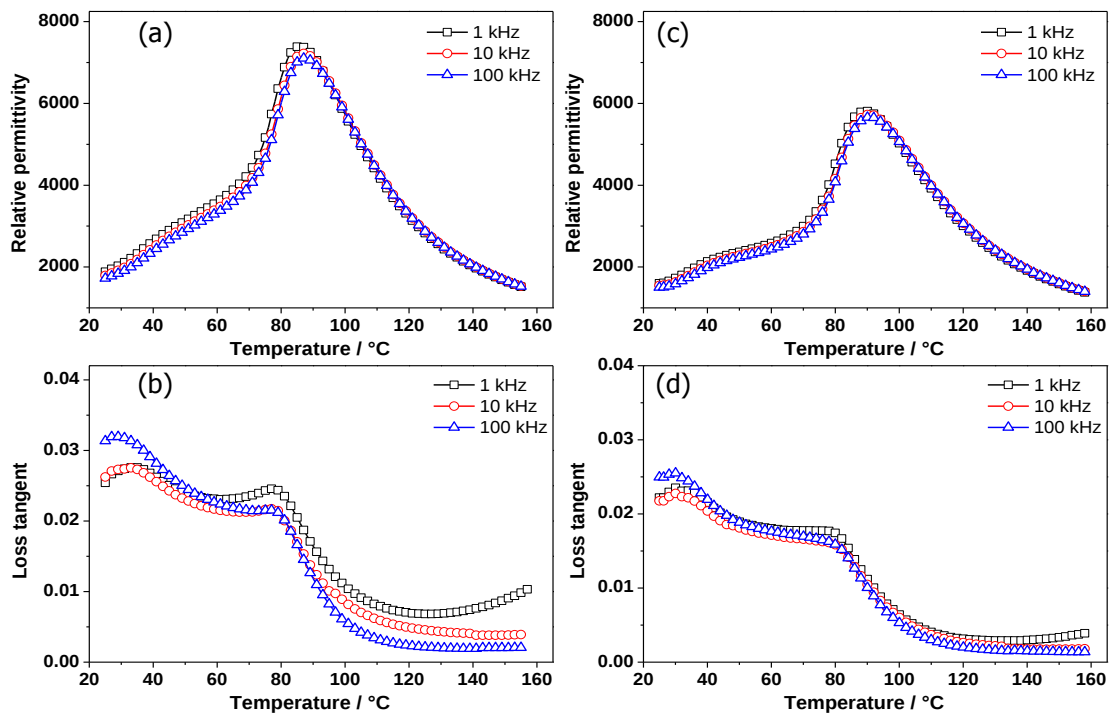


Figure 5.36 Relative permittivity and loss tangent as a function of the temperature for (a)-(b) BCZT-2G1 and (c)-(d) BCZT-2G2 sintered at 1300 °C measured at frequencies of 1, 10 and 100 kHz, respectively.

5.3.4.3 Influence of sintering temperature for glass-modified BCZT

The influence of sintering temperature on the temperature-dependence of relative permittivity and loss for the BCZT-G1 and BCZT-G2 ceramics is illustrated by the results presented in Figure 5.37. In common with the case for pure BCZT, the use of higher sintering temperatures yields improved densification and crystallinity, leading to higher relative permittivity values and a more clearly-defined peak at the Curie temperature, as shown in Figure 5.37 (a) and (c) for BCZT-2G1 and BCZT-2G2, respectively. However, reductions in relative permittivity between 1200 and 1300 °C are consistent with the reduction in relative density reported in section 5.3.1 above. An additional shoulder is clearly apparent on the ϵ_r -T curves for the materials sintered at temperatures above 1200 °C, which is attributed to the thermally-induced O-T transformation. Since a dominant orthorhombic phase was detected at room temperature, as described in section 5.3.2 above, it is likely that the further transformation to a single rhombohedral phase would occur at temperatures below room temperature, giving rise to further anomalies in the ϵ_r -T and $\tan\delta$ -T relationships.

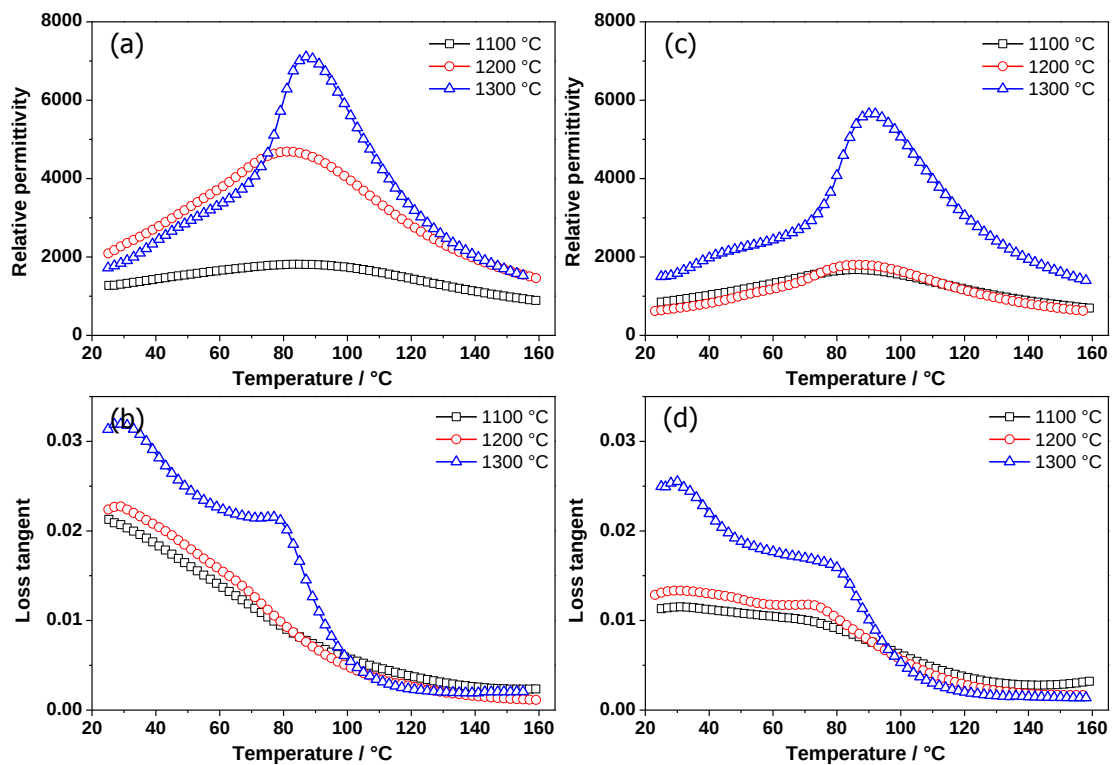


Figure 5.37 Influence of temperature on relative permittivity and loss tangent for (a)-(b) BCZT-2G1 and (c)-(d) BCZT-2G2 sintered at 1100 °C-1300 °C, measured at a frequency of 100 kHz.

5.3.4.4 Influence of glass content for glass-modified BCZT

BCZT-BBS ceramics prepared with various glass contents all exhibited a clear shoulder in their ϵ_r -T curves at temperatures ranging from 40 to 60 °C, as shown in Figure 5.38. If it is assumed that this anomaly is associated with the O-T transformation, then it appears that the addition of BBS leads to a slight increase in T_{O-T} . This was interpreted in section 5.3.4.2 above in terms of the selective dissolution of CaTiO_3 into the liquid phase during sintering, thereby reducing the Ca/Zr ratio of the crystalline perovskite phase and hence stabilising the orthorhombic phase at room temperature. According to Figure 5.38, it is evident that T_{O-T} increased systematically with increasing glass content. For example, in the case of BCZT-G1 T_{O-T} increased from ≈ 40 to 60 °C for glass contents of 2 and 15 % respectively. Furthermore, it is apparent that the main peak in relative permittivity at the Curie point shifts to lower temperatures with increasing glass content. These observations support the view that the chemical composition of the perovskite phase is significantly affected by the presence of the BBS liquid phase during sintering, resulting in a reduction of the Ca/Zr ratio.

An additional anomaly is evident in the ϵ_r -T curves for glass contents of 10 and 15% at a temperature of approximately 120 °C. Although the origin of this anomaly is not obvious at present, it could also be caused by chemical heterogeneity. For example, the selective dissolution of both Ca and Zr from the perovskite BCZT grains would lead to the formation of some pure BaTiO_3 grains, which would exhibit a higher Curie temperature, in the range 120 to 130 °C [49]. Therefore, the occurrence of chemical heterogeneity, resulting from the dissolution of dopants into the liquid phase can in principle explain the observed changes in both T_C and T_{O-T} [15, 185]. Further evidence, in the form of more precise micro-chemical analysis, would help to support this argument.

For a sintering temperature of 1300 °C, increasing glass content in BCZT ceramics led to a general reduction in relative permittivity values as a result of the low relative permittivity of the BBS glass phase ($\epsilon_r \approx 10.5$ and 7.5 for G1 and G2, respectively), which acts as a screening layer between the higher relative permittivity BCZT grains. On the other hand, the slight increases in relative permittivity between 2 and 5% glass content, observed for both G1 and G2, are attributed to the reduction in porosity and, possibly, grain size effects [67].

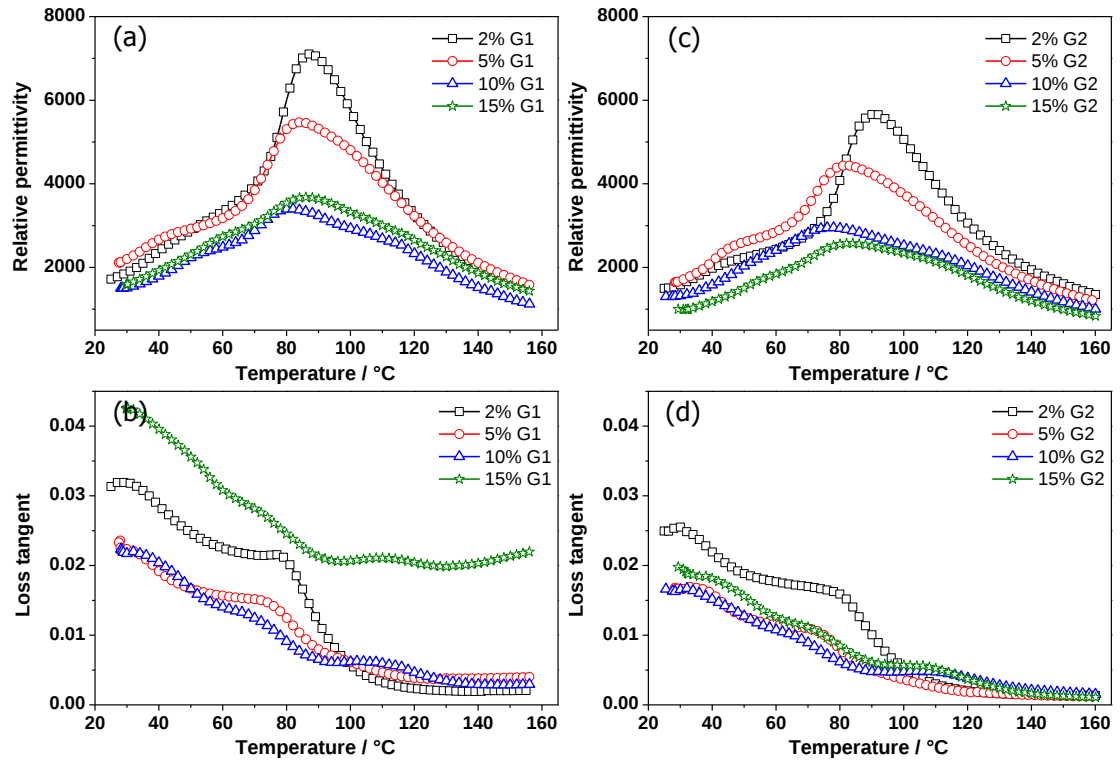


Figure 5.38 Relative permittivity and loss tangent as a function of the temperature for (a)-(b) BCZT-xG1 and (c)-(d) BCZT-xG2 with $x=2, 5, 10$, and 15 sintered at $1300\text{ }^{\circ}\text{C}$ measured at frequencies of 100 kHz , respectively.

5.3.4.5 Thermally-induced phase transformations

From the BCT-BZT phase diagram, Figure 2.18 and Figure 2.19 [62], it can be seen that the tilt in the MPB of the BCZT system leads to the possibility to approach the MPB by changing temperature as well as by changing the composition. Therefore, the in-situ XRD study provides a chance to understand the phase changes that might occur on approaching or crossing the MPB.

The temperature-dependent in-situ SXPD patterns for BCZT-5G1 sintered at $1200\text{ }^{\circ}\text{C}$ are shown in Figure 5.39, which presents the changes in the $\{200\}$ peak profile on heating from 30 to $140\text{ }^{\circ}\text{C}$. It is expected that a chemically-homogeneous BCZT ceramic should transform to a cubic structure at temperatures above the Curie point. In the present case, the transition to the cubic phase occurred above the Curie temperature of $\approx 90\text{ }^{\circ}\text{C}$. Furthermore, significant changes in the peak profiles are evident in the intermediate temperature range. These results are generally in agreement with the dielectric property measurements, shown in Figure 5.37 above, where the two transition temperatures, corresponding to the O-T and T-C transformations of BCZT-5G1, were determined as approximately 45 and $90\text{ }^{\circ}\text{C}$, respectively.

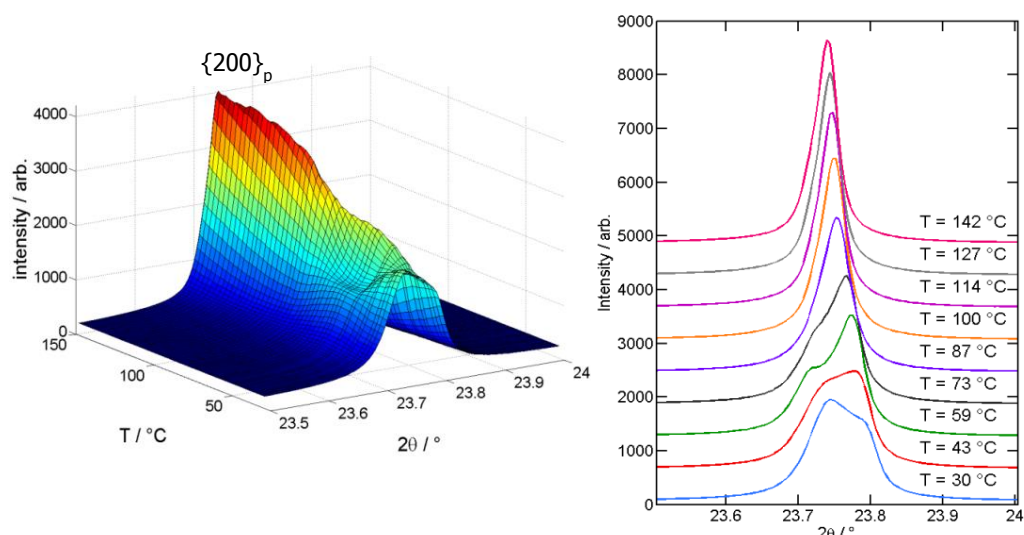


Figure 5.39 Changes in SXPD peak profile for $\{200\}_p$ reflection of BCZT-5G1 ceramic, sintered at 1200 °C, on heating from 30 to 140 °C.

The results of full-pattern refinement of temperature-dependent SXPD patterns for the BCZT-5G2 ceramic during heating from 30 to 150 °C are presented in Figure 5.40. In this case, increasing the temperature caused a gradual transformation from the coexisting O and R phases at room temperature to a single T phase at 60 °C, as confirmed by the full-pattern fitting results included in Table 5.5. The presence of the minor rhombohedral phase at 30 °C indicates that the R-O transformation temperature is most likely located slightly below room temperature, in accordance with the results presented by Keeble [64]. It was anticipated that the T to C transformation would occur at the ferroelectric Curie temperature (≈ 85 °C). However, a shoulder was apparent on both the $\{200\}$ and $\{111\}$ peak profiles up to approximately 150 °C. These results are consistent with the presence of chemical heterogeneity in the glass-modified BCZT ceramics, which takes the form of 2 distinct perovskite phases, one being the BCZT solid solution and the other comprising 'pure' BT, as proposed in section 5.3.4.4 above. The major BCZT phase transforms to cubic at ≈ 85 °C, while the minor BT phase retains the tetragonal structure above 85 °C and transforms to cubic around 120 °C. Therefore, the full pattern fitting at 150 °C, Figure 5.40-(f), indicates the presence of two cubic phases represented by BCZT and BT.

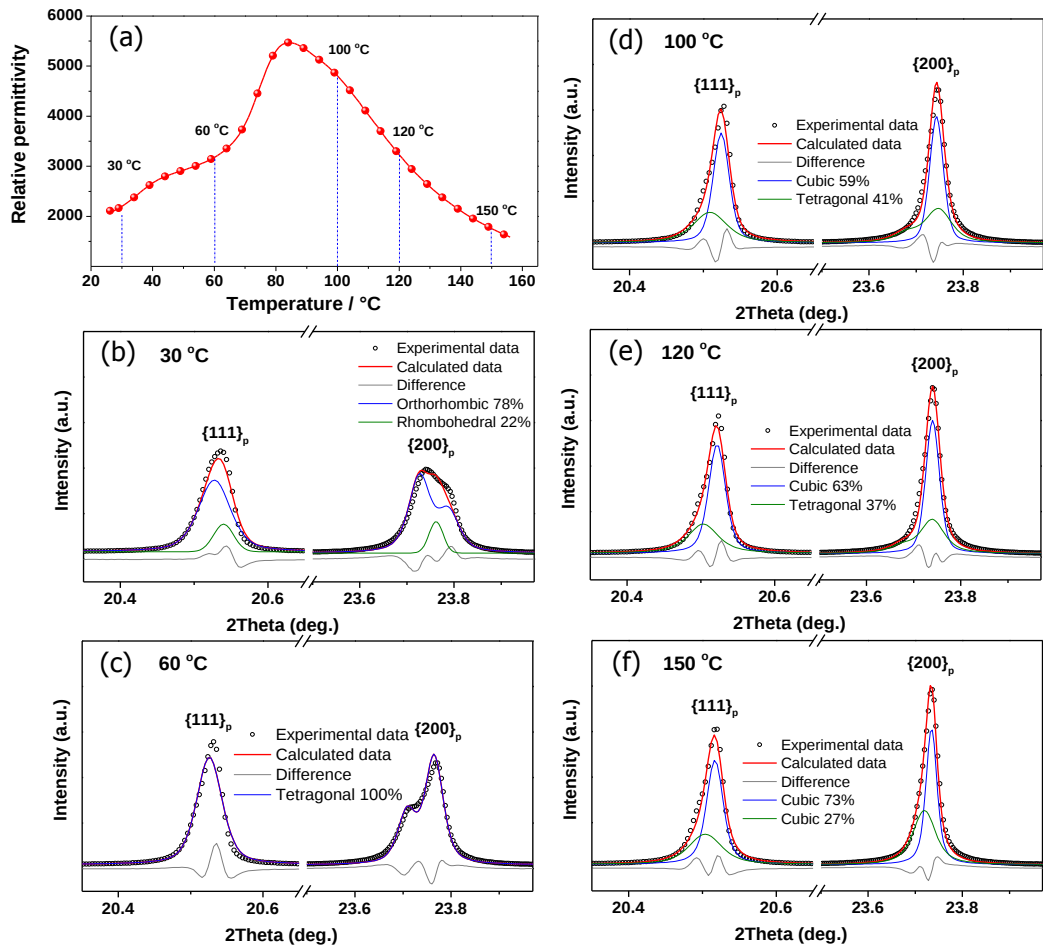


Figure 5.40 (a)-(f) In situ SXPD profile of BCZT-5G1 during heating for 30 to 150 °C. (a) ϵ_r -T curve and (b)-(f) the measured, calculated and difference data obtained by full-pattern refinement showing $\{111\}_p$ and $\{200\}_p$ reflections of (b) coexisting phases O-R phases at 30 °C, (c) single T phase at 60 °C, (d)-(e) C-T coexisting phases at 100-120 °C and (f) C-C coexisting phases (BCZT and BT) at 150 °C, respectively.

Table 5.5 Coexisting phases, phase fractions, lattice parameters, χ^2 and R_{wp} obtained by full-pattern refinement for BCZT-5G1 ceramic during heating for 30 to 150 °C. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

Composition during heating	Phase fraction (%)	Lattice parameter				χ^2	R_{wp}
		a (Å)	b (Å)	c (Å)	$\alpha(^{\circ})$		
30 °C	O = 78(2)	$a_o = 5.6776(2)$	$b_o = 4.0059(3)$	$c_o = 5.6816(3)$	--	5.71	4.53
	R = 22(1)	$a_r = 4.0102(3)$	--	--	89.9		
60 °C	T = 100	$a_T = 4.0128(4)$	--	$c_T = 4.0221(4)$	--	5.98	4.21
100 °C	C = 59(3)	$a_C = 4.0141(3)$	--	--	--	6.71	5.53
	T = 41(2)	$a_T = 4.0131(3)$	--	$c_T = 4.0268(5)$	--		
120 °C	C = 63(2)	$a_C = 4.0150(1)$	--	--	--	7.21	6.57
	T = 37(3)	$a_T = 4.0151(3)$	--	$c_T = 4.0258(4)$	--		
150 °C	C = 73(2)	$a_C = 4.0158(2)$	--	--	--	6.82	6.13
	C = 27(1)	$a_C = 4.0183(3)$	--	--	--		

5.3.5 Ferroelectric properties

5.3.5.1 Ferroelectric properties of pure BCZT

The P-E hysteresis loops obtained for pure BCZT ceramics at room temperature are presented in Figure 5.41. In the case of pure BCZT, a sintering temperature of 1400 °C yielded a well-defined ferroelectric loop having saturation polarisation (P_s) remanent polarisation, (P_r) and coercive field (E_c) values of 0.19, 0.09 C m⁻² and 0.30 kV mm⁻¹, respectively. In contrast, the P-E loops of the pure BCZT ceramics sintered at 1300 and 1350 °C were poorly saturated and exhibited a 'rounded' appearance, indicating high losses. Loops of this form are commonly observed in specimens having high porosity and therefore can be attributed to the poor densification achieved in pure BCZT at sintering temperatures lower than 1400 °C. The low polarisation values result from poor crystallinity and very fine grain size [67], while the 'rounding' effect is caused by conduction currents associated with poor insulation resistance [186].

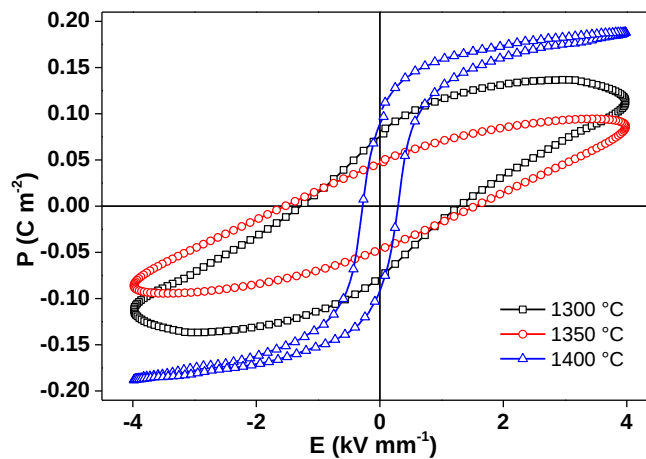


Figure 5.41 P-E hysteresis loops obtained for pure BCZT sintered at 1300 to 1400 °C measured at 4 kV mm⁻¹, 2 Hz.

5.3.5.2 Influence of sintering temperature for glass-modified BCZT

The influence of sintering temperature on the ferroelectric behaviour of BCZT-2G1 and BCZT-2G2 ceramics is illustrated by the results presented in Figure 5.42. In the case of the G1-modified material, well-formed P-E loops with relatively high polarisation values were obtained for sintering temperatures of 1200 and 1300 °C, while that of the ceramic sintered at 1100 °C yielded lower values as a result of the lower density. The results obtained for BCZT-2G2 were similar, but with generally lower polarisation values.

The saturation and remanent polarisation values were reduced somewhat relative to those of the pure BCZT ceramic sintered at 1400 °C, due to the presence of the low-relative permittivity glass phase between the ferroelectric BCZT grains. For example, the BCZT-2G1 ceramic sintered at 1300 °C yielded P_s and P_r values of 0.129 and 0.0678 C m⁻², respectively, which were approximately 27 % lower than the pure BCZT ceramic sintered at 1400 °C. On the other hand, the BCZT-2G1 ceramic sintered at 1200 °C yielded a slightly higher P_s value of 0.148 C m⁻² but a lower P_r value of 0.0398 C m⁻². The observed variations in ferroelectric switching behaviour with sintering temperature can be correlated with the ϵ_r -T relationships shown in Figure 5.37, where it is apparent that the BCZT-2G1 ceramic sintered at the highest temperature of 1300 °C exhibited a more well-defined Curie point but the relative permittivity at room temperature was slightly higher for the ceramic sintered at 1200 °C.

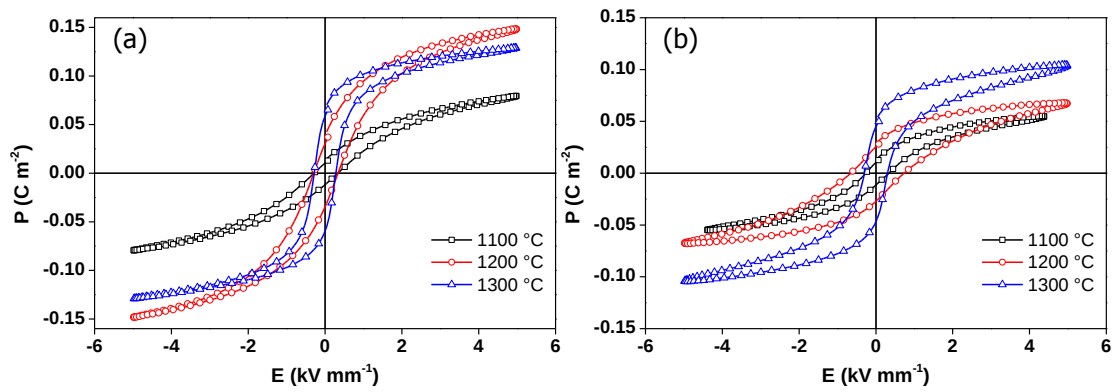


Figure 5.42 P-E hysteresis loops of (a) BCZT-2G1 and (b) BCZT-2G2 sintered at temperatures of 1100 °C to 1300 °C measured at field 5 kV mm⁻¹, 2 Hz, respectively.

5.3.5.3 Influence of glass content for glass-modified BCZT

For a given sintering temperature of 1200 °C, increasing glass content in BCZT ceramics had little influence on P_r and E_c , but led to significant reductions in P_s , as shown in Figure 5.43. This effect was most strongly pronounced for BCZT-G2 ceramics sintered at 1200 °C. Increasing the sintering temperature to 1300 °C generally had a beneficial effect on the P-E hysteresis loops, yielding a narrower switching field region and improved remanent polarisation values, particularly for the lower glass contents.

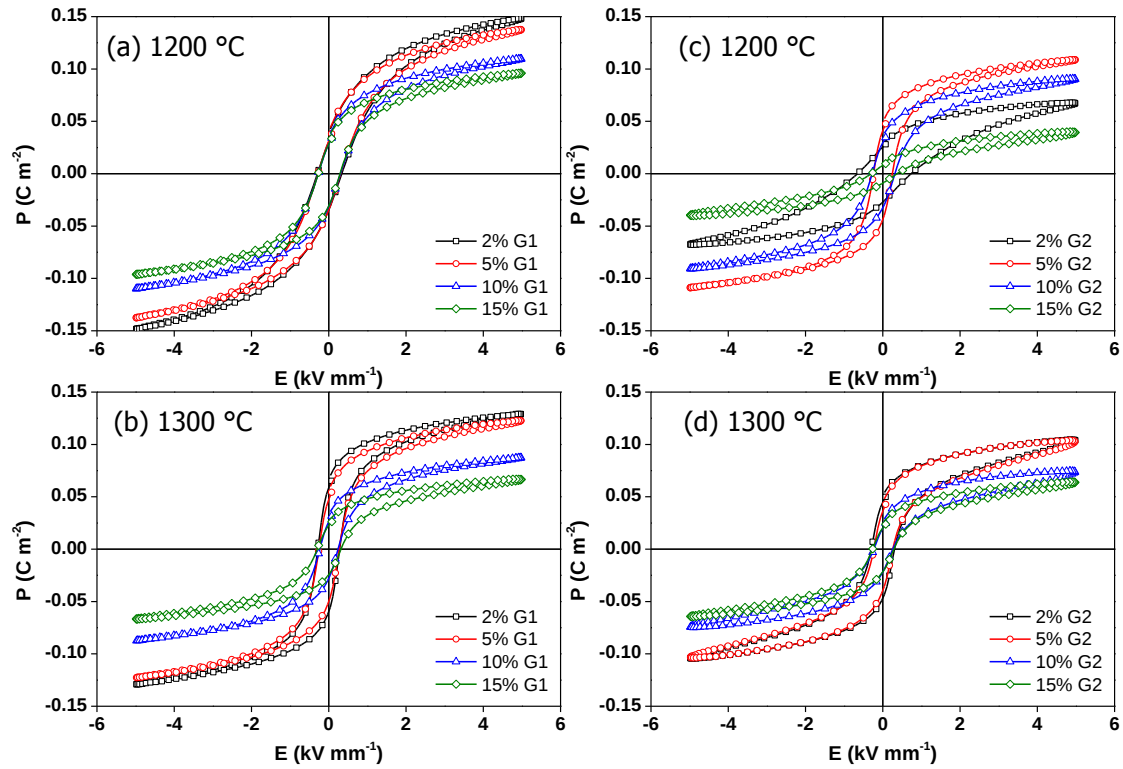


Figure 5.43 P-E hysteresis loops of (a)-(b) BCZT-G1 and (c)-(d) BCZT-G2 ceramics sintered at 1200 °C and 1300 °C.

The resulting variations in P_s and P_r as a function of BBS content and sintering temperature are summarised in Figure 5.44. The highest P_s values were obtained for the BC-G1 ceramics sintered at 1200 °C, while the higher sintering temperature of 1300 °C yielded the highest P_r values. The lower polarisation values of the BCZT-G2 ceramics are attributed to the lower relative permittivity of the G2 glass and the poorer densification behaviour of these materials in comparison with BCZT-G1. Further work is required to optimise the ferroelectric switching behaviour of these materials, and hence to obtain improved remanent polarisation values. This could include investigations into the properties of BCZT-BBS ceramics sintered at an intermediate temperature in the range 1200 to 1300 °C, for example.

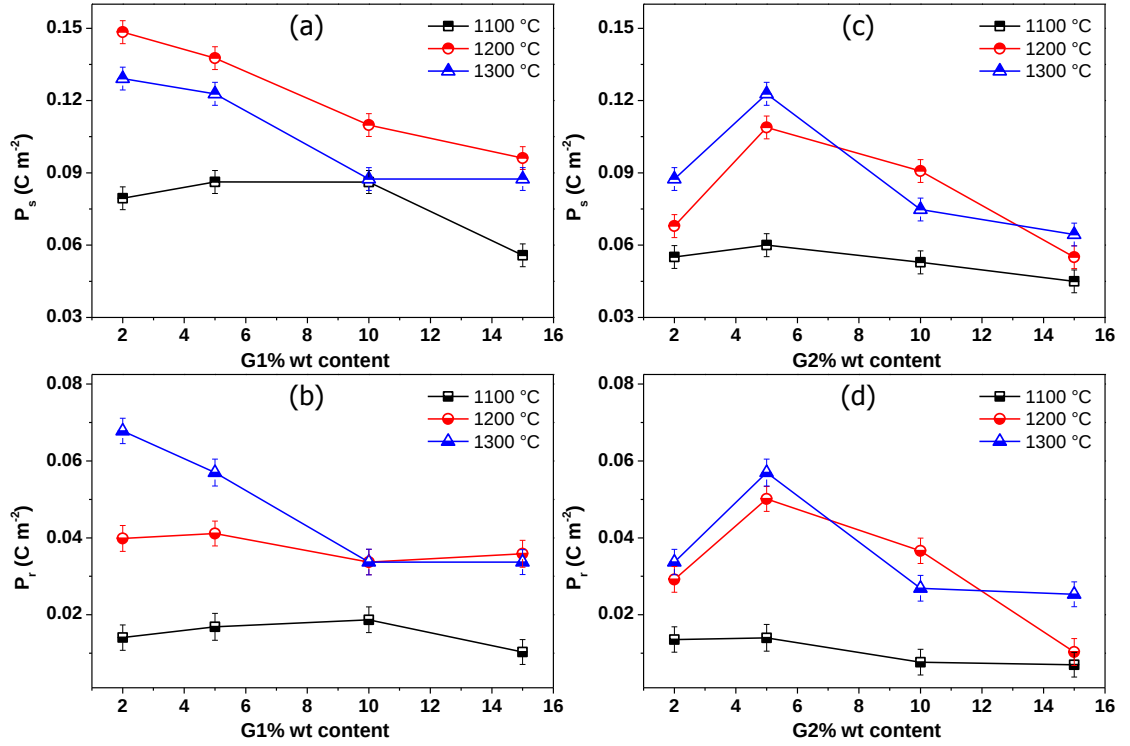


Figure 5.44 Influence of BBS content on P_s and P_r of (a)-(b) BCZT-G1 and (c)-(d) BCZT-G2 ceramics as a function of glass content sintered at 1100-1300 °C measured at field 5 kV mm^{-1} and 2 Hz, respectively.

5.3.5.4 Influence of temperature for glass-modified BCZT

The influence of temperature on ferroelectric properties was evaluated by recording the P-E hysteresis loops of BCZT ceramics with 0, 5 and 10 wt% glass content over a range of temperatures from 25 to 140 °C, as illustrated by the results presented in Figure 5.45. The P-E loops generally decreased in height with increasing temperature but did not collapse fully into linear loss-free behaviour at temperatures up to 140 °C. The P_s values reduced gradually over the full temperature range, while P_r dropped relatively sharply between 80 and 100 °C due to the ferroelectric phase transformation. The coercive field values varied little over this temperature range. Significant nonlinearity and finite P_r values above 100 °C could be caused by electric field-induced paraelectric-ferroelectric phase transformations in the region of T_C , as reported by Tian et al. [187].

The temperature-dependent polarisation values obtained for BCZT ceramics with different glass contents are summarised in Figure 5.45 (c)-(d). The superiority of the G1 glass and the relatively rapid loss of remanent polarisation above 80 °C are clearly apparent in these results. However, it is also clear that significantly nonlinearity in dielectric properties occurs even above the Curie point. For example, the saturation

polarisation, P_s , for BCZT-5G1 at 140 °C was measured as 0.061 C m⁻² at an electric field of 5 kV mm⁻¹. This is lower than the predicted value of 0.088 C m⁻², assuming a linear dielectric with a relative permittivity of 2000 at an electric field of 5 kV mm⁻¹.

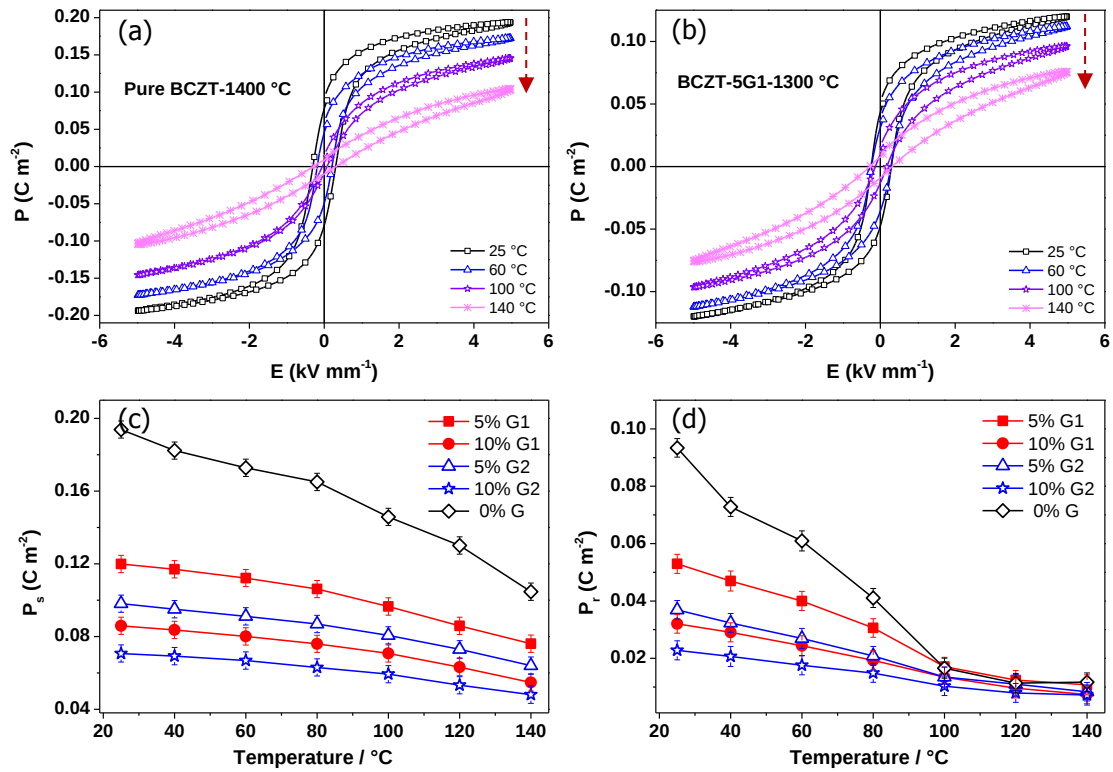


Figure 5.45 Influence of temperature on (a) and (b) P-E hysteresis loops of pure BCZT sintered at 1400 °C and BCZT-5G1 sintered at 1300 °C, (c) P_s and (d) P_r of pure BCZT and BCZT-BBS measured at temperatures from 25 to 140 °C. Arrow indicates increasing temperature.

5.4 Pure and glass-modified ($\text{K}_{0.5}\text{Na}_{0.5}$) NbO_3 ceramics

Currently, KNN-based ceramics are promising candidates for replacing PZT in some piezoceramic devices as a result of their good electromechanical properties and high Curie temperatures. However KNN-based materials are reported to suffer from some difficulties in processing, for example during the powder synthesis and the sintering of the powder compact; these issues are largely related to the high volatility of the alkali metal oxides, which leads to problems in control of stoichiometry and in densification. In spite of these drawbacks, KNN is considered to be one of the most attractive and viable lead-free piezoceramics [188-190].

In this chapter, the addition of excess alkali carbonates (Na_2CO_3 and K_2CO_3) has been investigated as a means to reduce the sintering temperature and improve the ferroelectric/dielectric properties of KNN ceramics. For this reason, 5 mol% excess of each of the Na_2CO_3 and K_2CO_3 were added to the starting mixture of KNN. In addition, the influence of two different glasses (G3 and G4) on the microstructure and ferroelectric/dielectric properties of KNN will be discussed. The glasses were added to the calcined KNN powder in varying proportions $(1-x)\text{KNN}-x\text{G3}$, G4 with $x=5, 10$ and 15 wt% using a sintering temperature in the range 1050 to 1150 °C.

5.4.1 Preparation of pure KNN

5.4.1.1 Relative density analysis

The densities of KNN ceramics sintered at different temperatures are shown in Figure 5.46. It can be seen that the density increased as the sintering temperature increased, with relative densities of 77 to 82 % being achieved for sintering temperatures in the range 1110 to 1200 °C. The use of higher temperatures resulted in excessive evaporation of the volatile K_2O and Na_2O oxides, leading to reduced final density values [69]. This level of relative density is too low for practical applications due to the continuously-connected porosity (see Figure 5.50 below) and the associated issues with adsorption of atmospheric moisture, giving rise to high electrical conductivity and instability under high electric field conditions. Therefore, two different types of glass were subsequently added to the KNN ceramic in order to improve its densification behaviour (described in section 5.4.2 below).

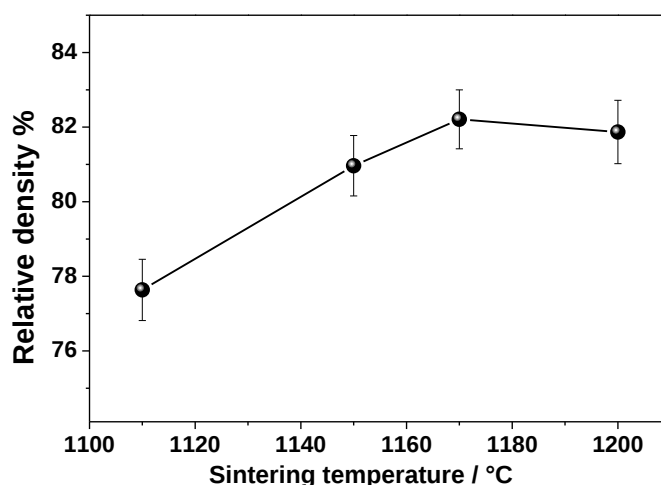


Figure 5.46 Relative density of KNN ceramic sintered with 5 mol% excess of Na_2CO_3 and K_2CO_3 at temperatures from 1110 to 1200 °C.

5.4.1.2 Lab XRD results

The XRD patterns of KNN powder calcined at 700 and 900 °C, with and without the excess alkali carbonate addition, respectively, are presented in Figure 5.47. It can be seen that the patterns correspond to the perovskite phase without any obvious secondary phase. Splitting and narrowing of the pseudo-cubic diffraction peaks, indicating a well crystallised KNN phase, became apparent after calcination at only 700 °C for the *alkali excess* powder, similar to the results reported by Bomlai et al. [131]. In contrast, the initially stoichiometric powder exhibited broad and overlapping diffraction peaks, even after calcination at 900 °C, indicating poor crystallinity. Consequently, only the *alkali excess* powder was chosen for subsequent sintering and characterisation studies.

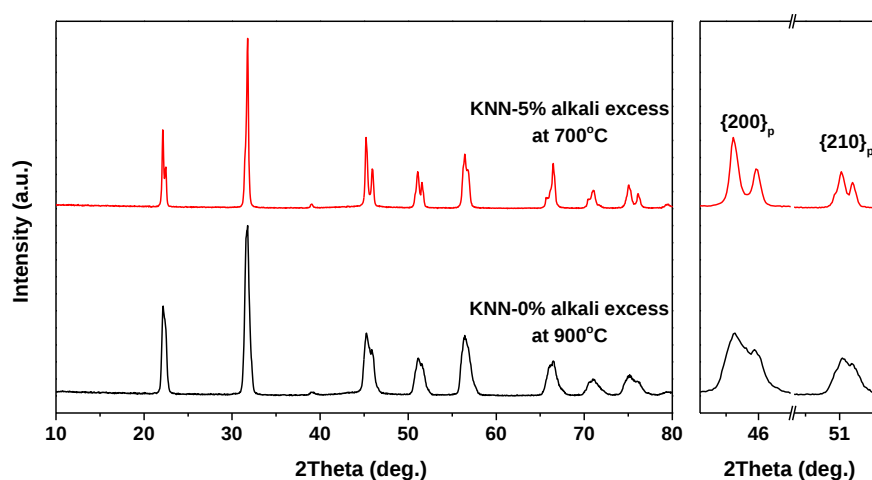


Figure 5.47 XRD patterns of KNN powders calcined at 700 °C (alkali excess) and 900 °C (stoichiometric), showing the influence of the different processing parameters.

The orthorhombic structure of the *alkali excess* KNN powder, calcined at 700 °C, was confirmed by full-pattern refinement giving the results shown in Figure 5.48. It was found that the best fit was obtained using a single phase orthorhombic structure [191].

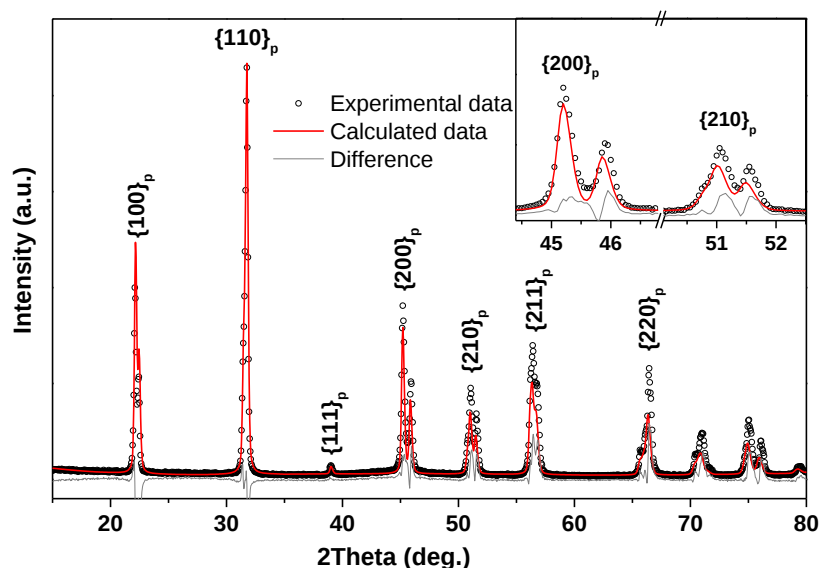


Figure 5.48 Full-pattern fitting of XRD results for *alkali-excess* KNN powder calcined at a temperature of 700 °C, indicating orthorhombic (O) structure.

The XRD pattern obtained for the sintered KNN ceramic, prepared using the *alkali excess* powder, is shown in Figure 5.49. The results of full-pattern fitting were similar to those of the calcined powder, although with slight improvements in the separation of the split diffraction peaks indicating enhanced crystallinity. The crystallographic parameters obtained for the calcined and sintered KNN are summarised in Table 5.6.

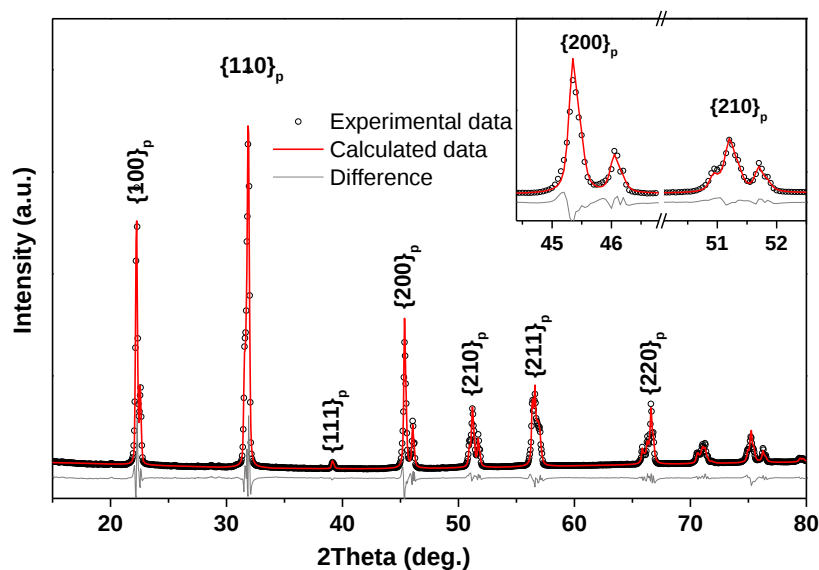


Figure 5.49 Full-pattern fitting of XRD results for KNN ceramic sintered at 1150 °C.

Table 5.6 Phase fractions, lattice parameters, χ^2 and R_{wp} of pure-KNN ceramics. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

Composition	Phase fraction (%)	Lattice parameter			χ^2	R_{wp}
		a (Å)	b (Å)	c (Å)		
KNN/700 °C	O = 100	$a_0=5.6588(2)$	$b_0=3.9560(1)$	$c_0=5.6851(2)$	5.86	10.39
KNN/1150 °C	O = 100	$a_0=5.6365(1)$	$b_0=3.9396(3)$	$c_0=5.6684(3)$	5.66	7.89

5.4.1.3 Microstructure analysis

The particle size and morphology of the *alkali excess* KNN powder after calcination at 700 °C are shown by the SEM micrograph presented in Figure 5.50 (a). It is apparent that the crystal size is in the range $0.35\pm0.05\ \mu\text{m}$, but the particles are strongly agglomerated. The grain size of the KNN ceramic sintered at 1150 °C, measured as $14.2\pm3.2\ \mu\text{m}$, was dramatically larger than that of the starting powder, as shown in Figure 5.50 (b). The grains exhibited a cuboid morphology, typical of KNN ceramics, and there was a high residual porosity, consistent with the low relative density reported in section 5.4.1.1 above.

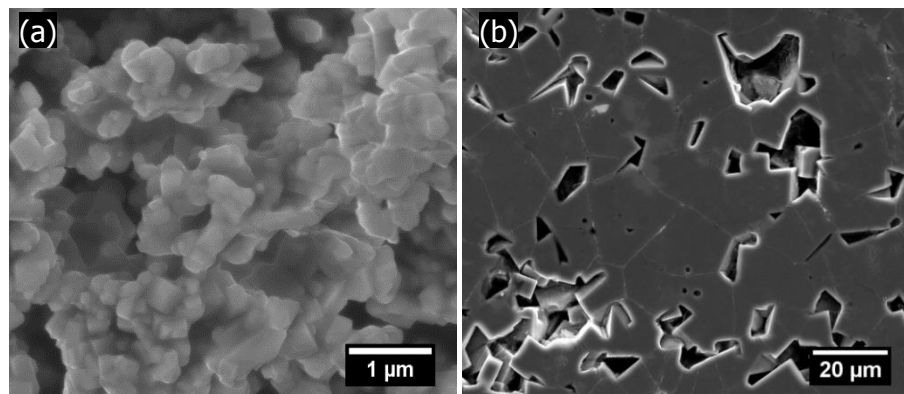


Figure 5.50 SEM micrographs for (a) *alkali excess* KNN powder calcined at 700 °C and (b) KNN ceramic sintered at 1150 °C.

5.4.1.4 Dielectric properties

The temperature-dependence of relative permittivity and loss tangent for the pure KNN ceramic is shown in Figure 5.51. The relative permittivity was in the region of 350 at room temperature, increasing to a peak of approximately 3700 at the Curie temperature of 410 °C. An additional transition occurred at a temperature of approximately 200 °C, which is attributed to the orthorhombic-tetragonal phase transformation (T_{O-T}) [192].

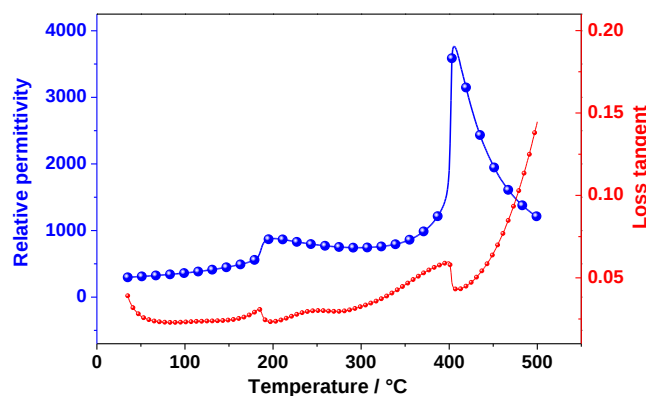


Figure 5.51 Relative permittivity and loss tangent as a function of the temperature for KNN ceramic sintered at 1150 °C, measured at a frequency of 100 kHz.

5.4.1.5 Ferroelectric properties

The ferroelectric P-E hysteresis loops obtained for the pure KNN ceramic, measured using a maximum electric field of 2.5 kV mm⁻¹, are shown in Figure 5.52. The remanent polarisation, P_r , increased up to a maximum level of around 0.12 C m⁻², but a fully-saturated state could not be obtained due to electrical breakdown at higher fields. The tendency for electrical arcing at relatively low electric field levels is attributed to the internal porosity of the pure KNN ceramic [186].

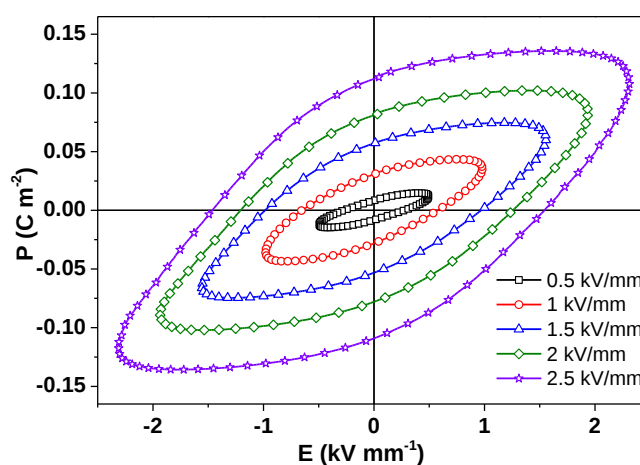


Figure 5.52 P-E hysteresis loops obtained for KNN sintered at 1150 °C measured at various different electric field levels at a frequency of 2 Hz.

5.4.2 Glass-modified KNN ceramics

5.4.2.1 Relative density analysis

The influence of glass content on the relative densities of the glass-modified KNN ceramics, sintered at different temperatures, is shown in Figure 5.53. Here, the figure insert illustrates the changes in theoretical density of the composite KNN-glass

materials as a function of the glass content, calculated according to the method described in section 4.6.1. It can be seen that the theoretical density decreases with increasing glass content for G3 but increases for G4. This effect can be understood in terms of the different chemical compositions of the glasses, with G4 containing a higher proportion of heavy metal oxides.

For the G3-modified KNN ceramics sintered at 1050 °C, the relative density increased from approximately 60 to 80 % as the glass content increased from 5 to 15 wt%, as shown in Figure 5.53 (a). However, the density did not improve significantly at higher temperatures. On the other hand, the G4-modified KNN ceramics exhibited higher relative densities, greater than 90 %, which improved with increasing glass content and sintering temperature, as shown in Figure 5.53 (b). The slight reduction in density for KNN-15G4 at the highest sintering temperature of 1150 °C might be due to the partial volatilization of boron and bismuth oxides [193]. The highest relative densities of 92 and 96 % were obtained for KNN-5G4 sintered at 1150 °C and KNN-15G4 sintered at 1050 °C, respectively. In this case, the densities are higher than those results reported by Zhao et al. [194] and Park et al. [195]. The sintering temperatures for KNN-G3 ceramics were limited to a maximum of 1110 °C due to issues with melting.

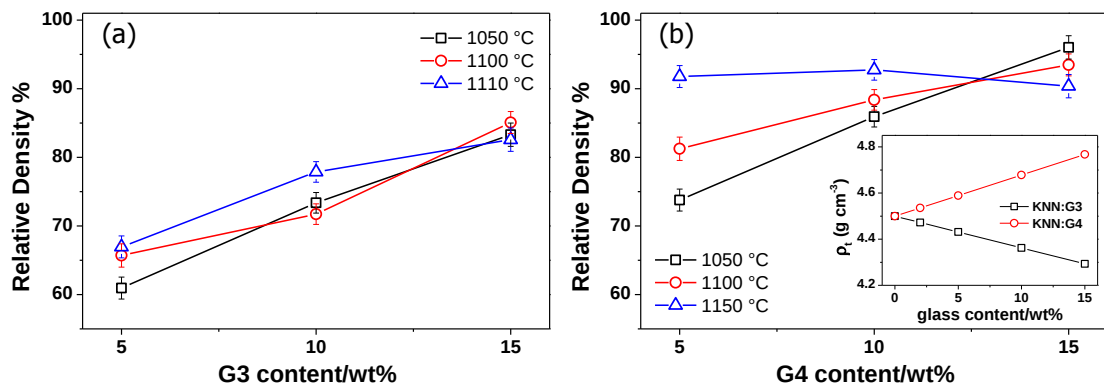


Figure 5.53 Influence of glass content and sintering temperature on the relative density for (a) KNN-xG3 and (b) KNN-xG4, where x= 5, 10 and 15 wt%. The inserted figure is theoretical density of the KNN-(G3, G4) ceramic-glass composite as a function of the glass content.

5.4.2.2 Lab XRD results

The XRD patterns of KNN-10G3 and KNN-10G4 sintered at temperatures between 1050 and 1150 °C are presented Figure 5.54. The type of glass used clearly has a strong influence on the patterns, which correspond to coexisting orthorhombic (O) and

rhombohedral (R) phases with a perovskite structure, with either barium niobate or bismuth niobate secondary phases occurring at high glass contents.

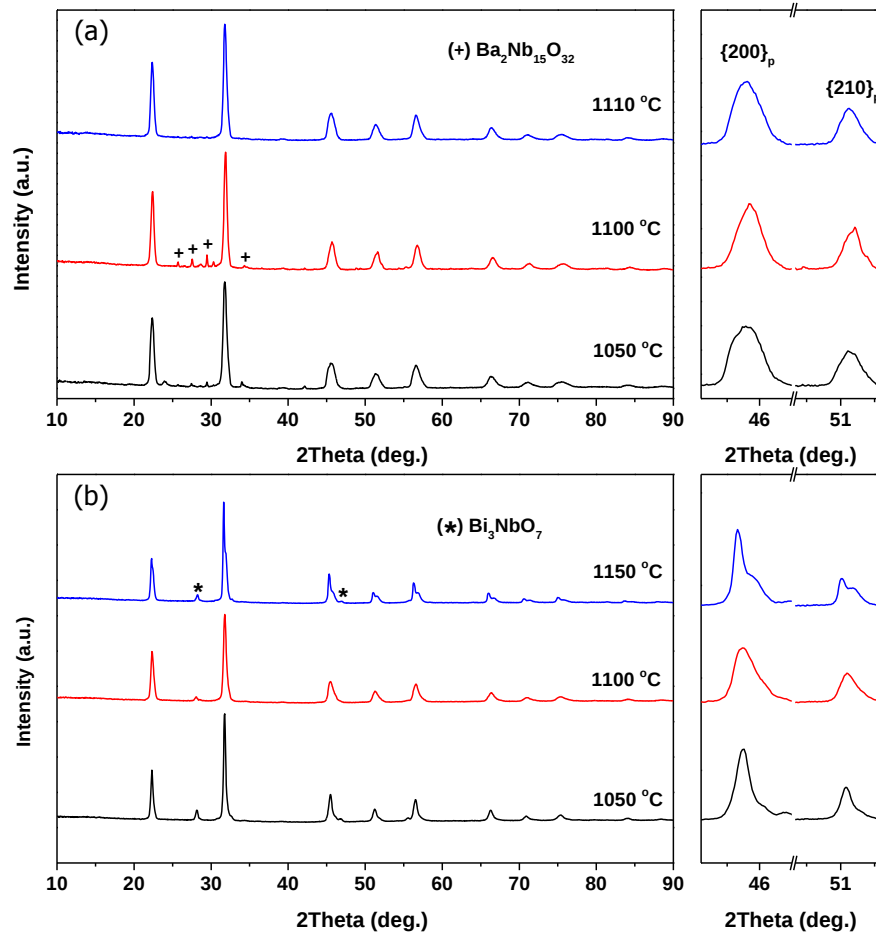


Figure 5.54 XRD patterns of (a) KNN-10G3 and (b) KNN-10G4 sintered ceramics. Second phases are identified as (+) $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$ and (*) Bi_3NbO_7 .

The presence of O-R coexisting phases in the glass-modified KNN ceramics was confirmed by full-pattern refinement, as shown in Figure 5.55 and Table 5.7. The incorporation of glass additives leads to a reduction of the O phase fraction to 82 % and 51 % for KNN-10G3 and KNN-10G4, respectively. These results generally disagree with those reported by Li et al. [136], since the addition of the BBS-glass additive into pure KNN did not result in any structural changes or the occurrence of second phases. The separation of the split diffraction peaks was improved for KNN-10G4, which could be related to increases in grain size and crystallinity.

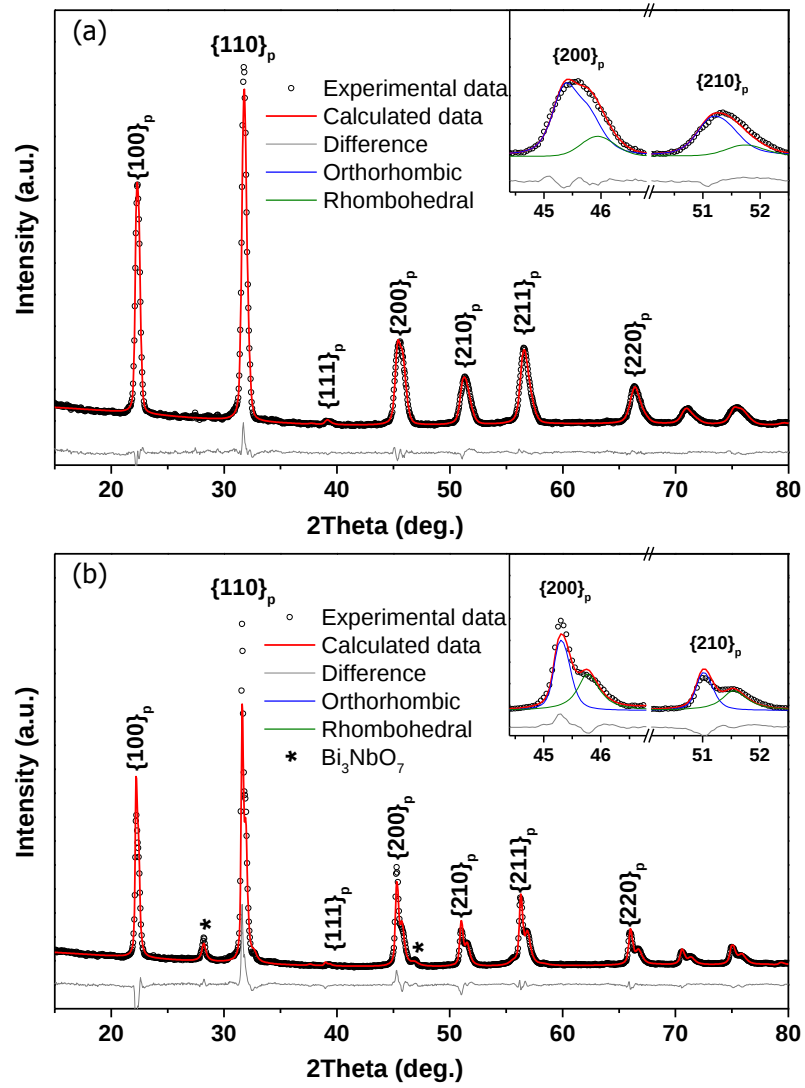


Figure 5.55 The experimental and calculated XRD peak profiles of (a) KNN-10G3 and (b) KNN-10G4 sintered at 1110 °C and 1150 °C, respectively.

Table 5.7 Coexisting phases, phase fractions, lattice parameters, χ^2 and R_{wp} of glass-modified KNN ceramics. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

Composition	Phase fraction (%)	Lattice parameter			χ^2	R_{wp}
		a (Å)	b (Å)	c (Å)		
KNN-10G3/1110 °C	O = 82(1)	$a_0=5.6500(4)$	$b_0=3.9616(2)$	$c_0=5.6552(4)$	2.92	3.23
	R = 18(2)	$a_R=5.5833(5)$	--	$c_R=13.694(4)$		
KNN-10G4/1150 °C	O = 51(3)	$a_0=5.6662(4)$	$b_0=3.9942(1)$	$c_0=5.6616(3)$	5.71	7.28
	R = 49(2)	$a_R=5.6025(3)$	--	$c_R=13.741(2)$		

5.4.2.3 Microstructure analysis

The effects of the glass additives on the microstructures of the KNN ceramics are illustrated by the SEM micrographs presented in Figure 5.56. It is noticeable that the grain size of the sintered ceramics with glass additions is not significantly larger than that of the calcined powder, being in the range 0.3 to 0.6 μm . In this case, the use of quantitative grain size analysis was hindered by the fine grain size, lack of contrast at grain boundaries and the presence of porosity.

Furthermore, the microstructure improved as the G3 content increased from 5 wt% to 15 wt% at the same sintering temperature of 1050 $^{\circ}\text{C}$. This is associated with the increase in density of the ceramics, as reported in Figure 5.53 (a) above. The improvement in densification behaviour of KNN was enhanced further by the G4 glass, as illustrated in Figure 5.56 (d). In this case, the presence of the bismuth-rich glass phase can be discerned as the irregular, lighter regions between grains.

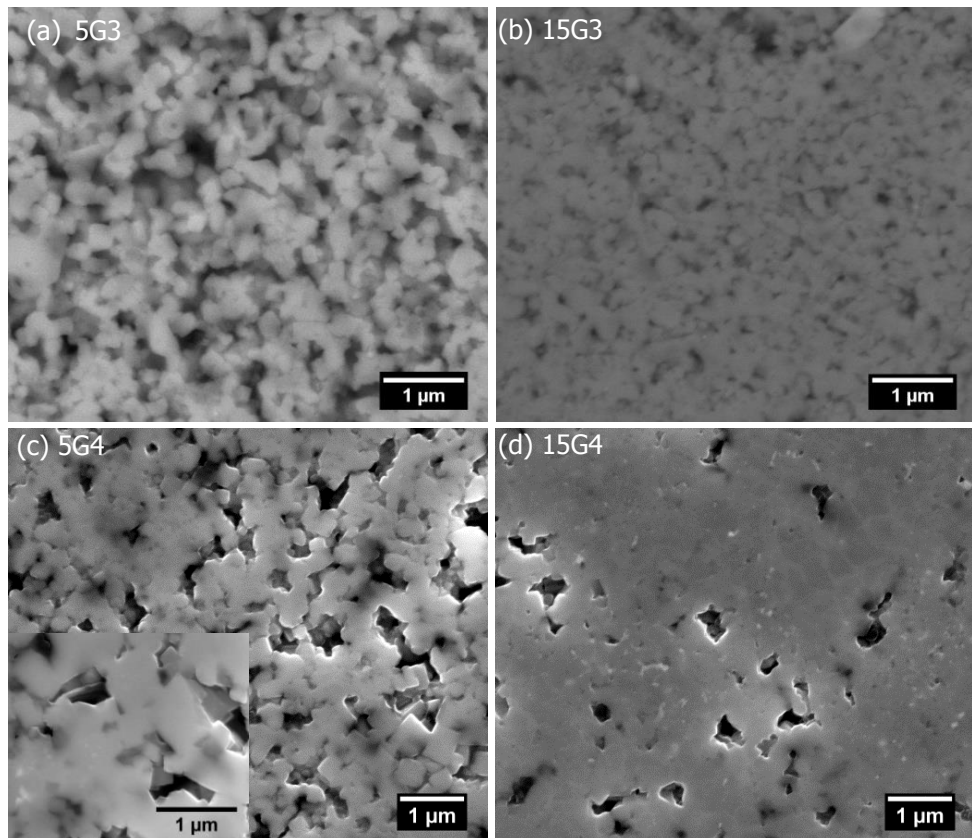


Figure 5.56 SEM micrographs of (a) KNN-5G3, (b) KNN-15G3, (c) KNN-5G4 and (d) KNN-15G4 sintered at 1050 $^{\circ}\text{C}$.

5.4.2.4 Temperature dependence of dielectric properties

The influence of the glass additives on the dielectric behaviour of KNN ceramics is illustrated by the results presented in Figure 5.57 to Figure 5.59, which show the temperature-dependence of relative permittivity and loss for KNN-G3 and KNN-G4 ceramics prepared using various sintering temperatures (1050 to 1150 °C) and glass contents (5 to 15 wt%).

The results obtained KNN-10G3 and KNN-10G4 sintered at 1100 °C at various measurement frequencies from 1 to 100 kHz are presented in Figure 5.57. These results suggest the occurrence of two phase transitions in the glass-modified KNN ceramics, indicated by the lower temperature shoulder and the main peak in the ϵ_r -T relationship. The anomalies in the relative permittivity curves correspond to the orthorhombic-tetragonal transformation (T_{O-T}) at approximately 200 °C and the tetragonal-cubic (T_{T-C}) transformation at the Curie temperature of approximately 400 °C. The dielectric properties are affected significantly by measurement frequency, particularly at high temperatures, although the transition temperatures are frequency-invariant. The latter observation suggests that the frequency dispersion of relative permittivity and loss is not due to relaxor ferroelectric behaviour. Instead, the increase in relative permittivity at low frequencies is attributed to an interfacial space-charge polarisation mechanism and is associated with increasing electrical conductivity, indicated by the increase in loss tangent [196].

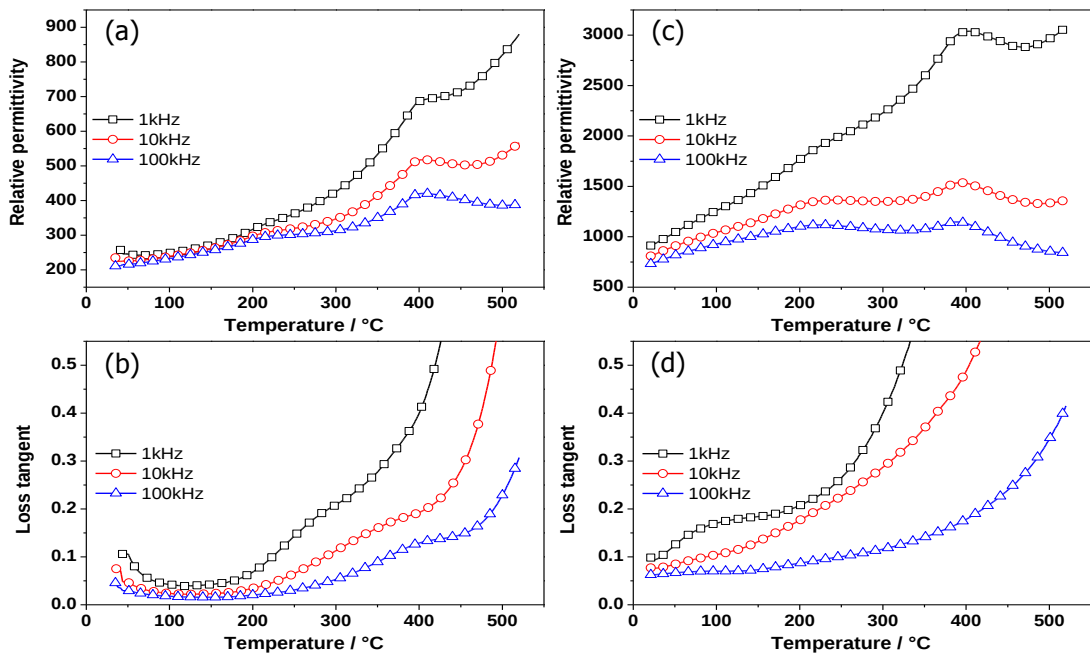


Figure 5.57 ϵ_r -T and $\tan\delta$ -T relationships for (a)-(b) KNN-10G3 and (c)-(d) KNN-10G4 sintered at 1100 °C, measured at frequencies of 1, 10 and 100 kHz.

The influence of sintering temperature on the temperature-dependence of relative permittivity and loss tangent for the KNN-15G3 and KNN-15G4 ceramics is shown in Figure 5.58. The relative permittivity decreased slightly due to the presence of G3 in comparison with the results for pure KNN represented in Figure 5.51 above. This could possibly be due to the reduction in relative density of the ceramic samples sintered with G3, reported in 5.4.2.1 above. Furthermore, the two phase transitions (T_{O-T} and T_{T-C}) of KNN-15G3 ceramic, Figure 5.58 (a), are slightly shifted to lower temperatures especially at the high sintering temperature, 1110 °C. An additional anomaly is evident in the ϵ_r -T curves for KNN-15G3 at a temperature of approximately 55 °C. Although the origin of this anomaly is not confirmed at present, it could potentially indicate the R-O transformation, which might be shifted to a higher temperature due to the presence of the G3 glass.

The presence of the G4 glass additive, Figure 5.58 (c), leads to generally higher relative permittivity values ($\epsilon_r \approx 740$ at room temperature). In addition, the two phase transitions (T_{O-T} and T_{T-C}) are generally shifted to lower temperatures. On the other hand, the highest sintering temperature of 1150 °C caused clearly a reduction in the ϵ_r -T curves of KNN-15G4. This might be due to the partial volatilization of boron and bismuth oxides as described in section 5.4.2.1 above.

The higher permittivities of KNN-G4, in comparison with KNN-G3, can be understood in terms of the improved densification and higher relative permittivity of the G4 glass in comparison with that of G3 ($\epsilon_r \approx 6.5$ and 24 for G3 and G4, respectively), which cause an increase the room-temperature relative permittivity from approximately 300 to 740 for KNN-G3 and KNN-G4, respectively.

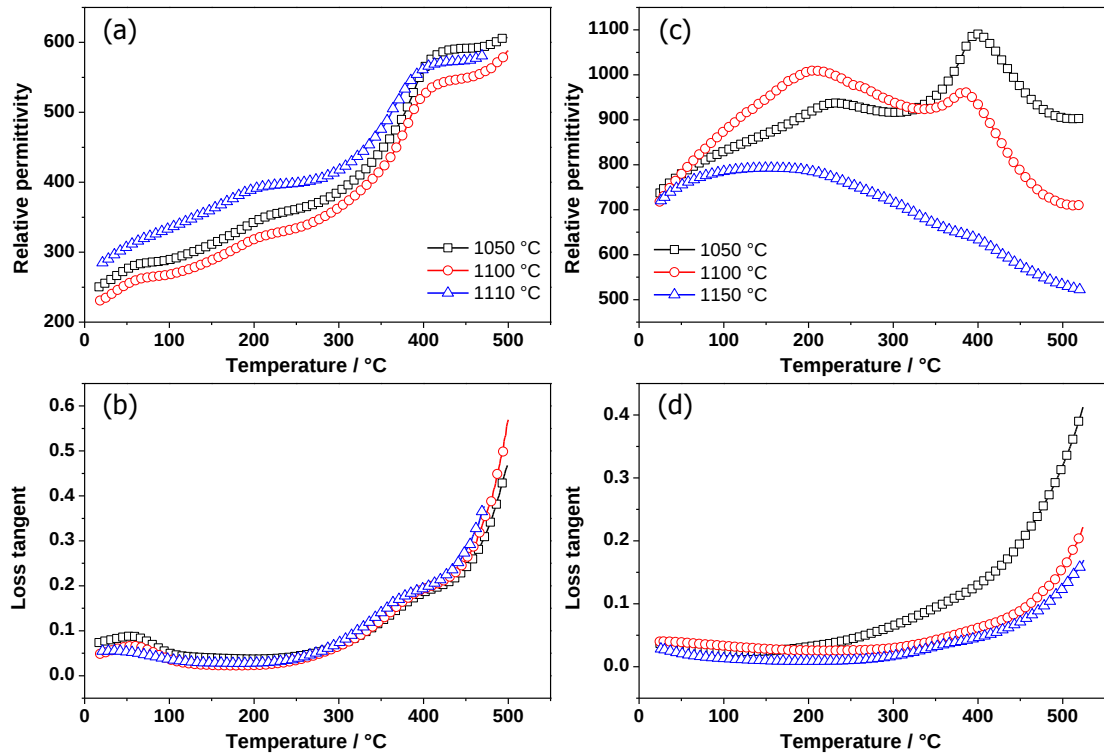


Figure 5.58 Relative permittivity and loss tangent as a function of the temperature for (a)-(b) KNN-15G3 and (c)-(d) KNN-15G4 sintered at 1050 to 1150 °C measured at a frequency of 100 kHz, respectively.

The influence of glass content on the temperature-dependence of dielectric properties of KNN ceramics is shown in Figure 5.59. In the case of G3, the high glass content (15 wt%) led to the highest relative permittivity values. However, the ϵ_r -T and $\tan\delta$ -T curves for this composition are most prominent at high temperatures and low frequencies, which indicate an interfacial polarisation mechanism associated with a relatively high electrical conductivity.

On the other hand, increasing G4 glass content from 5 to 10 wt% in KNN ceramics led to an increase in permittivity, with a slight reduction being apparent for the highest glass content of 15 wt%. This trend can be understood in terms of the reduction in porosity, which acts to increase ϵ_r at low glass contents, and the low relative permittivity of the glass (in comparison with the crystalline KNN grains), which acts to reduce ϵ_r in the more dense specimens with higher glass contents.

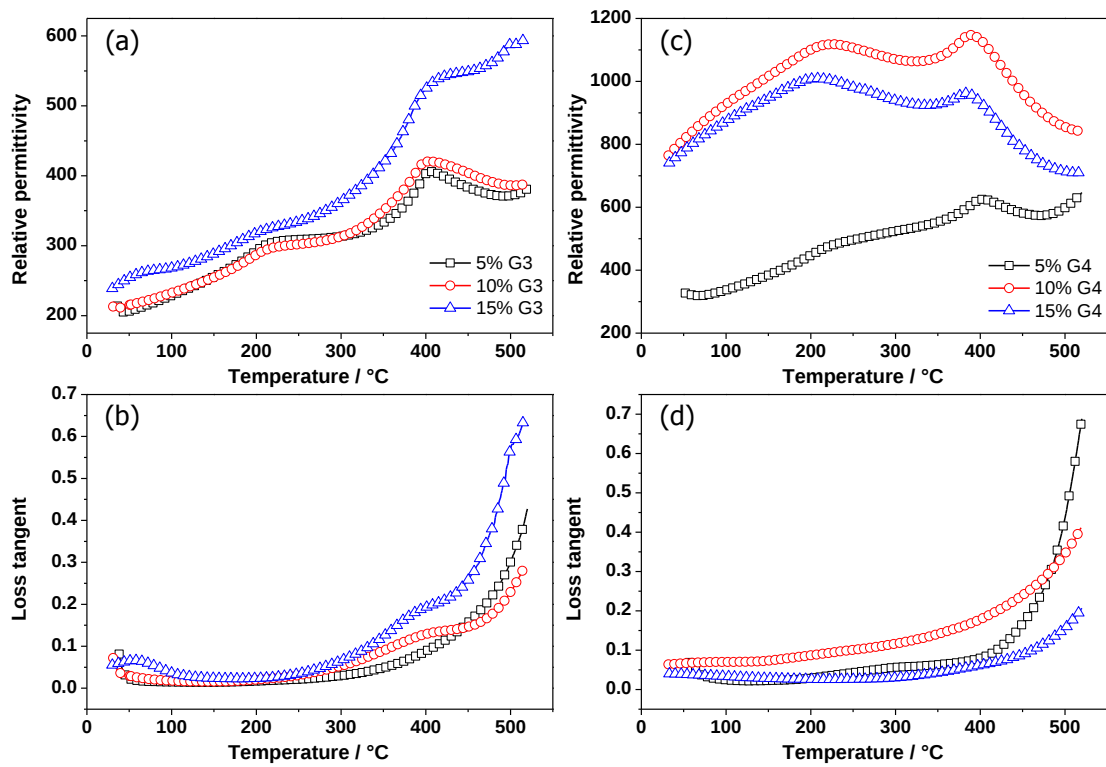


Figure 5.59 Relative permittivity and loss tangent as a function of the temperature for (a)-(b) KNN-xG3 and (c)-(d) KNN-xG4 with $x=5, 10$, and 15 wt% sintered at 1100 °C measured at frequencies of 100 kHz, respectively.

5.4.2.5 Ferroelectric properties

The influence of glass additives on the ferroelectric P-E hysteresis loops of KNN ceramics are illustrated by the results presented in Figure 5.60. Strongly rounded loops were obtained for the G3-modified KNN ceramics, which were attributed to the effects of a relatively high electrical conductivity [186], consistent with the dielectric results presented Figure 5.57 (a) and (b) in section 0 above. This effect could be associated with the high porosity of these ceramics. Rounded loops were also evident for KNN-G4 ceramics, although a slim loop was obtained for KNN-15G4.

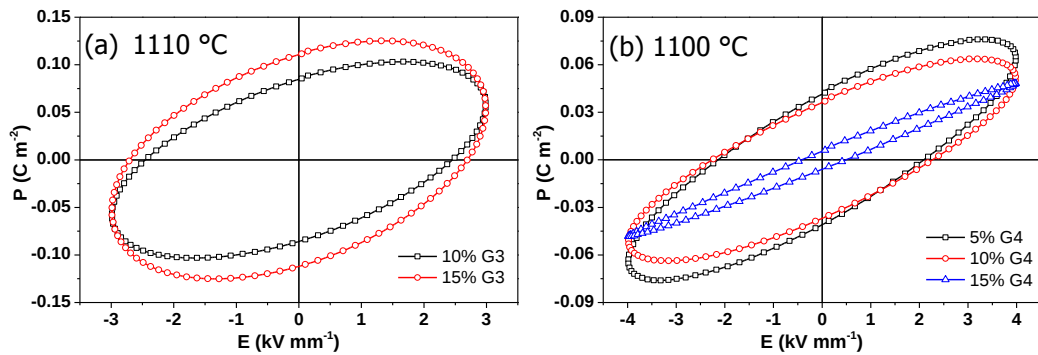


Figure 5.60 P-E hysteresis loops obtained for (a) KNN-(10, 15)G3 sintered at 1110 °C and (b) KNN-(5, 10, 15)G4 sintered at 1100 °C measured at frequency 2 Hz.

The influence of sintering temperature on the ferroelectric behaviour of KNN-15G4 ceramics obtained for sintering temperatures of 1050 to 1150 °C is presented Figure 5.61. In the case of the G4-modified material, slim P-E loops with relatively low polarisation values were obtained for each of the different sintering temperatures.

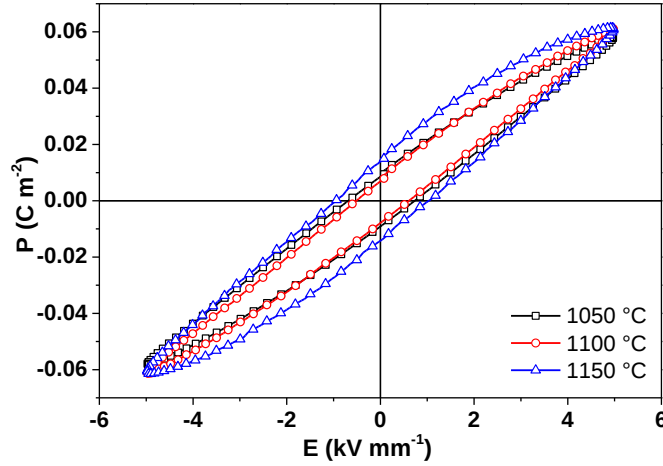


Figure 5.61 P-E hysteresis loops of KNN-15G4 sintered at 1050 to 1150 °C measured at field 5 kV mm⁻¹, 2 Hz.

The electric field-dependent dielectric behaviour for KNN-15G4 sintered at temperatures from 1050 to 1150 °C is illustrated by the ferroelectric P-E loops shown in Figure 5.62(a). It is evident that the maximum polarisation increased gradually as the electric field increased but in a non-linear fashion. The effective relative permittivity values obtained from these P-E loops appeared to show an almost linear increase in ϵ_r with increasing field amplitude up to ≈ 2 kV mm⁻¹, as shown in Figure 5.62 (b), described by the empirical Rayleigh Law. For KNN-15G4 sintered at 1150 °C, the Rayleigh coefficient was determined as 95×10^{-6} m V⁻¹.

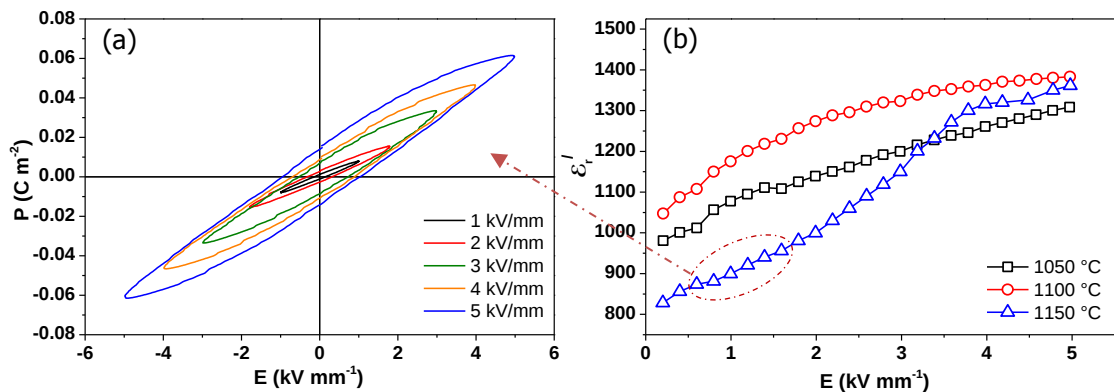


Figure 5.62 (a) P-E hysteresis loops obtained for KNN-15G4 sintered at 1150 °C and (b) electric field-dependence of relative permittivity for KNN-15G4 sintered at 1050 to 1150 °C, measured at a frequency of 2 Hz.

5.5 Glass-modified KBN ceramics

In practise, KNN ceramics are generally modified chemically to further enhance their piezoelectric properties and hence meet the needs for practical applications. Consequently, there have been many publications on suitable dopants for KNN ceramics. Amongst these, the combination of Sb, Bi and Zr has been identified in recent publications as a particularly attractive option [85, 197].

In this section, the influence of G3 and G4 glasses on the microstructure and dielectric properties of $0.96(\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3)-0.04(\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$ (KBN) will be discussed. The glasses were added to the calcined KBN powder in varying proportions according to the formula $(1-x) \text{KBN}-x\text{G3}$, G4 with $x=5, 10$ and 15 wt%, using a sintering temperature in the range 1050 to 1150 °C.

5.5.1 Relative density analysis

In pure KBN, the sintering temperature plays an important role in the densification of ceramics. In the present work, the relative density was found to increase from approximately 85 to 92 % as the sintering temperature increased from 1150 to 1170 °C. The use of temperatures above 1170 °C resulted in excessive evaporation of the volatile K_2O and Na_2O oxides, leading to reduced final density values [85].

The influence of glass additives on the relative densities of the KBN ceramics is shown in Figure 5.63., while the figure insert shows the changes in theoretical density of the KBN-glass composites as a function of the glass content, calculated according to the method described in section 4.6.1. The relative densities of the KBN-G3 ceramics sintered at a temperature of 1050 °C were all in the range of approximately 77 to 88 %, Figure 5.63 (a), indicating poor densification. At a G3 glass content of 2 wt%, increasing the sintering temperature from 1050 to 1110 °C resulted in an increase in relative density to values in the range 76 to 87 %, which is still considered to be low. On the other hand, it is apparent that the use of the G4 glass yielded improvements in the density, Figure 5.63 (b). At a high sintering temperature of 1150 °C, the relative density of KBN-5G4 was approximately 91%. Then it decreased slightly to 89% as the glass content increased. The latter effect could be due to volatilisation of both boron and bismuth oxides at high temperatures, as reported by Lai [119].

Furthermore, with increasing sintering temperature, the relative density increased to approximately 94 % for KBN-10G4 and 95% for KBN-15G4 sintered at 1100 °C and 1050 °C, respectively.

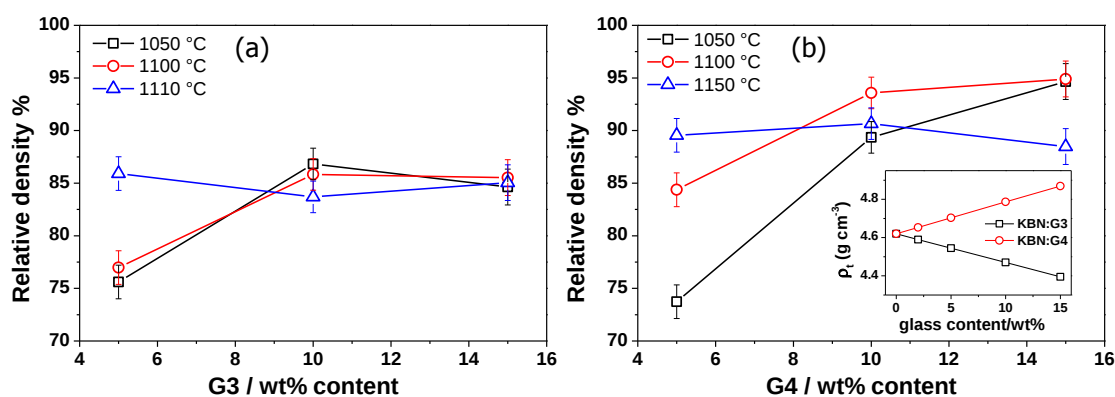


Figure 5.63 Influence of glass content on the relative density for (a) KBN-xG3 and (b) KBN-xG4 sintered ceramics. The figure inset shows the theoretical densities of the KBN-(G3, G4) ceramic-glass composites as a function of the glass content.

5.5.2 Lab XRD results

XRD patterns of the sintered pure KBN ceramics are presented in Figure 5.64. These patterns are consistent with a pseudo-cubic perovskite phase, with no evidence to indicate the presence of any other crystalline second phases. Moreover, the ceramics mainly comprise orthorhombic (O) and rhombohedral (R) coexisting phases, as confirmed in Figure 5.66 (a) and Table 5.8, below.

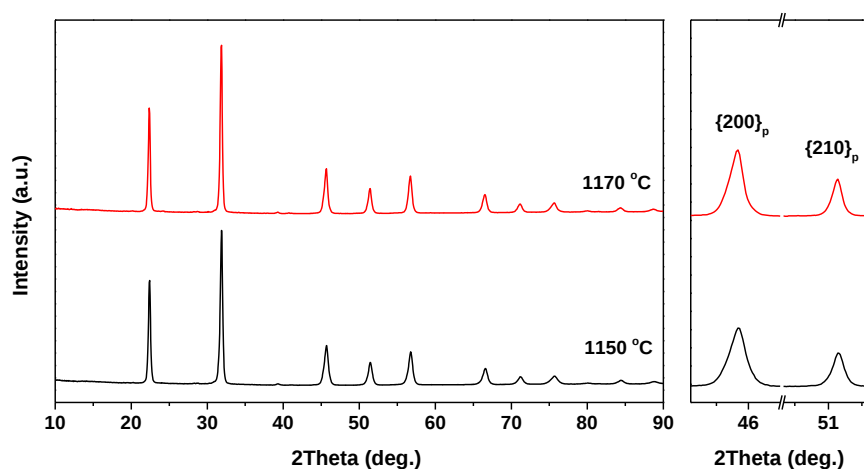


Figure 5.64 The XRD pattern of KBN ceramic sintered at temperatures 1150 °C and 1170 °C.

The XRD patterns obtained for KBN-10G3 and KBN-10G4 sintered at temperatures between 1050 and 1100 °C are shown in Figure 5.65. There is no dramatic change due to the presence of the glass, other than the presence of second phases, identified as either barium niobate or bismuth niobate, at high glass contents. In common with the unmodified KBN ceramics, these materials comprise coexisting orthorhombic (O) and rhombohedral (R) phases with a perovskite structure. A subtle change occurred for the KBN-10G4 ceramic sintered at 1150 °C, where both $\{200\}_p$ and $\{210\}_p$ peaks showed

evidence of splitting, indicated by the appearance of a shoulder on the left side of the main peak. In addition, the diffraction peaks for G3 are asymmetric, which indicates the occurrence of a small structural distortion together with peak broadening due to the small grain sizes.

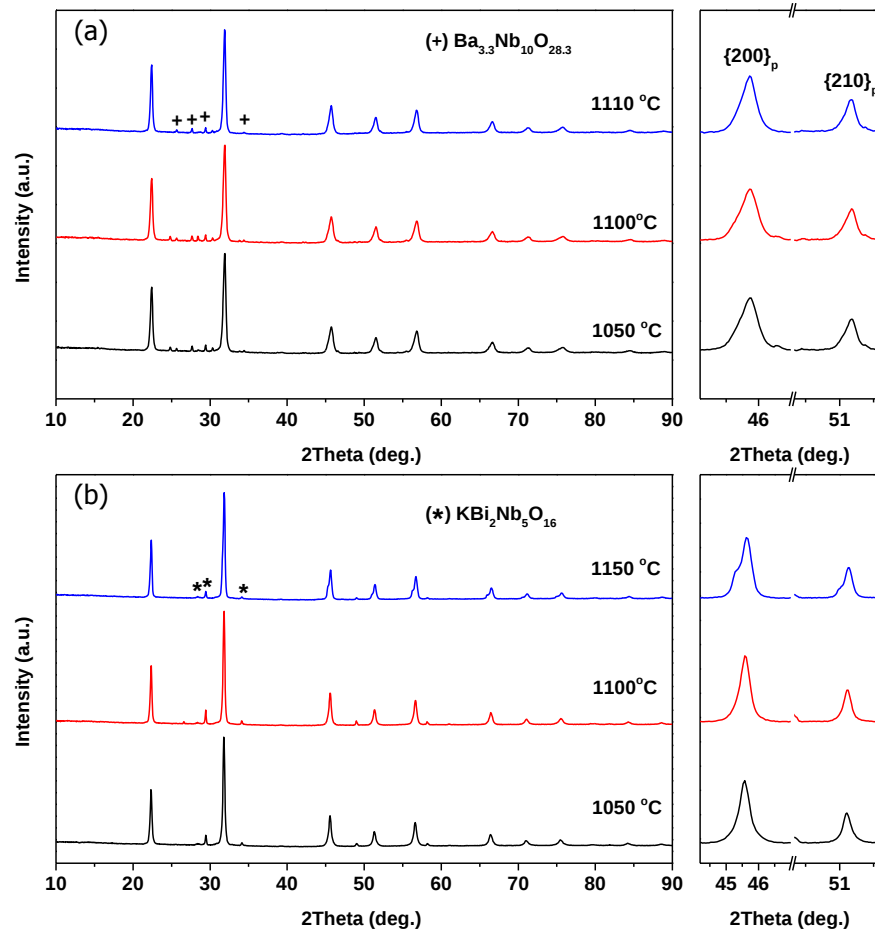


Figure 5.65 XRD patterns of (a) KBN-10G3 and (b) KBN-10G4 ceramic sintered at 1050 °C to 1150 °C, where (+) $\text{Ba}_{3.3}\text{Nb}_{10}\text{O}_{28.3}$ and (*) $\text{KBi}_2\text{Nb}_5\text{O}_{16}$.

The presence of O-R coexisting phases in the pure and glass-modified KBN ceramics was confirmed by full-pattern refinement, as shown by the results presented in Figure 5.66. and Table 5.8. In the case of pure KBN sintered at 1170 °C, shown in Figure 5.66 (a), the structure was found to comprise coexisting orthorhombic (O) and rhombohedral (R) phases with an O phase fraction of approximately 74 %.

The O-R coexisting phase structures for KBN-10G3 and KBN-10G4, sintered at 1110 °C and 1150 °C, respectively, were confirmed by full-pattern refinement as shown in Figure 5.66 (b)-(c). The glass-modified KBN-10G3 and KBN-10G4 ceramics were found to have O phase fractions of 67 % and 58 %. The impact of the glass additives on the crystal structures of KBN ceramics could be caused by minor changes in the chemical

composition of the grains, which may also be responsible for the variations in dielectric properties described in section 5.3.5 below.

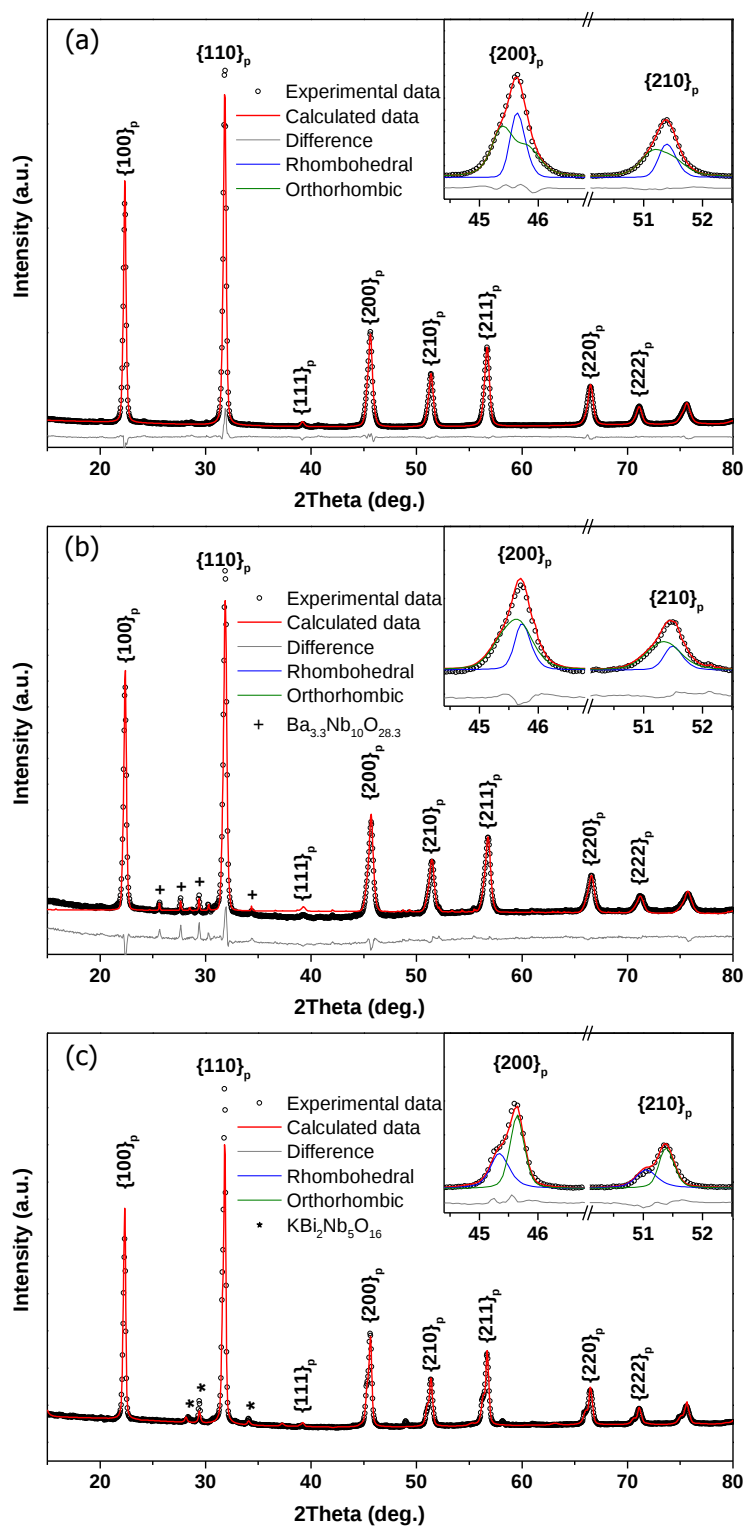


Figure 5.66 Comparison of experimental and calculated XRD peak profiles of (a) pure KBN ceramic sintered at 1170 °C, (b) KBN-10G3 sintered at 1110 °C and (c) KBN-10G4 ceramic sintered at 1150 °C.

Table 5.8 Coexisting phases, phase fractions, lattice parameters, χ^2 and R_{wp} of KBN ceramics. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

Composition	Phase fraction (%)	Lattice parameter				χ^2	R_{wp}
		a (Å)	b (Å)	c (Å)	α (°)		
Pure KBN/ 1170 °C	O = 74(1)	$a_o=5.6154(2)$	$b_o=3.9957(5)$	$c_o=5.6154(3)$	--	5.3	3.94
	R = 26(2)	$a_R=3.9672(3)$	--	--	89.94(1)		
KBN-10G3/ 1110 °C	O = 67(3)	$a_o=5.6481(3)$	$b_o=3.9580(4)$	$c_o=5.6519(3)$	--	6.32	4.94
	R = 33(2)	$a_R=3.9741(5)$	--	--	89.89(2)		
KBN-10G4/ 1150 °C	O = 58(1)	$a_o=5.6161(1)$	$b_o=3.9818(2)$	$c_o=5.6182(1)$	--	5.72	6.97
	R = 42(2)	$a_R=3.9993(2)$	--	--	89.97(1)		

5.5.3 Microstructure analysis

The SEM micrographs of KBN ceramics modified with G3 and G4 glasses sintered at different temperatures are shown Figure 5.67 and Figure 5.68. The incorporation of the glass additives generally leads to an improvement in densification during sintering, which is reflected in the changing microstructures of the KBN-based ceramics.

For G3, the increasing glass content appeared to have little effect on the grain sizes of the sintered ceramics, which are in the range 0.3-0.7 μm , but there was a noticeable reduction in porosity, which is consistent with the increase in density reported in Figure 5.63 above.

The influence of G4 on microstructure was more dramatic since the KNN-G4 ceramics exhibited improved densification behaviour, which yielded clear reductions in porosity and increased grain growth. Furthermore, the development of a 'core-shell' type microstructure was clearly evident, as shown for KBN-15G4 in Figure 5.67 (d). In addition, there is evidence for lighter regions of a Bi-rich second phase, identified by XRD as $\text{KBi}_2\text{Nb}_5\text{O}_{16}$ (see section 5.5.2), and the Bi-containing glassy phase [198, 199]. The core-shell microstructures can be formed because of the excess of dopants above the solubility limit, leading to controlled or suppressed diffusion processes [198]. In the present case, the light grey shell regions could represent the bismuth- and zirconia-rich solid solution with the lighter grey core regions being a lightly-doped KNN phase.

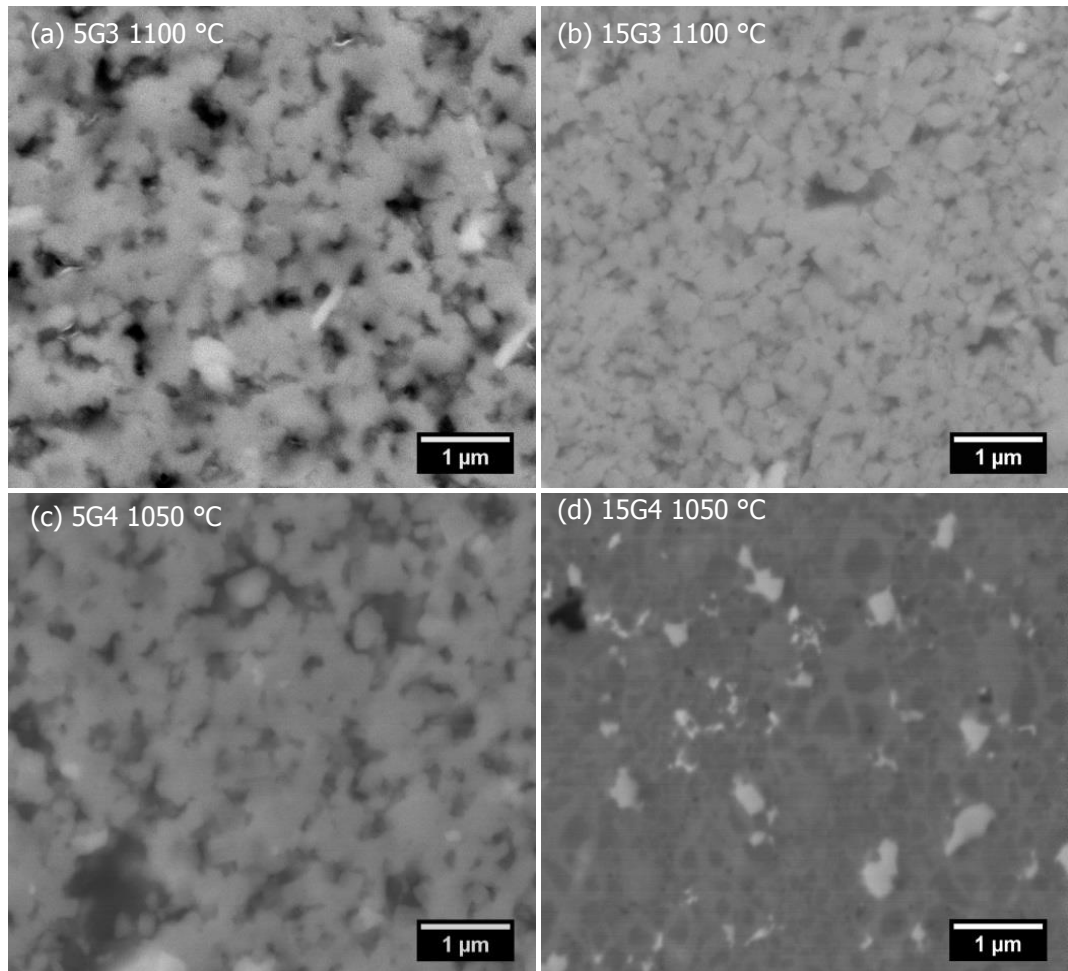


Figure 5.67 SEM micrographs for (a)-(b) KBN-(5,15)G3 sintered at 1100 °C and (c)-(d) KBN-(5,15)G4 sintered at 1050 °C.

EDS spectra were recorded in the form of line-scans to help identify the distribution of elements in the KBN-15G4 ceramic, as illustrated by the results shown in Figure 5.68. It is evident that the Nb, K and Na, are distributed uniformly throughout the crystalline KBN grains while the heavy elements, represented by Bi, are concentrated in the glassy phase, which occurs as light areas between the grains.

The Si-rich areas, which are expected to correspond to the glass phase, are not well defined, perhaps due to the limit of resolution of the EDX analysis and the weaker signals from light elements.

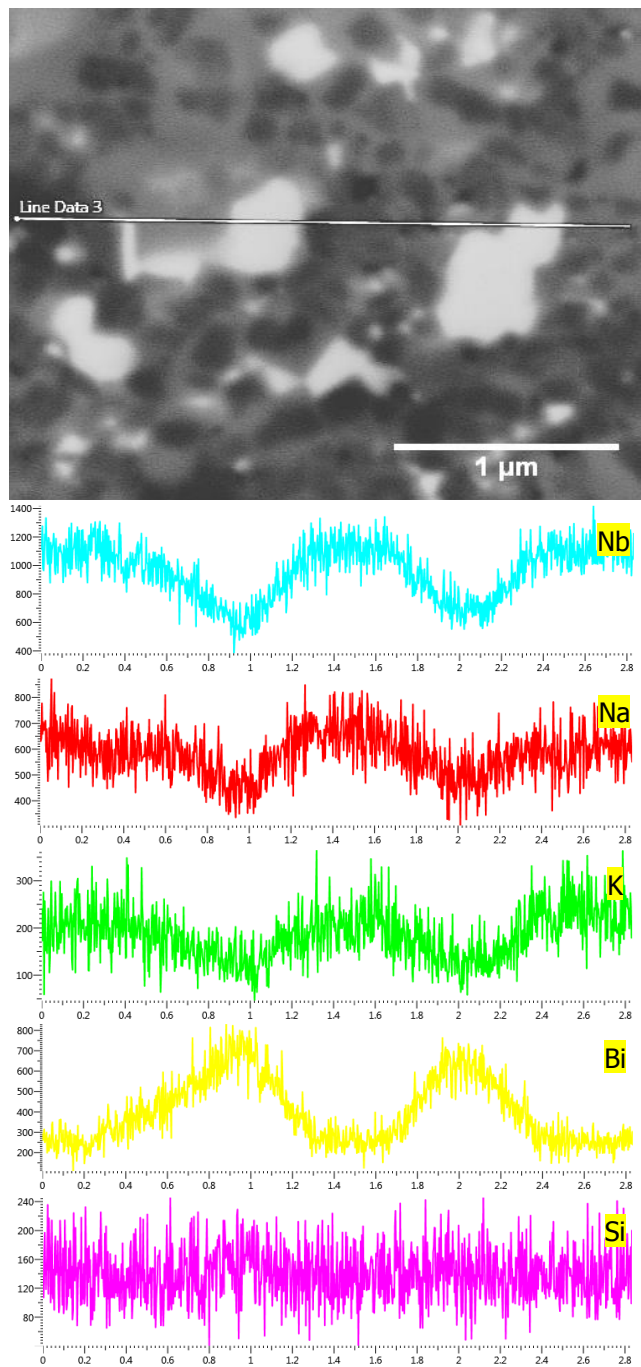


Figure 5.68 SEM image and EDS spectra of KBN-15G4 sintered at 1050 °C with corresponding chemical composition.

5.5.4 Temperature dependence of dielectric properties

The temperature-dependence of relative permittivity and loss tangent for the KBN ceramic, measured at various frequencies, is shown in Figure 5.69. It is evident that the formation of the solid solution between BNKZ and KNN causes dramatic shifts in the transition temperatures, reducing T_C from approximately 410 °C to 220 °C and T_{O-T} from 200 °C to about 50 °C, where there is a slight change in relative permittivity near 50 °C. These results are in agreement with those reported by Wang et al. [85].

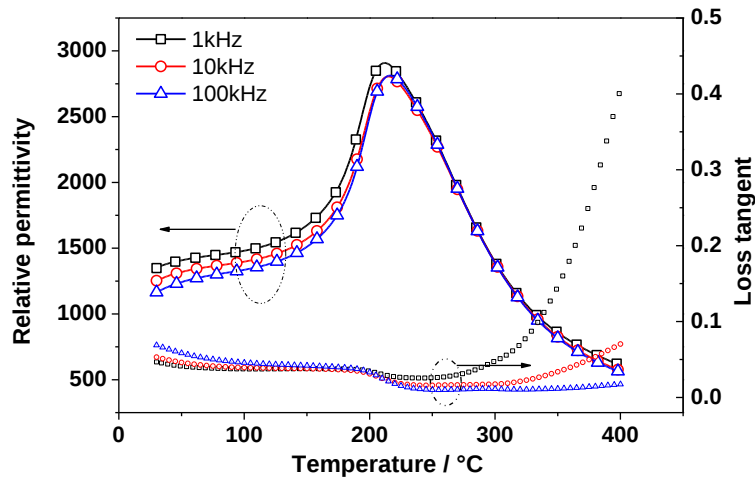


Figure 5.69 (a) Relative permittivity and (b) loss tangent as a function of temperature for pure KBN sintered at 1170 °C, measured at frequencies of 1, 10 and 100 kHz.

The influence of the glass additives on the dielectric behaviour of the KBN ceramics is illustrated by the results presented in Figure 5.70 to Figure 5.72, which show the temperature-dependence of relative permittivity and loss tangent for KBN-G3 and KBN-G4 ceramics prepared using various sintering temperatures (1050 to 1150 °C) and glass contents (5 to 15 wt%).

The dielectric properties are affected significantly by glass additives, causing anomalies in the ϵ_r -T curves corresponding to two phase transitions in the glass-modified KBN ceramics, occurring at temperatures similar to those of the phase transformations in pure KNN ceramics, as shown in Figure 2.23 in section 2.2.4.1 [79]. Figure 5.70 shows the influence of temperature on the relative permittivity and loss tangent for KBN-5G3 and KBN-5G4 ceramics sintered at 1100 °C, at various measurement frequencies from 1 to 100 kHz. The obvious frequency-dependence in both parameters at high temperatures indicates the influence of conduction and associated interfacial polarisation [196].

Although the origin of these changes in the ϵ_r -T curves is not completely clear, it could potentially be caused by heterogeneous dissolution and reprecipitation of dopant elements in the glass phase, leading to the formation of some lightly-doped KNN grains that transform in a similar way to the pure KNN ceramic. Similar effects were observed in the glass-modified BCZT ceramics described in section 5.3 above. The identification of bismuth-rich second phases in the structural and microstructural studies described in sections 5.5.2 and 5.5.3 above provides some evidence to support this interpretation. Further micro-chemical analysis of these materials using wavelength dispersive x-ray spectroscopy (WDS) would help to resolve this point. The generally higher relative permittivity values for the G4-modified KBN ceramics (in comparison with G3) are attributed to the improvements in densification behaviour and the higher relative permittivity of this glass.

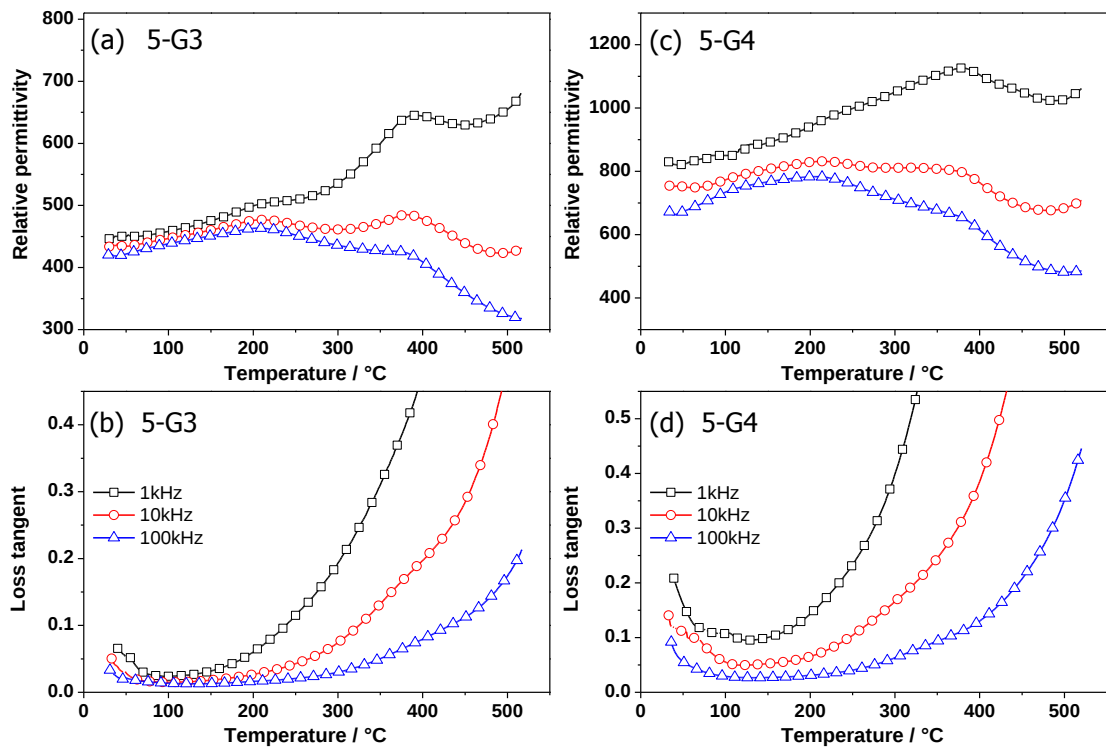


Figure 5.70 ϵ_r -T and $\tan\delta$ -T relationships for (a)-(b) KBN-5G3 and (c)-(d) KBN-5G4 sintered at 1100 °C, measured at frequencies of 1, 10 and 100 kHz.

The relative permittivity values were reduced further at a higher glass content of 15%, as shown in Figure 5.71. However, a peak in ϵ_r (≈ 400) near 120°C was apparent for KBN-15G3 ceramics sintered at 1110 °C, as shown in Figure 5.71. Furthermore, high ϵ_r values (≈ 1000) were obtained for the KBN-15G4 ceramic from room temperature up to 50 °C. These observations indicate significant shifts in the phase transformation

temperatures due to the presence of the glass, which is attributed to micro-scale chemical heterogeneity, as indicated in Figure 5.67 and Figure 5.68 above.

Furthermore, increasing sintering temperature generally led to improvements in the relative permittivity. In this case, at the highest sintering temperatures used in the present study, the KBN-15G3 and KBN-15G4 ceramics gave ϵ_r values around 370 and 950 for specimens sintered at 1110 and 1150 °C, respectively.

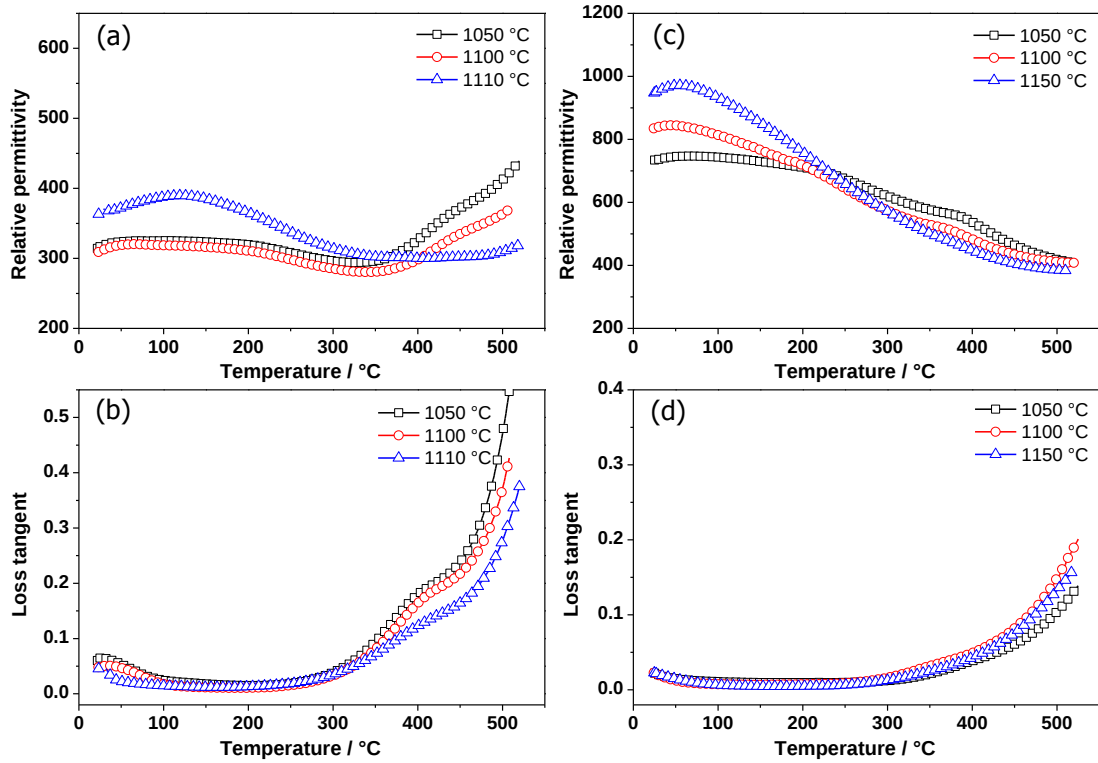


Figure 5.71 Relative permittivity and loss tangent as a function of the temperature for (a)-(b) KBN-15G3 and (c)-(d) KBN-15G4 sintered at 1050 to 1150 °C, measured at a frequency of 100 kHz.

The influence of glass content on the phase transformation temperatures, as indicated by anomalies in ϵ_r -T and $\tan\delta$ -T relationships, is illustrated further by the results presented in Figure 5.72. In the case of low glass contents (5 wt% of G3 and G4), there are two clear anomalies, which correspond to the orthorhombic-tetragonal (O-T) transformation at approximately 200 °C and the tetragonal-cubic (T-C) transformation at the Curie temperature of approximately 400 °C, as noted above in Figure 5.70.

With increasing glass content, there was a general decrease in relative permittivity values due to the presence of the low- relative permittivity glass phase between grains, as discussed previously. However, anomalously high relative permittivity values were obtained in certain temperature ranges, which are associated with the phase

transformation temperatures. Interactions between the glass and KBN crystalline phases lead to changes in the composition of the KBN phase and micro-heterogeneity, which in turn influences the phase transformation temperatures. For example, for the KBN ceramics containing 10 to 15 wt% G3 and G4, the increases in relative permittivity around a temperature of 50 °C could be associated with the R-O transformation (occurring at approximately -120 °C for pure KNN), which is shifted to higher temperatures due to changes in composition of the KBN grains during heat treatment.

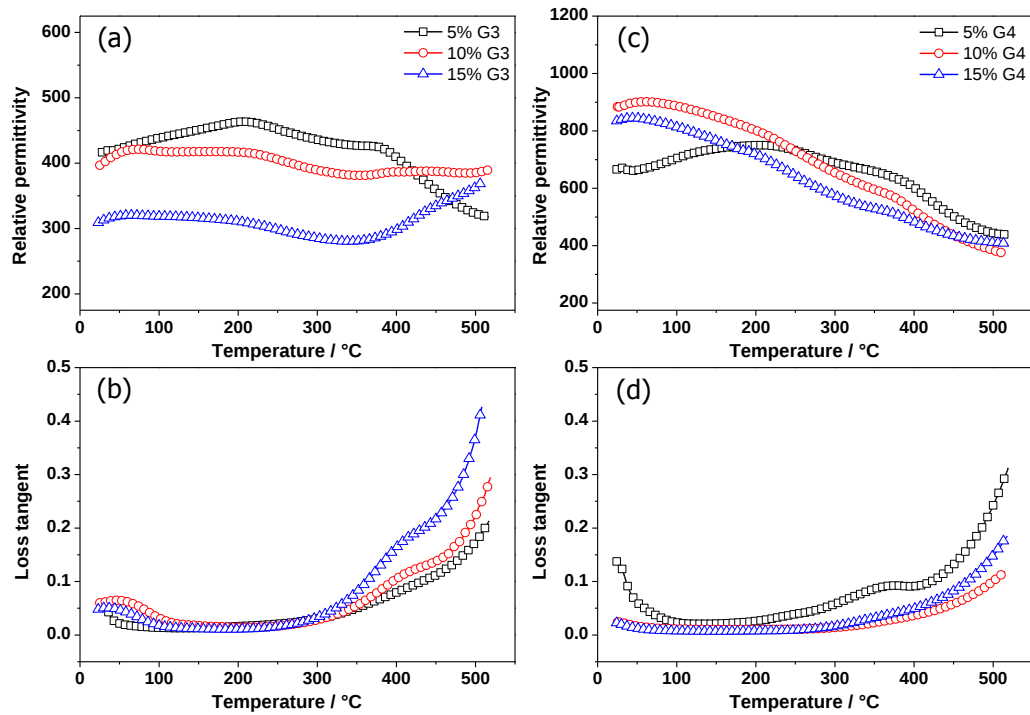


Figure 5.72 Relative permittivity and loss tangent as a function of the temperature for (a)-(b) KBN-xG3 and (c)-(d) KBN-xG4 with $x=5, 10$, and 15 wt% sintered at 1100 °C, measured at a frequency of 100 kHz, respectively.

5.5.5 Ferroelectric properties

The influence of the sintering temperature and glass content on the ferroelectric behaviour of glass-modified KBN ceramics are illustrated by the results presented in Figure 5.73 to Figure 5.75. For KBN ceramics modified with 15 wt% G3 additives, the P-E loops displayed a rounded appearance, as shown in Figure 5.73 (a). This is attributed to the effects of a relatively high electrical conductivity, associated with the glassy phase [186]. On the other hand, the G4-modified KBN ceramics yielded slim but unsaturated P-E loops with maximum polarisation values in the range 0.041 to 0.054 C m⁻² at a maximum electric field amplitude of 5 kV mm⁻¹, Figure 5.73.

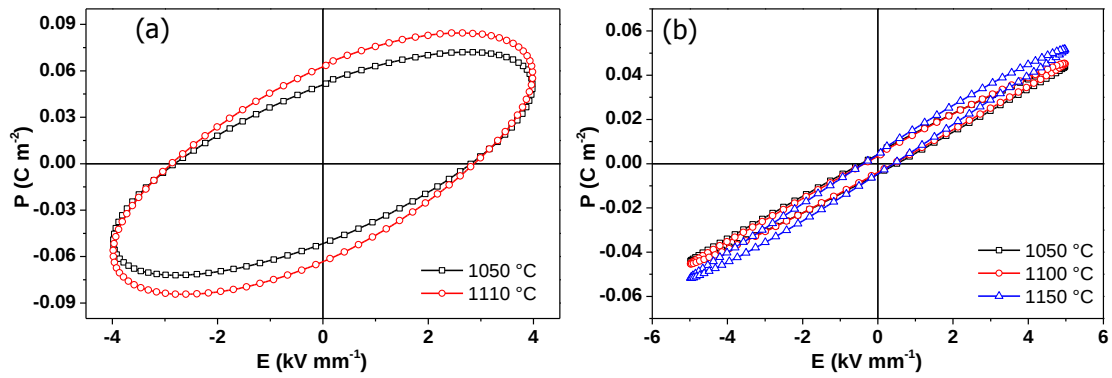


Figure 5.73 P-E hysteresis loops obtained for (a) KBN-15G3 and (b) KBN-15G4 sintered at various temperatures.

At a fixed sintering temperature of 1150 °C, the P-E loops of the KBN-10G4 and KBN-15G4 ceramics were both slim in appearance, but a rounded 'lossy' loop was obtained for KBN-5G4 (Figure 5.74). This effect can be correlated with the reduction in density for this composition at high sintering temperatures; the presence of open porosity can lead to the adsorption of atmospheric moisture on internal pore surfaces and hence cause a relatively high electrical conductivity and dielectric loss.

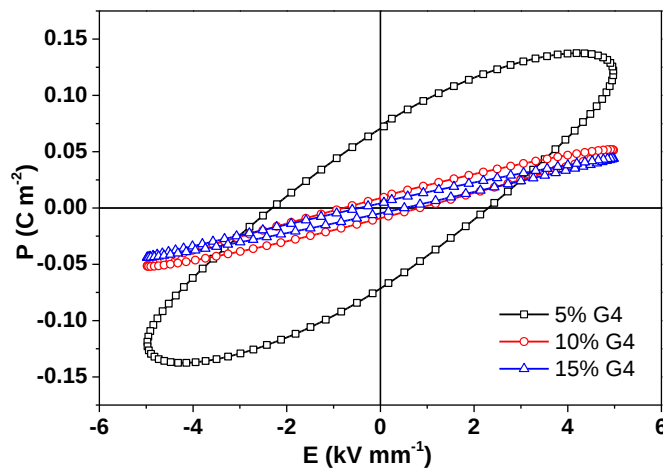


Figure 5.74 P-E hysteresis loops of KBN-xG4 sintered at 1150 °C, with x = 5, 10, and 15 wt% measured at field 5 kV mm⁻¹, 2 Hz.

Field-dependent P-E hysteresis loop measurements for KBN-15G4, shown in Figure 5.75, indicated a predominantly linear behaviour. The corresponding relative permittivity values increased slightly with increasing field amplitude and were generally in agreement with the low-field dielectric measurements reported in section 5.5.4 above.

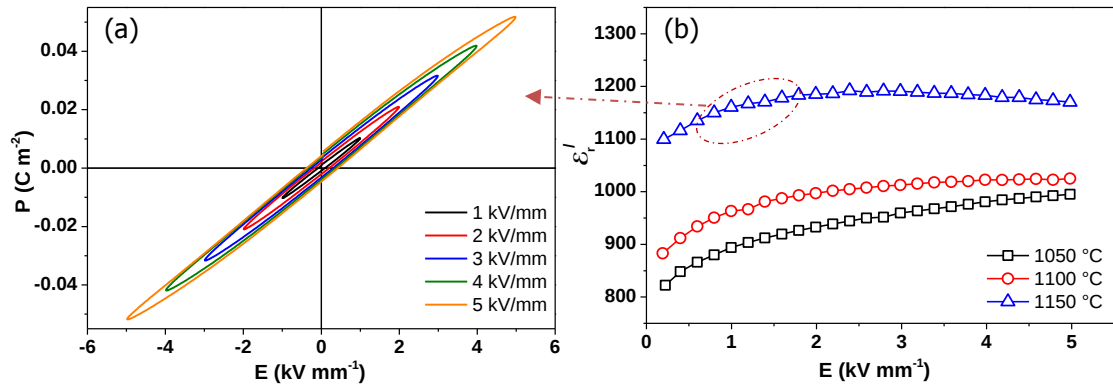


Figure 5.75 (a) P-E hysteresis loops obtained for KBN-15G4 sintered at 1150 °C measured at the different electric field and (b) relative permittivity calculated from P-E hysteresis loops of KBN-15G4 sintered at 1050 to 1150 °C measured at a field of 5 kV mm^{-1} , 2 Hz.

5.6 Crystallization of KNN-based glass-ceramics

Glass-ceramics containing ferroelectric ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$) (KNN) can potentially combine the desirable characteristics of glasses and ferroelectric crystals, giving rise to novel materials having pore-free and fine-grained microstructures; such materials have potential applications in high energy density capacitors and electro-optic devices [200, 201].

The aim of this work was to develop glass-ceramics containing high levels of perovskite KNN phase using potassium and sodium-modified barium borosilicate glass (denoted BBSKN or previously G2), with different KNN contents ranging from 50 to 80 mol% (denoted K-50 to K-80), with a view to applications as energy storage dielectrics. Experiments were conducted to determine the crystallisation behaviour, microstructure and dielectric/ferroelectric properties of such glass-ceramics.

5.6.1 Thermal analysis

Differential scanning calorimetry (DSC) results, was carried out on the as-quenched glass samples to analyse the thermal parameters, including the glass transition (T_g) and crystallisation temperatures (T_{cr}). Then, these parameters were employed for selection of the heat treatment processes. The DSC results obtained for the K-50 to K-80 glass samples during heating up to 900 °C, are shown Figure 5.76. Endothermic peaks are generally interpreted as resulting from the glass transition, while exothermic peaks are usually associated with crystallisation processes.

The glass transition (at T_g) was observed at temperatures around 540 °C and was more clearly evident for K-80 and K-70 than the other glasses. Another feature in the DSC curves was a broad exothermic peak (labelled as *) at ≈ 575 °C, which could be due to liquid-liquid phase separation (*liquation*) of the glass [202, 203]. The main exothermic peak (at T_{cr}) has a sharp line-shape and indicates the precipitation of the first crystalline phases from the glass matrix at temperatures in the range 615 to 620 °C. It is noted that T_{cr} for K-50 was approximately 620 °C, while it shifted to the lower temperature of approximately 615 °C for the remaining samples. This could be related to the higher content of glass-forming oxides in K-50. Multiple exothermic peaks (labelled as +) were observed at temperatures up to 900 °C for K-70 and K-80, which might be associated with phase transitions or further crystallisation processes [132].

Therefore, the glasses were subsequently heat treated at temperatures between 600 °C and 850 °C in order to identify the crystalline phases present at each crystallisation step.

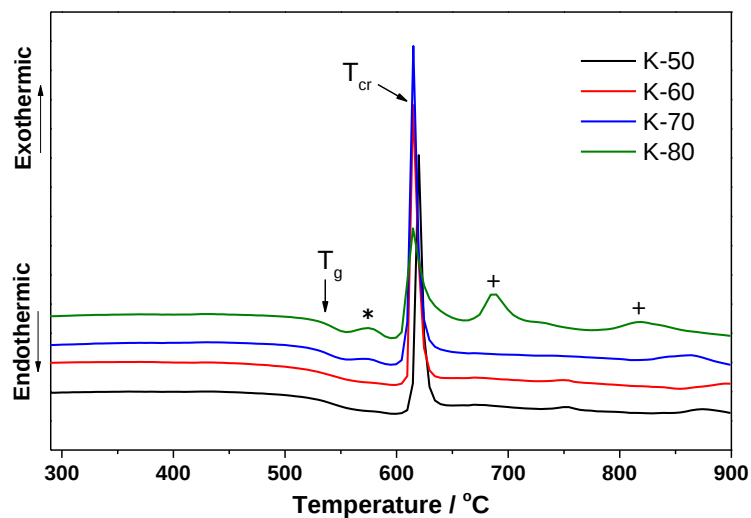


Figure 5.76 The DSC results of glass samples showing endothermic and exothermic peaks for the heating cycle at a temperature up to 900 °C. The exothermic peaks are labelled as (T_{cr}) crystallisation peak, (T_g) glass transition, (*) phase separation of the glass and (+) secondary crystallisation peaks.

5.6.2 Physical appearance and density

The physical appearances of the K-50 glass-ceramics subjected to different heat treatment conditions are presented in Figure 5.77. It is clear that the fully amorphous and transparent glass became opaque during the heat treatment, indicating the occurrence of the crystallisation processes. The surface 'sheen' on all of the specimens is a direct indication that a significant amount of glassy phase is still present after heat treatment at temperatures up to 800 °C.

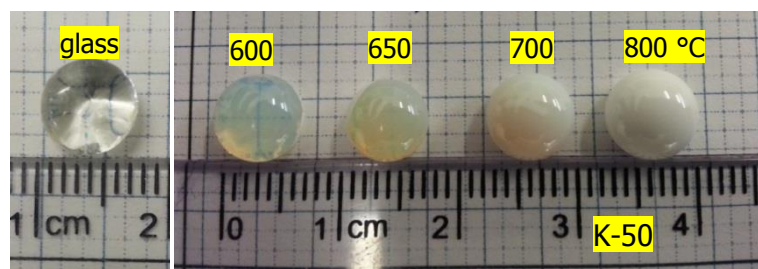


Figure 5.77 The physical appearances of glass and glass-ceramics heat treated at different temperatures, showing the change in the transparency due to the crystallisation process.

The density results of glass-ceramics with several different KNN contents heated at a temperature in the range between 650 and 850 °C are presented in Figure 5.78. Note that the figure insert shows the changes in theoretical density of the glass-ceramics as a function of KNN content, calculated using the method described in section 4.6.1.

It can be seen that the theoretical density of the glass-ceramics increased with increasing KNN content. As would be expected, the increase in the heat treatment temperature and KNN content caused a general increase in the density of all glass-ceramic samples. Moreover, the average increase in density after heat treatment up to 850 °C is about 15 %, while the average change due to the increase in KNN content at a fixed heat treatment temperature was approximately 8 %. These results are consistent with the changes in crystal structure and microstructure reported in sections 5.6.3 and 5.6.4 below.

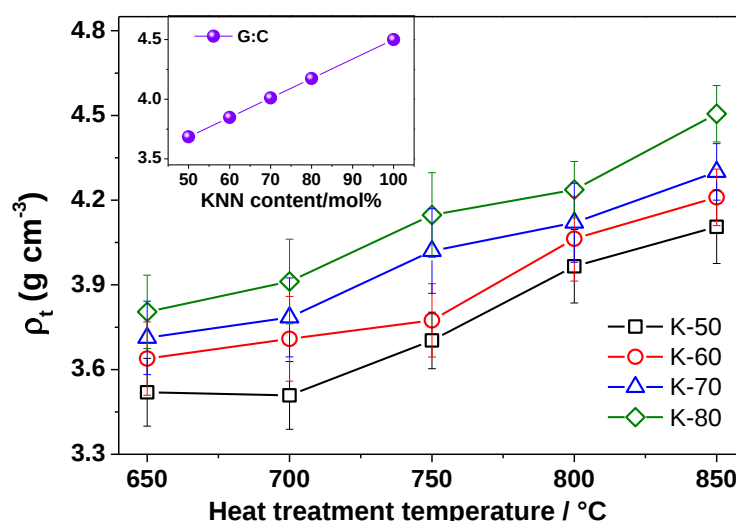


Figure 5.78 The bulk density (total) of glass-ceramics samples versus heat treatment temperature. The figure insert is the theoretical density of the KNN-BBS ceramic-glass as a function of the KNN content.

5.6.3 Lab XRD results

The glass and glass-ceramic samples were examined by XRD to identify the amorphous and crystalline phases obtained by the heat treatment process. Figure 5.79 shows examples of the changes in the XRD patterns for K-50 and K-70 during heat treatment between 600 and 800 °C. It can be observed first that all of the glasses exhibit an amorphous nature in the as-quenched state. Secondly, the initial crystallisation occurs at temperatures between 600 and 650 °C, in agreement with DSC results (Figure 5.76 above). In this case, the crystallisation happens at temperatures slightly lower than those results reported by Hanyu et al. [129] and Pu et al. [204]. Furthermore, the

intensity of the diffraction peaks at 2θ values in the range 22 to 30° (which is identified as the second phase in Figure 5.80 below) decreased with increasing KNN content. In addition, the initial crystallisation temperature was reduced slightly for the higher KNN content.

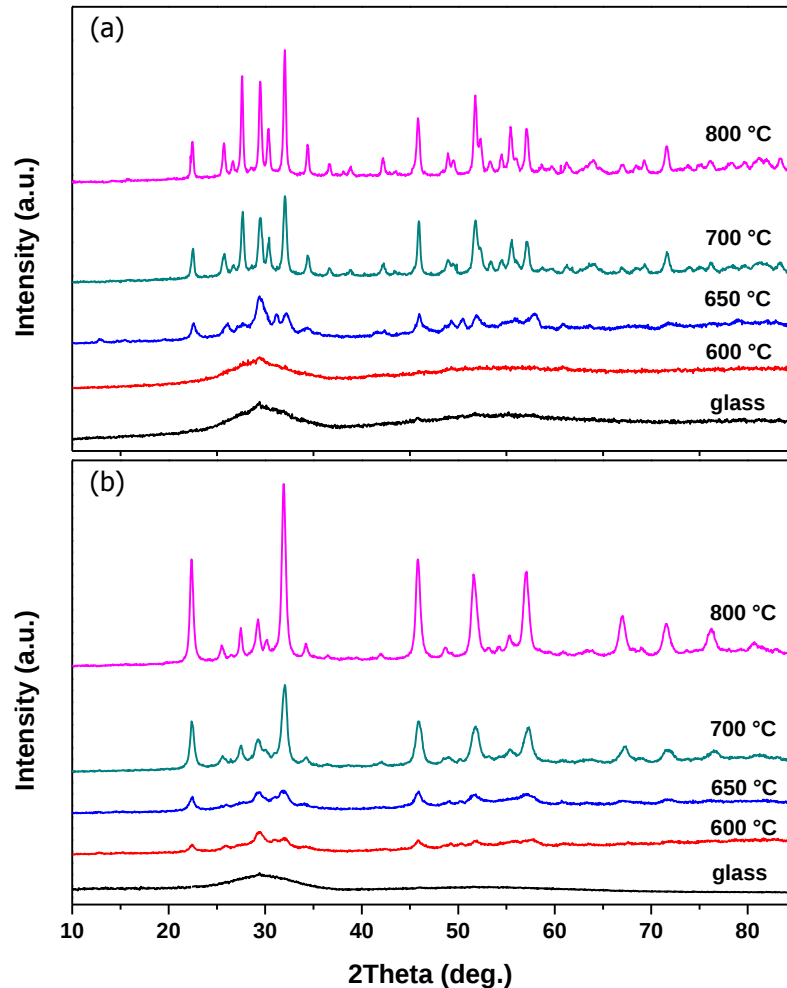


Figure 5.79 The XRD patterns for (a) K-50 and (b) K-70 of glass and glass-ceramics heated at temperatures from 600 to 800°C , showing the crystallization development during heat treatment process.

The XRD pattern of K-80, together with the full pattern refinement used to quantify the crystalline phases, is presented as an example in Figure 5.80. The best fit, in this case, was obtained with 79 wt% of the major KNN perovskite phase (labelled as $*$) with 21 wt% second phase of barium niobate (labelled as $+$). The broad background hump between 15 and $40^\circ 2\theta$ is attributed to the remaining glassy phase.

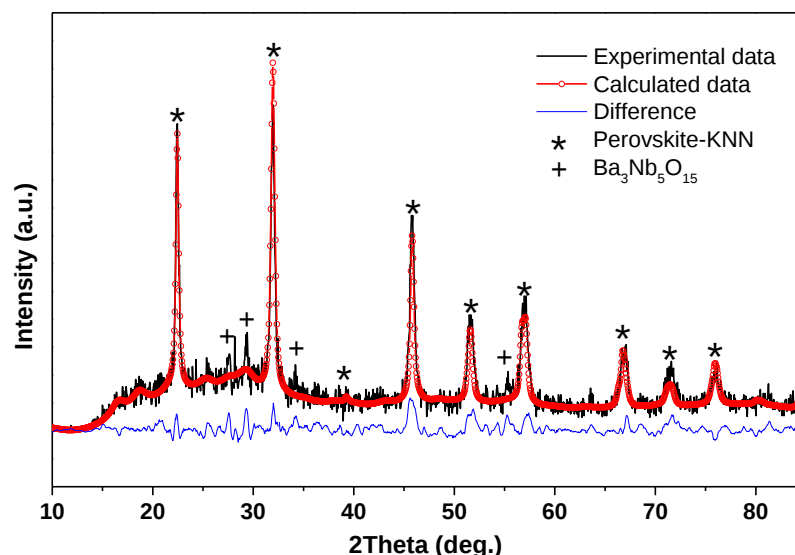


Figure 5.80 The XRD full pattern refinement for K-80 heated at 800 °C. The KNN perovskite phase is labelled as (*) and the barium niobate second phase as (+).

In order to provide further information on/and understanding of the crystallisation of the glass-ceramics, in-situ high resolution synchrotron x-ray diffraction powder experiments were conducted during heat treatment, as discussed in section 5.6.7 below.

5.6.4 Microstructure analysis

According to previous literature, it is anticipated that in KNN glass-ceramics the liquid-liquid phase separation should occur at the nanoscale during heating of the quenched glass due to immiscibility; the phase separated regions can then act as nucleation sites for crystallisation during further heat treatment [142]. Therefore, the microstructures of the glass-ceramics at different stages during heat treatment were studied by analytical scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The BSE micrographs of K-50 heated at temperatures in the range between 650 and 850 °C are presented in Figure 5.81. Visibly, the microstructures of glass-ceramics are clearly affected by heat treatment. The sample in Figure 5.81 (a), heat treated at 650 °C, shows a high glass volume with some dispersed nanoscale crystallites, in agreement with the XRD results, which indicated that the initial stages of crystallisation occurred between 600 and 650 °C (Figure 5.79 above). In BSE imaging mode, the lighter regions generally contain the heavier elements on average and are attributed to the crystalline phases. As the heat treatment temperature increased, the lighter

regions increased in size, indicating growth or clustering of the crystalline phases. The crystalline agglomerates were separated by regions of the darker glassy phase.

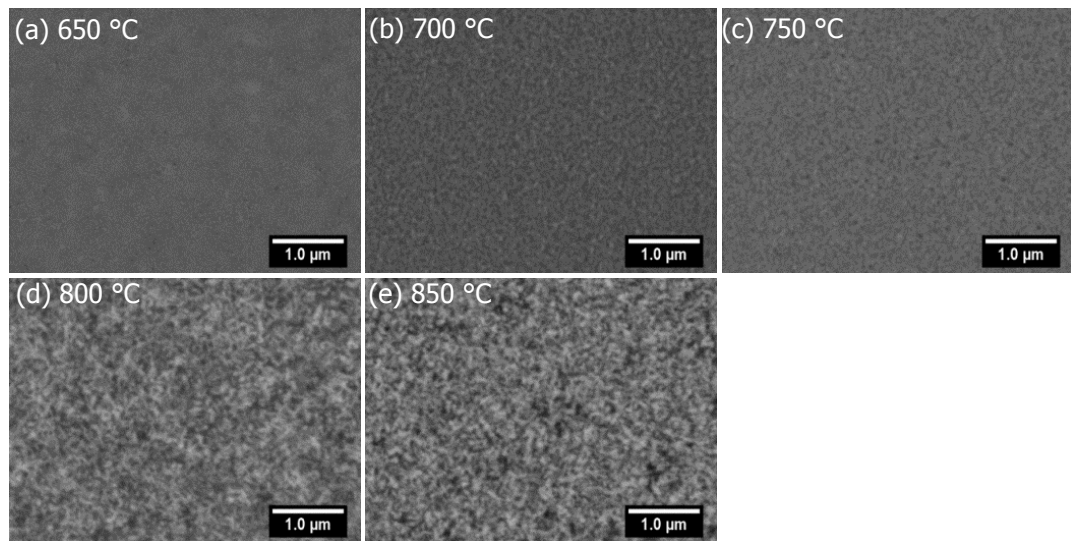


Figure 5.81 (a)-(e) SEM (BSE) micrographs for K-50 glass-ceramics showing the crystallisation process due to heat treated at temperatures in the range between 650 and 850 °C,

TEM micrographs of the K-50 glass-ceramic heat treated at 800 °C are shown in Figure 5.82. Contrast can be observed between the two different areas (labelled as 1 and 2), where the darker area (1) corresponds to the crystalline/ferroelectric phases, while the brighter area (2) corresponds to the residual glass. Furthermore, it can be observed that individual crystallites are 30 ± 7 nm in size, have a fairly regular isometric morphology, and are surrounded by the remaining glass. The crystal size, in this case, is smaller than those reported by Hanyu, which were in the range 70 to 100 nm [129].

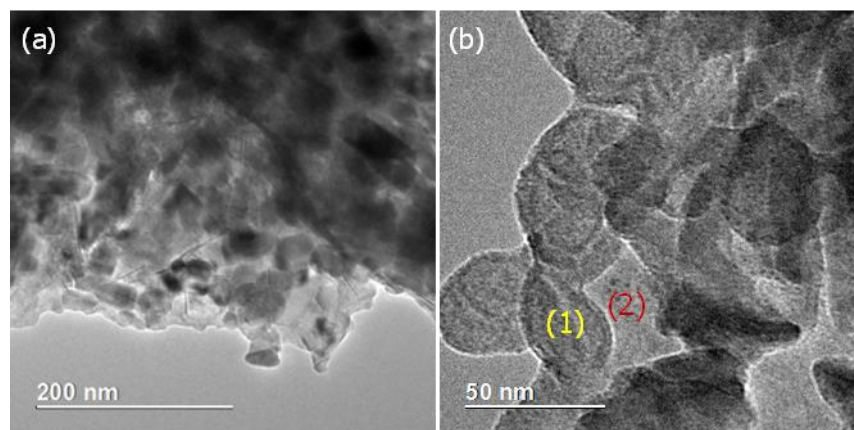


Figure 5.82 TEM micrographs for K-50 glass-ceramics heat treated at 800 °C, with different scale bars (a) 200 nm and (b) 50 nm, showing the contrast between the crystalline phases labelled as '1' and residual glass as '2', respectively.

The SEM images for K-80 heated at a temperature in the range between 650 and 850 °C are shown in Figure 5.83. In comparison with K-50 heated at 650 °C, Figure 5.81 (a), it can be observed that the K-80 sample heated at the same temperature shows more crystallites as bright spots, corresponding to the higher KNN content. These spots grow larger with increasing temperature producing clearly-defined agglomerates of crystalline phases surrounded by the residual glass.

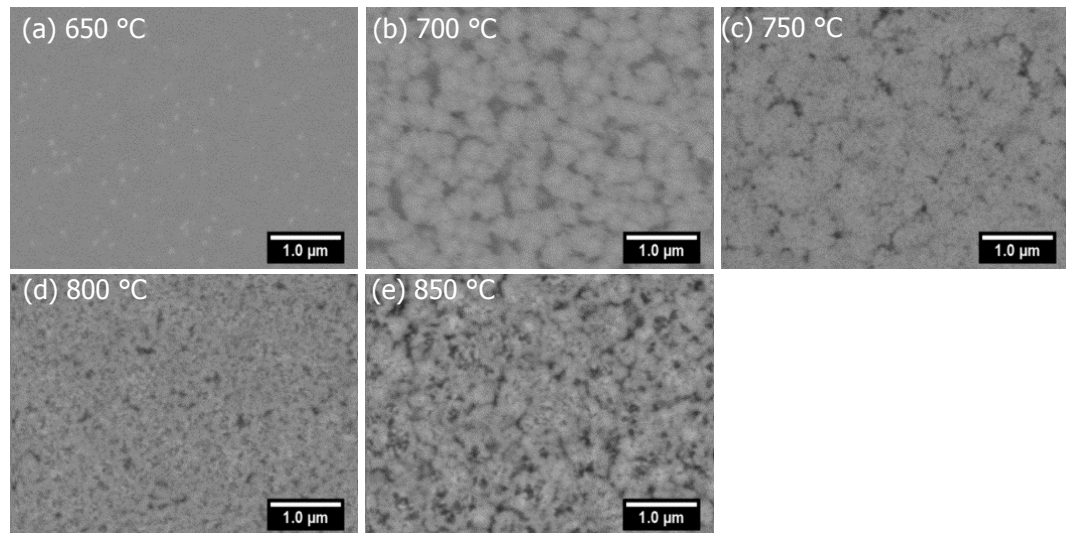


Figure 5.83 SEM (BSE) micrographs for K-80 glass-ceramics heat treated at temperatures in the range between 650 and 850 °C.

The SEM micrographs obtained for glass-ceramics with different KNN contents (K-50 to K-80) after heat treatment at 700 °C are shown in Figure 5.84. The increase in both the agglomerate size and in the size of the glassy regions as a function of increasing KNN content is clearly evident in this figure.

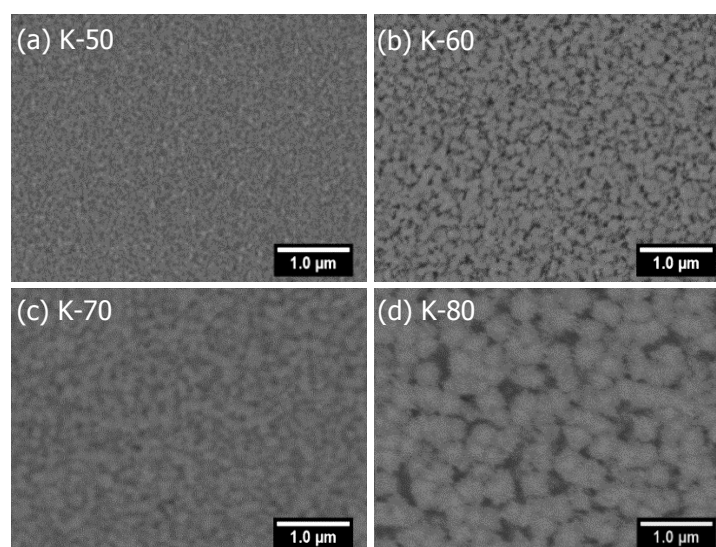


Figure 5.84 SEM (BSE) micrographs for glass-ceramics heat treated at 700 °C (a) K-50 (b) K-60, (c) K-70 and (d) K-80, showing the crystallisation of the intermediate phase.

For a higher heat treatment temperature of 850 °C (Figure 5.85), the increase in crystalline phase content and reduction of the residual glassy phase with increasing KNN content are indicated by the increasing proportion of the lighter phase. Furthermore, the boundaries between the crystalline agglomerates are less well-defined than those observed at 700 °C, due to the general increase in crystalline content at this temperature. These results are consistent with the XRD patterns presented in Figure 5.79, but it was not possible to distinguish between the morphologies of different crystalline phases (e.g. KNN and BN) in these images.

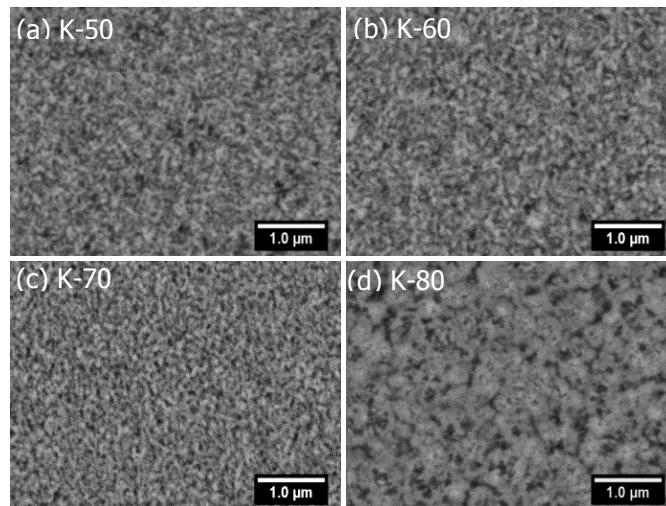


Figure 5.85 SEM (BSE) micrographs for glass-ceramics heat treated at 850 °C (a) K-50 (b) K-60, (c) K-70 and (d) K-80.

5.6.5 Temperature dependence of dielectric properties

The relative permittivity and loss tangent were measured as a function of temperature and frequency to evaluate the influence of the crystalline phases on the dielectric behaviour and polymorphic phase transformations associated with KNN.

The changes in relative permittivity and loss tangent over the temperature range from room temperature up to 500 °C for K-50 and K-80 glass-ceramics heat treated at 850 °C are shown in Figure 5.86. It can be seen that the K-50 sample, Figure 5.86 (a)-(b), generally has a low relative permittivity and loss ($\epsilon_r \approx 95$ and $\tan\delta \approx 0.03$), which remain relatively independent of frequency and temperature up to ≈ 250 °C. In contrast, the K-80 sample, Figure 5.86 (c)-(d), exhibits a higher relative permittivity value at around 300, which increases slightly with temperature, as well as a broad peak at approximately 250 °C. Here, the relative permittivity (K-80 ≈ 300) was higher than those reported by Hanyu and Pu, which were approximately 190 [129, 204]. The reduction in the ferroelectric Curie temperature, relative to that of the KNN ceramics

described in section 5.4.1, is attributed to the fine particle size and poor crystallinity. The related aspect of particle size-induced broadening of the XRD peak profiles is also addressed in section 5.6.7 below.

The general increase in relative permittivity from K-50 to K-80 is attributed to the increase in the crystalline phase content, while the increases in relative permittivity and loss for both glass-ceramics samples at high temperatures and low frequencies indicates the influence of conduction and associated interfacial polarisation.

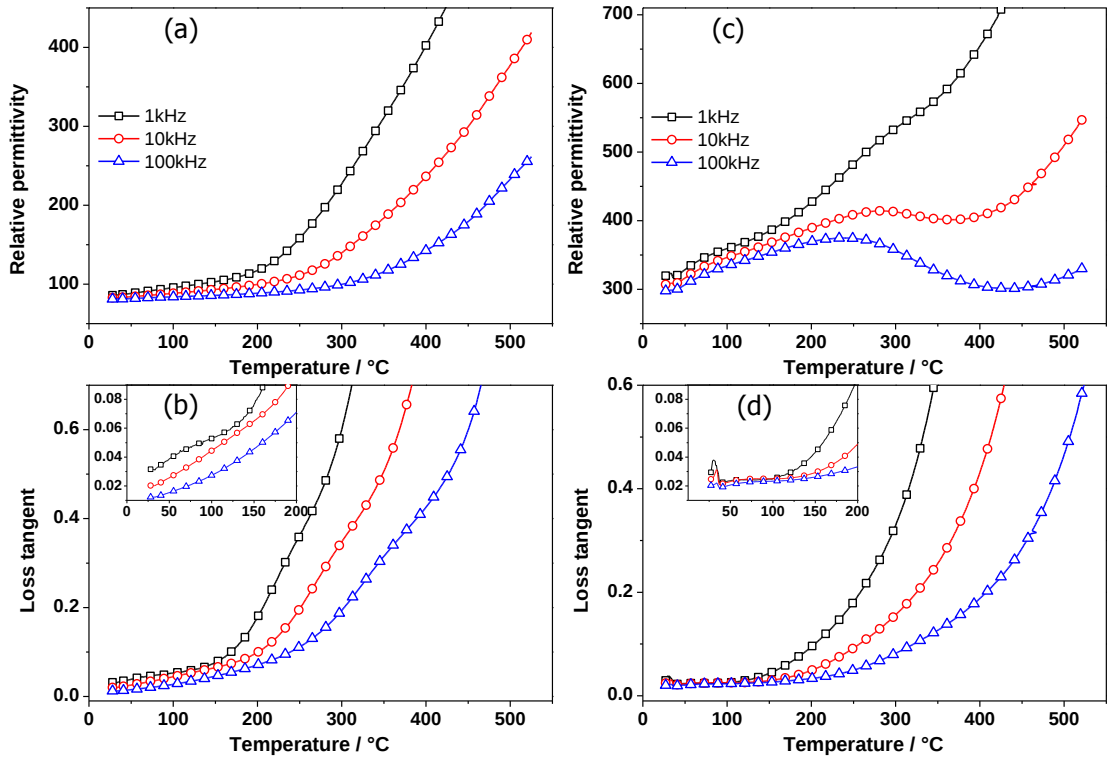


Figure 5.86 The temperature dependent relative permittivity and loss tangent of (a)-(b) K-50 and (c)-(d) of K-80 heat treated at 850 °C, measured at 1, 10 and 100 kHz.

The influence of heat treatment temperature on the ϵ_r -T and $\tan\delta$ -T relationships for K-50 and K-80 glass-ceramic samples is shown in Figure 5.87. It is apparent that both samples show a general increase in relative permittivity as the heat treatment temperature increased. K-50 glass-ceramics, Figure 5.87 (a)-(b), show a good stability of relative permittivity with temperature up to approximately 300 °C, for all heat treatments. This might be due to the small crystallite size (described in 5.6.4 above) and the presence of the low- relative permittivity glass phase between crystalline regions, which produces a 'field-screening' effect and could obscure the contribution from the high relative permittivity crystalline phases.

For the K-80 glass-ceramic sample Figure 5.87 (c)-(d), the relative permittivity values were generally higher than those of K-50 at each heat treatment temperature. Furthermore, the broad peak in relative permittivity obtained after heat treatment at temperatures from 750 to 850 °C shifts to higher temperatures with increasing heat treatment temperature. This is attributed to the increase in perovskite KNN phase content and the grain size effect.

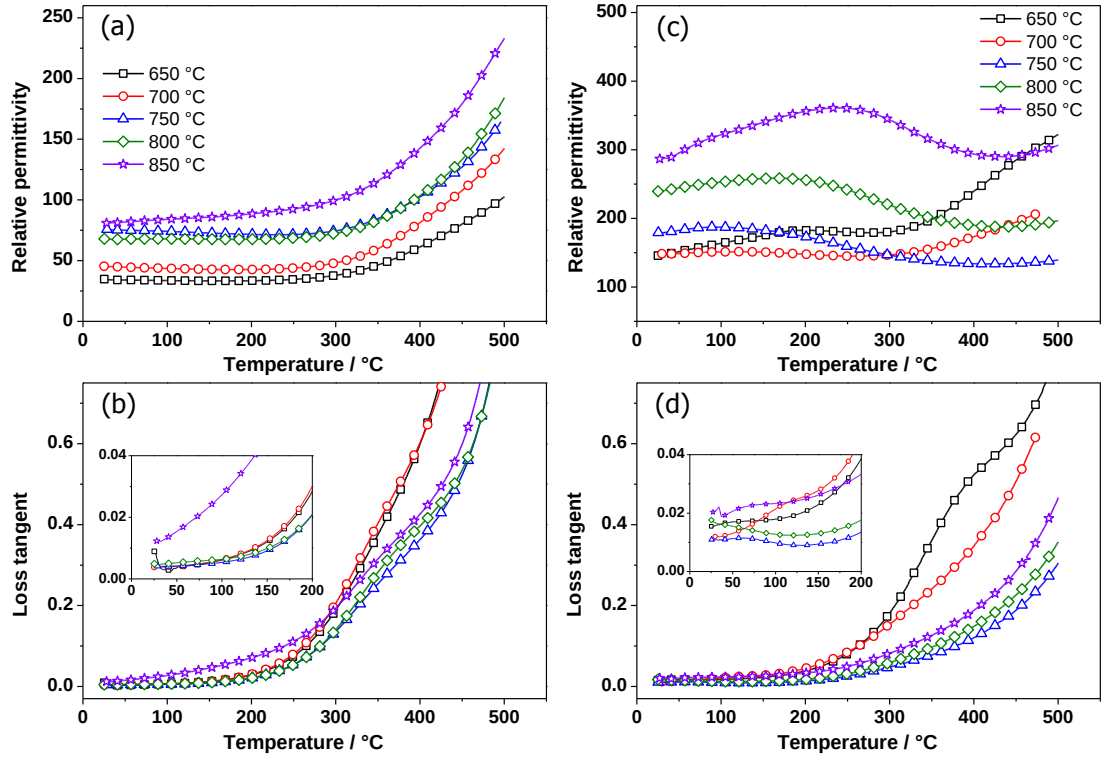


Figure 5.87 The temperature dependent relative permittivity and loss tangent at 100 kHz for K-50 (a)-(b) and K-80 (c)-(d), after heat treatment at 650 to 850 °C.

Figure 5.88 shows the effect of KNN content on the ϵ_r -T and $\tan\delta$ -T relationships for glass-ceramic samples heat treated at 650 and 850 °C, measured at a fixed frequency of 100 kHz. It is apparent K-50 to K-70 samples generally show a good stability of relative permittivity with temperature and no obvious evidence of the ferroelectric-paraelectric phase transformation, while K-80 has a higher relative permittivity than the other samples and also shows evidence of the ferroelectric transformation at the Curie temperature. The lack of clear evidence for the ferroelectric phase transformation in the dielectric results for the K50 to K70 glass-ceramics is attributed generally to the influence of crystal size and the interfacial screening effect of the glass phase between crystalline agglomerates [7, 77].

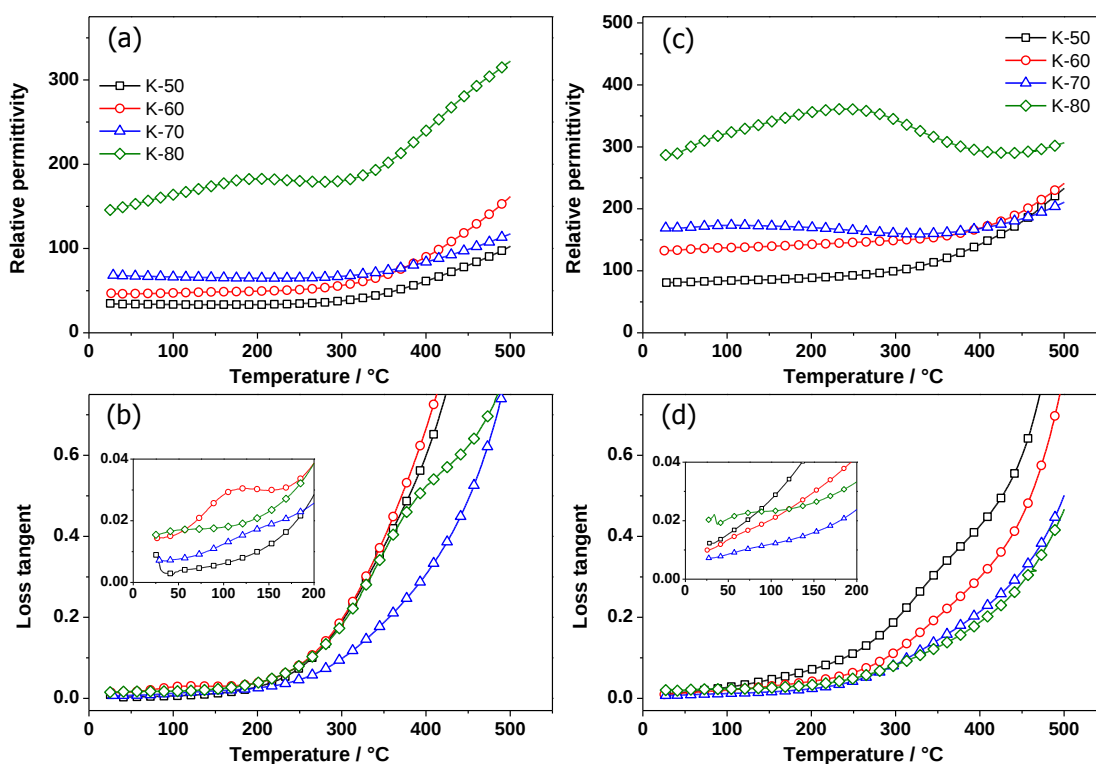


Figure 5.88 The temperature-dependent relative permittivity and $\tan\delta$ at 100 kHz of KNN-BBS glass-ceramics heat treated at (a)-(b) 650 °C and (c)-(d) 850 °C.

5.6.6 Nonlinear dielectric and ferroelectric properties

The study of the dielectric properties of the glass-ceramics at high electric field levels is important because of it can give information on the energy storage density, the relation between the high/low field electrical properties (dielectric nonlinearity) as well as the influence of electrical conduction at the high field. These measurements can be correlated with the other structural and microstructural studies. Thus, polarisation-electric field (P-E) hysteresis loops were measured at field levels up to 5 kV mm⁻¹ and at a frequency of 2 Hz at room temperature for all the glass-ceramic samples.

For K-80 heat treated at 850 °C, as shown in Figure 5.89, it is clear that the polarisation increased gradually with electric field amplitude. Some nonlinearity is evident, indicated by the increase in the average gradient of the loops, while the relatively large loop area indicates a significant increase in dielectric loss relative to the low-field measurements. The saturation polarisation (P_s) remanent polarisation, (P_r) and coercive field (E_c) values were recorded as 0.018, 0.0027 C m⁻² and 0.71 kV mm⁻¹ at the maximum field amplitude of 5 kV mm⁻¹. The effective ϵ_r and $\tan\delta$ values were calculated [205] as approximately 310 and 0.084 at 1 kV mm⁻¹, increasing to 412 and 0.14 at 5 kVmm⁻¹.

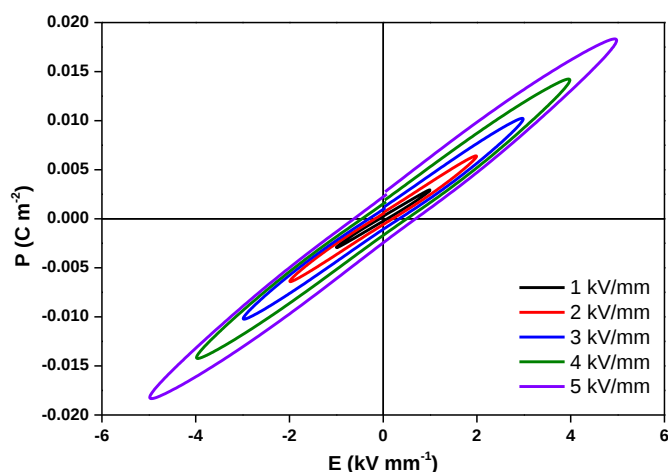


Figure 5.89 P-E hysteresis loops for K-80 glass-ceramics heat treated at 850 °C measured at an electric field up to 5 kV mm⁻¹ and frequency 2 Hz.

The influence of heat treatment temperature on the ferroelectric behaviour of glass-ceramics with different of KNN contents heat treated at temperatures in the range between 650 and 850 °C are plotted in Figure 5.90. It can be observed that the polarisation and hysteresis loss (loop area) gradually increase with increasing heat treatment, with similar behaviour being apparent for all glass-ceramic compositions.

The saturation polarisation values of the samples heated at 650 °C, were decreased relative to those of the sample heated at 850 °C, due to the lower content of crystalline phases and the presence of the low- relative permittivity glass phase between the ferroelectric KNN grains. For example, the K-50 glass-ceramic yielded relative permittivity values of 45 and 112 after heat treatment at 650 and 850 °C, respectively Figure 5.91 (b). A similar trend was evident for K-80, but the increase in permittivity, from 232 to 411 was even more dramatic. However, in the latter case, a slight reduction in relative permittivity occurred between 650 and 700 °C, which may be related to the changes in crystalline phase content, as discussed in section 5.6.7 below. The relative permittivity values derived from the P-E loops are generally consistent with those measured in the low field region, as discussed in section 5.6.5 above.

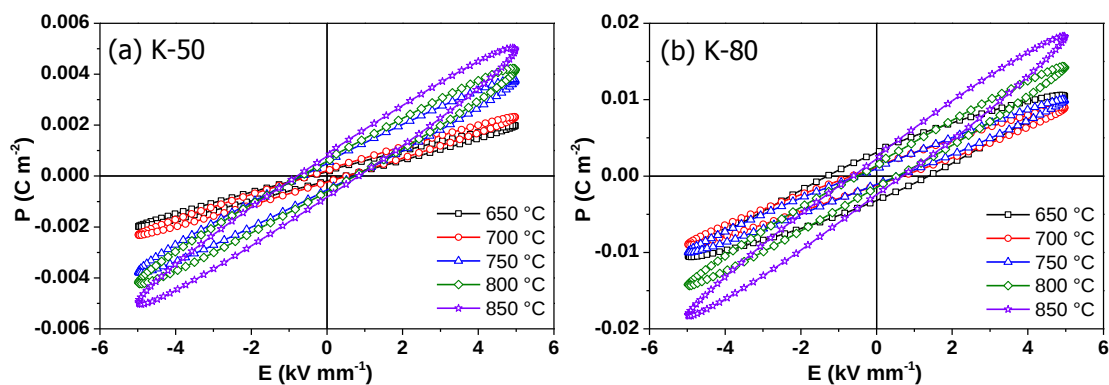


Figure 5.90 P-E hysteresis loops for (a) K-50 and (b) K-80 glass-ceramics heat treated at temperatures in the range between 650 and 850 °C, measured at an electric field amplitude of 5 kV mm⁻¹ and frequency 2 Hz.

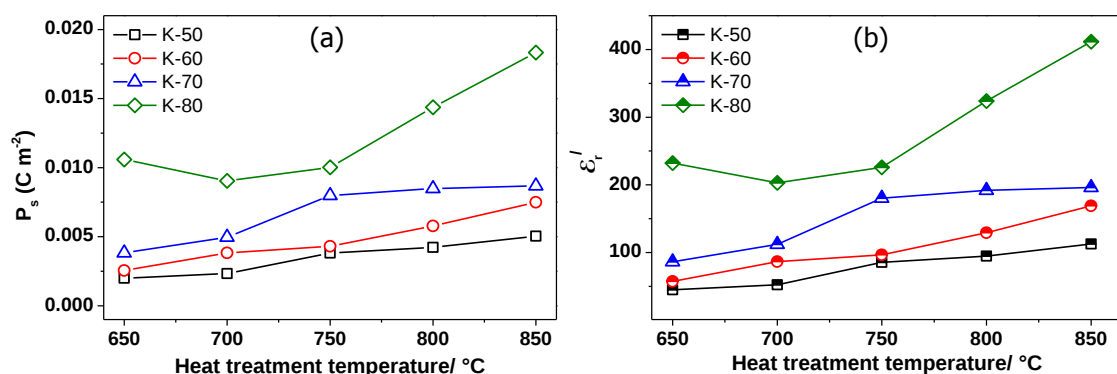


Figure 5.91 (a) P_s and (b) ϵ_r' , calculated from P-E hysteresis loops of K-50 to K-80 heated at temperatures in the range between 650 and 850 °C, showing the effect of the KNN content and the heat treatment on the permittivity, measured at an electric field amplitude of 5 kV mm⁻¹ and frequency 2 Hz.

According to the XRD and SEM results, combined with dielectric property measurements, the changes in polarisation behaviour are a consequence of the transformation from the amorphous (low permittivity) glass phase to the crystalline ferroelectric (high permittivity) phase, which is enhanced both by higher heat treatment temperatures as well as increase in KNN content. For K-80, the relative permittivity calculated from the P-E hysteresis loops showed an almost linear dependence on electric field amplitude up to 3 kV mm⁻¹, as illustrated in Figure 5.92 (a). A gradual tendency for saturation became evident beyond this level. To illustrate the nonlinear dielectric behaviour, the Rayleigh coefficients for nonlinearity, α' , were determined as 7.9 and 28 × 10⁻⁶ m V⁻¹ for K-80 heat treated at 700 and 850 °C, respectively. These values can be compared with typical results for soft and hard PZT ceramics, which were reported as 5.56 × 10⁻³ and 0.67 × 10⁻³ m V⁻¹, respectively [206], indicating that the KNN-based glass-ceramics exhibit relatively low dielectric nonlinearity in comparison with typical ferroelectric ceramics.

The variations in ϵ_r'' with electric field amplitude showed similar trends to ϵ_r' , as shown in Figure 5.92 (b). However, in this case, the 'low field' values were all low and relatively independent of the heat treatment temperature. An anomalous result was found for K-80 at 650 °C, which displayed a generally low relative permittivity but a high field-dependent loss. This could be associated with the presence of the intermediate phase at this temperature, as described in section 5.6.7 below.

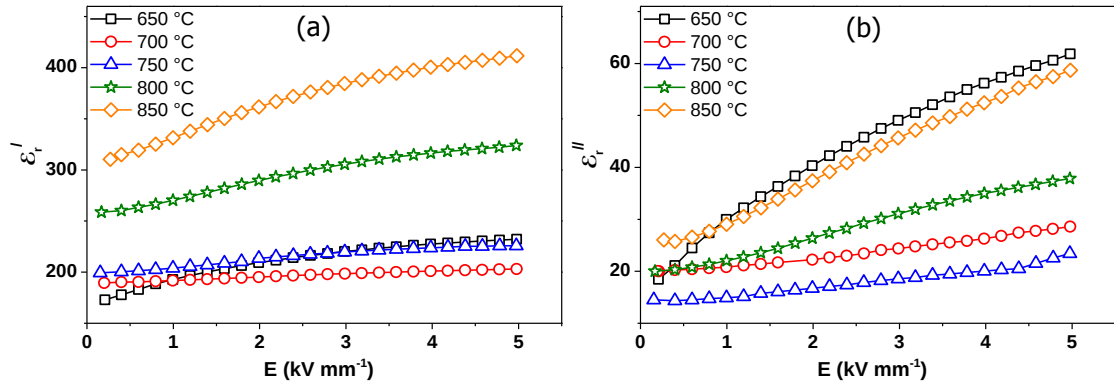


Figure 5.92 (a) and (b) real and imaginary part of relative permittivity calculated from P-E hysteresis loops of K-80 heated at temperatures of 650 to 850 °C, showing electric field dependence of the dielectric, measured at frequency 2 Hz.

For the given heat treatment temperatures of 650 and 850 °C, increasing KNN content in the glass-ceramic samples had little influence on P_r and E_c , but led to a significant increase in P_s , as shown in Figure 5.93. The real and imaginary parts of relative permittivity showed a gradual increase with KNN content up to 70 %, but then a step change between 70 and 80 %. This change could be related to the improvements in connectivity between the crystalline clusters at high KNN contents, as shown by the microstructures presented in Figure 5.84 and Figure 5.85 above.

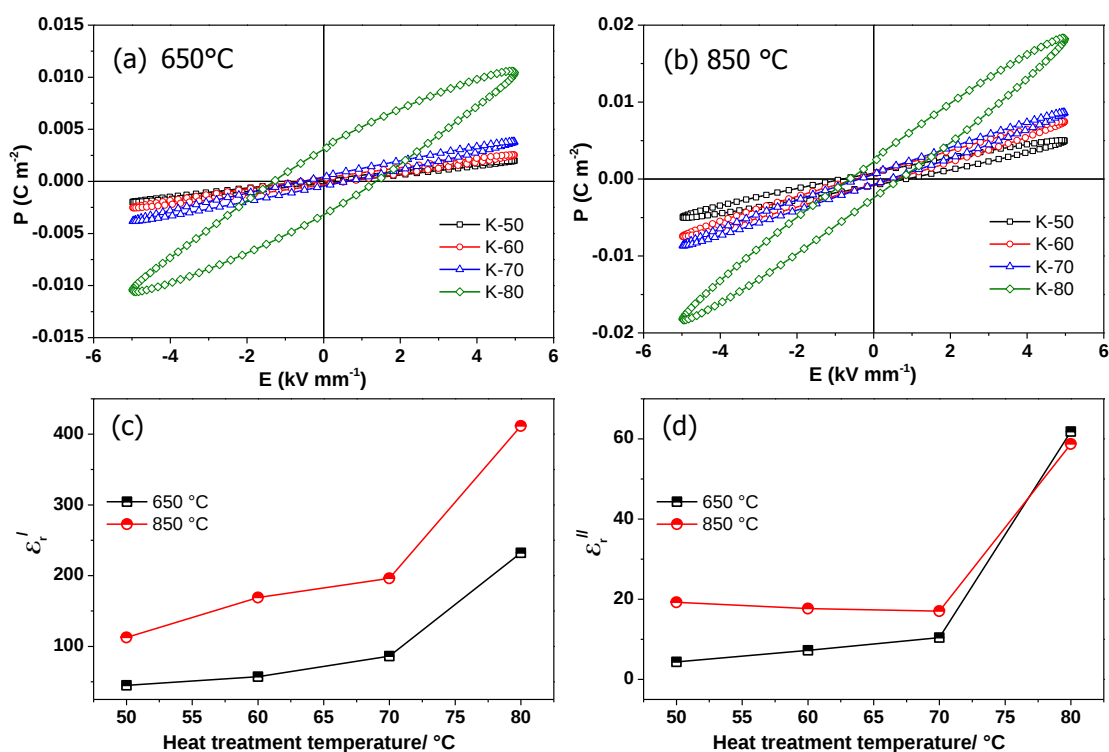


Figure 5.93 (a) and (b) P-E hysteresis loops for K-50 to K-80 glass-ceramics heat treated at temperatures 650 °C and 850 °C, respectively. (c) and (d) the real and imaginary parts of relative permittivity calculated from P-E loops, measured at an electric field amplitude of 5 kV mm⁻¹ and frequency 2 Hz.

5.6.7 In-situ synchrotron XRD results

In-situ high resolution synchrotron X-ray powder diffraction (SXPd) experiments were conducted for glass-ceramics samples to obtain further understanding of the development of crystalline phases in KNN glass-ceramics. The amorphous quenched glasses were heated up to 850 °C on the I11 beamline Diamond, using the PSD detector to continuously record high resolution diffraction patterns. According to the DSC results, the initial crystallisation occurs at temperatures between 600 and 650 °C. Therefore, two heat treatments were selected, using maximum temperatures of 650 and 850 °C with a heating rate of 10 °C min⁻¹.

SXPd data showing an overview of the main crystallographic transformations during heat treatment of the K-50 and K-80 glasses are shown in Figure 5.94. It can be seen that initial crystallisation occurs at temperatures between 600 and 650 °C, in agreement with the DSC results presented in section 5.6.1 above. Furthermore, the appearance and disappearance of some peaks is evidence that there are sequential changes in the crystalline phase content of the materials during heat treatment. One or more intermediate phases appear at temperatures around 600 °C, but these start to

decline above 700 °C and eventually disappear by 800 °C. Diffraction peaks associated with the perovskite KNN phase, accompanied by other second phases, become evident at temperatures above 700 °C and continue to increase in magnitude up to the highest temperature of 850 °C.

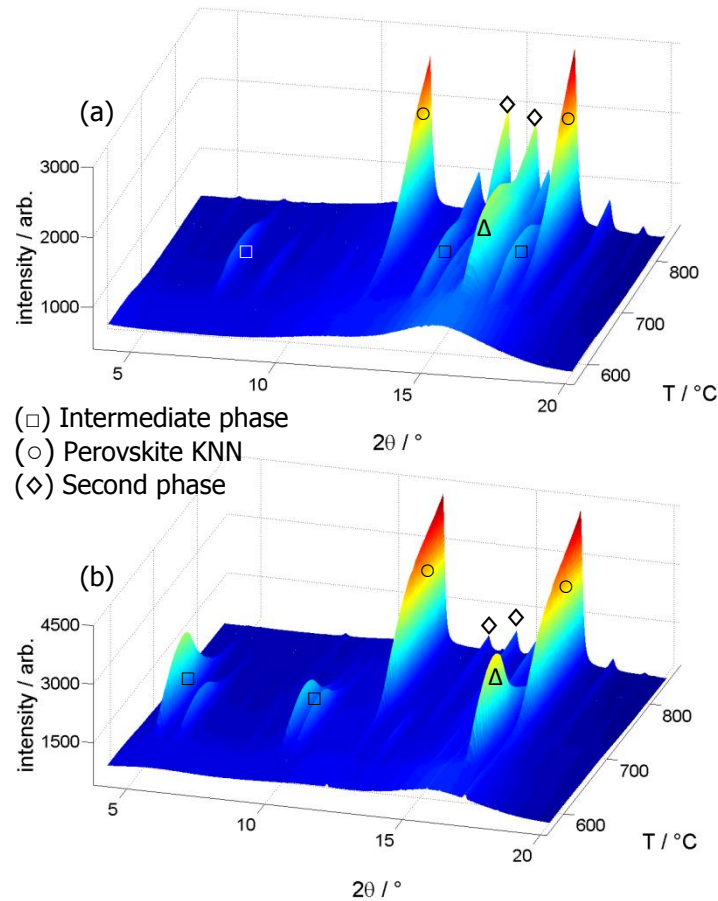


Figure 5.94 3-D representation of SXPD patterns of (a) K-50 and (b) K-80 glass-ceramics obtained during heating at a temperature up to 850 °C, showing phase formation sequence with peaks referring to the intermediate crystalline phase (Δ , $\square$), perovskite KNN ($\circ$) and the second phase ($\diamond$).

To demonstrate the phase development more clearly, the 2-D SXPD data showing the diffraction profiles at different temperatures are shown in Figure 5.95. The initial phase formation starts at a temperature of approximately 600 °C, where the liquid-liquid phase separation (liquation) occurs, initiating the nucleation of crystalline intermediate phases marked with ' Δ ' and ' $\square$ '. Some of the diffraction peaks at this stage appear to be associated with BaNbO_3 [207], marked with ' Δ ', but others are unidentified to date, marked with ' $\square$ '. The intermediate crystalline phases begin to transform to the mixture of KNN, marked ' $\circ$ ' and barium niobate ($\text{Ba}_3\text{Nb}_5\text{O}_{15}$), marked ' $\diamond$ ', at a temperature of approximately 700 °C, then conversion is completed by 800 °C. The final state is a

3-phase mixture of perovskite-KNN, barium niobate ($\text{Ba}_3\text{Nb}_5\text{O}_{15}$) and glass. In general, the broad peaks indicate a very small crystallite size ($\approx 15\text{-}30\text{ nm}$ calculated by analysis of single peak profiles, as shown in Figure 5.97 below) for all phases.

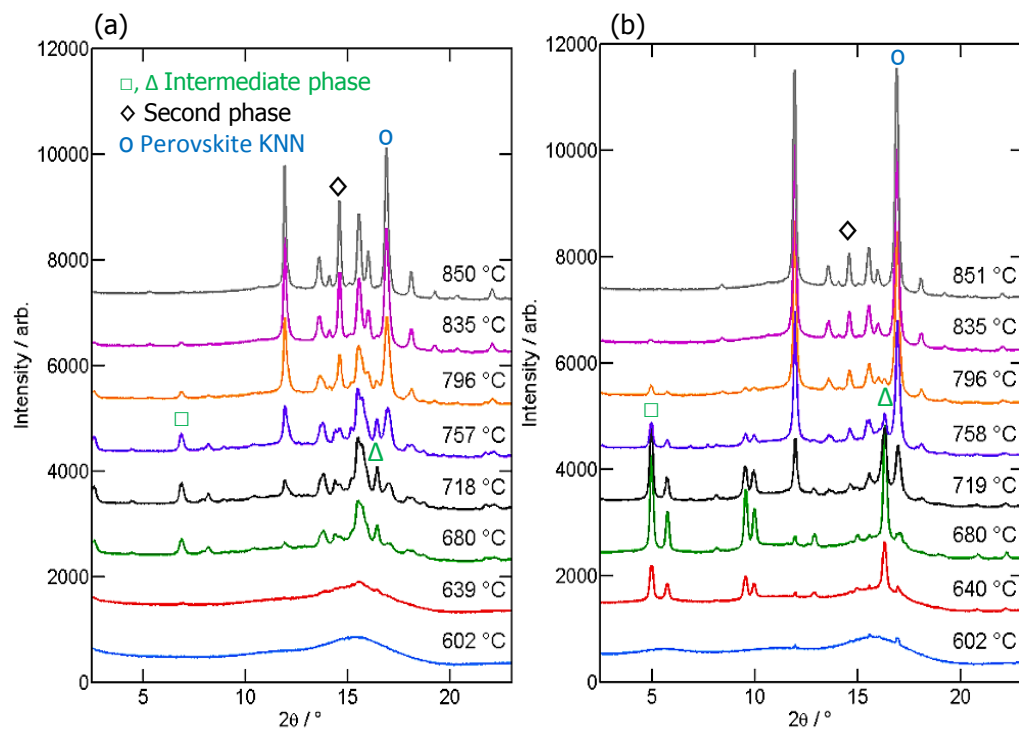


Figure 5.95 2-D temperature-dependent diffraction patterns (SXPD) of (a) K-50 and (b) K-80 glass-ceramics during heat treatment at a temperature up to 850 °C, showing phase formation sequence with peaks referring to the intermediate crystalline phase ($\square$), perovskite-KNN ($\circ$) and the second phase ($\diamond$).

The influence of heat treatment on the phase developments in the K-50 and K-80 glass-ceramics at a temperature up to 850 °C is shown in Figure 5.96. The intensity data are taken from the strongest peak of the intermediate phase and the perovskite KNN with the second phase of $\text{Ba}_3\text{Nb}_5\text{O}_{15}$, represented in Figure 5.95 above. As presented here, the intensity of the intermediate phase increases sharply at temperatures from 630 °C to 685 °C, followed by a gradual decrease towards zero at 850 °C. In contrast, the intensity of the diffraction peaks associated with KNN gradually increases at 705 °C towards the highest intensity at 850 °C. It seems that the growth of the perovskite KNN phase is directly associated with the loss of the intermediate phase(s). In addition, the growth of the second phase ($\text{Ba}_3\text{Nb}_5\text{O}_{15}$) starts to occur at a higher temperature around 750 °C.

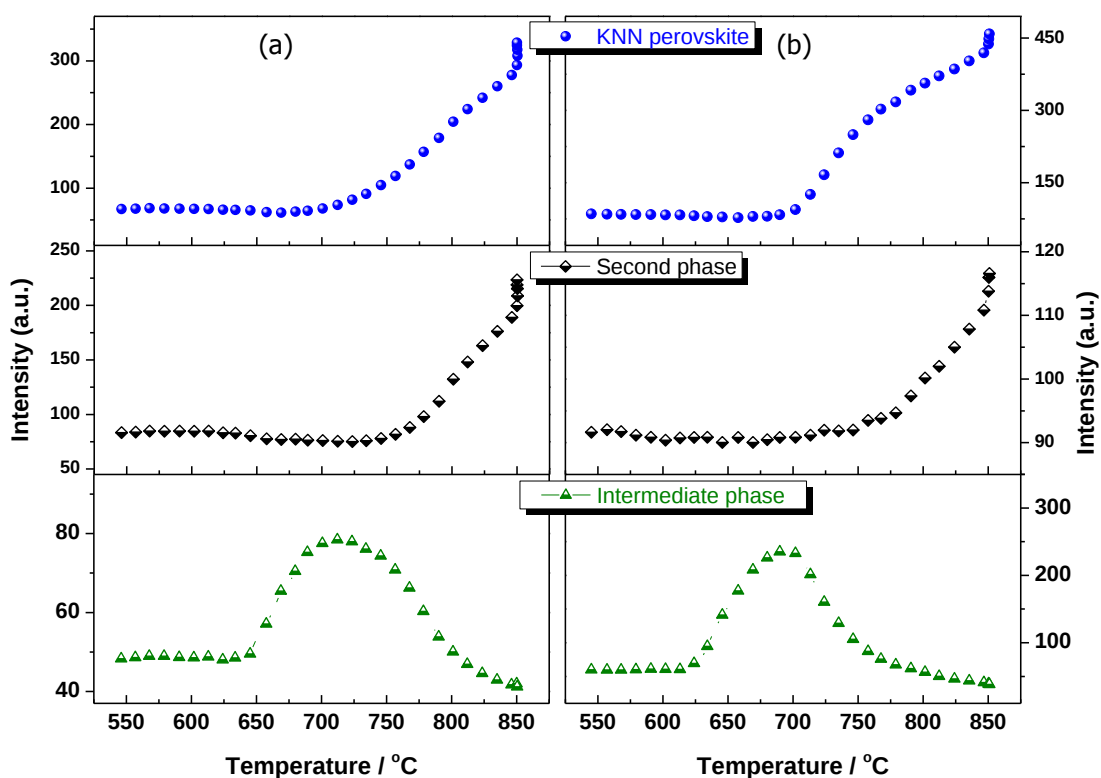


Figure 5.96 Changes in intensities of diffraction peaks for different phases in the series (a) K-50 and (b) K-80 sample as a function of the temperature. The intensity data are taken from the strongest peak of each phase (intermediate phase, second phase and perovskite-KNN), at approximately 5, 14 and 17 $^{\circ}2\theta$, respectively.

In order to evaluate the crystal growth during the crystallisation process, the mean crystallite sizes of intermediate phases BaNbO_3 and perovskite-KNN were determined using a single peak fitting using the 'FP' peak profile type analysis in Topas, giving the results shown in Figure 5.97. In the beginning, the BaNbO_3 -phase shows an increase in the crystallite size from approximately 14 to 24 nm when the temperature rises from around 625 to 690 $^{\circ}\text{C}$, then the crystallite size decreases when the temperature increases up to ≈ 715 $^{\circ}\text{C}$. Concomitantly, the perovskite KNN-phase crystals grew from 15 to 21 nm as the temperature increased from around 715 to 750 $^{\circ}\text{C}$. Upon further heating, the KNN-phase starts growing to approximately 23 nm at 850 $^{\circ}\text{C}$, then for a holding time of around 10 min at this temperature, the crystallite size increased to approximately 25 nm. Therefore, it is expected that the crystallite size can continue to increase gradually for longer holding times, as the TEM images show a crystallite size ≈ 50 nm using 4 hours of heating at 800 $^{\circ}\text{C}$, as shown in Figure 5.82 above.

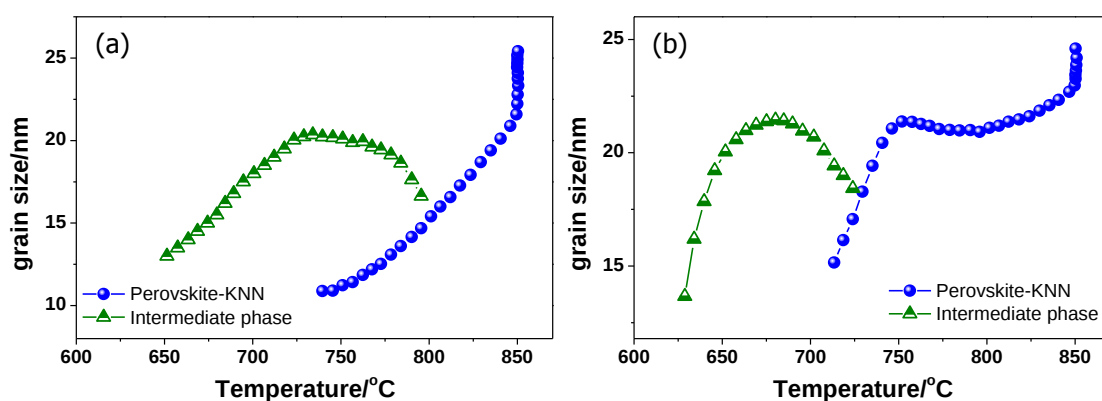


Figure 5.97 Influence of the heat treatment on the crystallite size of the phases formed during heating (a) K-50 and (b) K-80 glass-ceramic at temperatures up to 850 °C.

The SXPD data recorded at room temperature for all glass-ceramic samples (K-50 to K-80) after heat treatment at 850 °C are presented in Figure 5.98. All glass-ceramics show crystalline phases, which were identified as perovskite KNN with the tetragonal structure (shown below) as the main phase, as well as barium niobate ($\text{Ba}_3\text{Nb}_5\text{O}_{15}$) as a second phase. Furthermore, the intensities of the diffraction peaks associated with the second phase, between approximately 13 and 16.5°, decreased with increasing KNN content. This is attributed to a decrease in the ratio of barium oxide relative to sodium and potassium oxides. The relatively late appearance of $\text{Ba}_3\text{Nb}_5\text{O}_{15}$, at higher temperatures, also means that a greater proportion of the niobium oxide is already incorporated within the perovskite KNN phase before any reaction can occur with barium ions.

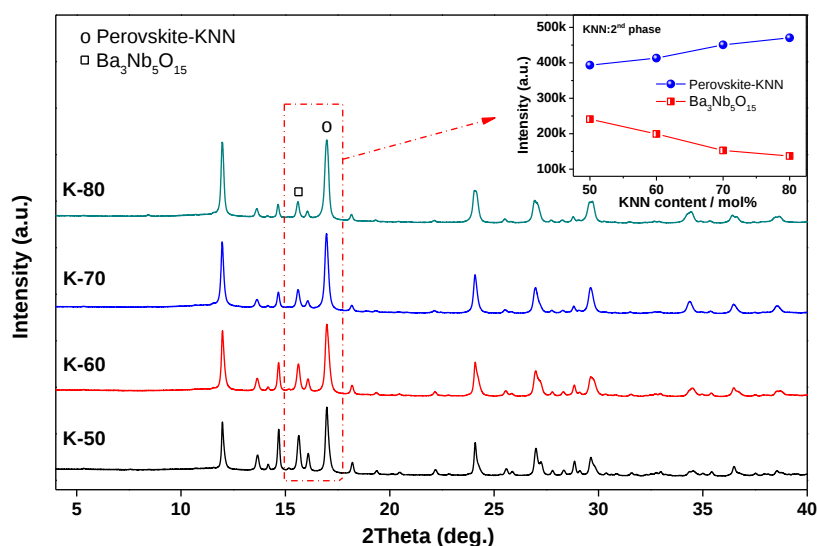


Figure 5.98 SXPD patterns of K-50 to K-80 glass-ceramics heat treated at a temperature up to 850 °C represent the effect of KNN content. The inserted figure is the intensity peaks depending on KNN content, the intensity data are taken from the strongest peak of (110) plane of perovskite-KNN and (011) of $\text{Ba}_3\text{Nb}_5\text{O}_{15}$.

The results of full-pattern fitting for K-50 and K-80 heated at 850 °C, shown in Figure 5.99, indicate that the K-80 comprised perovskite-KNN tetragonal phase and $\text{Ba}_3\text{Nb}_5\text{O}_{15}$ (BN) phase, with phase fractions of approximately 78 wt% and 23 wt%, respectively. The BN content increased to approximately 50 wt% for K-50.

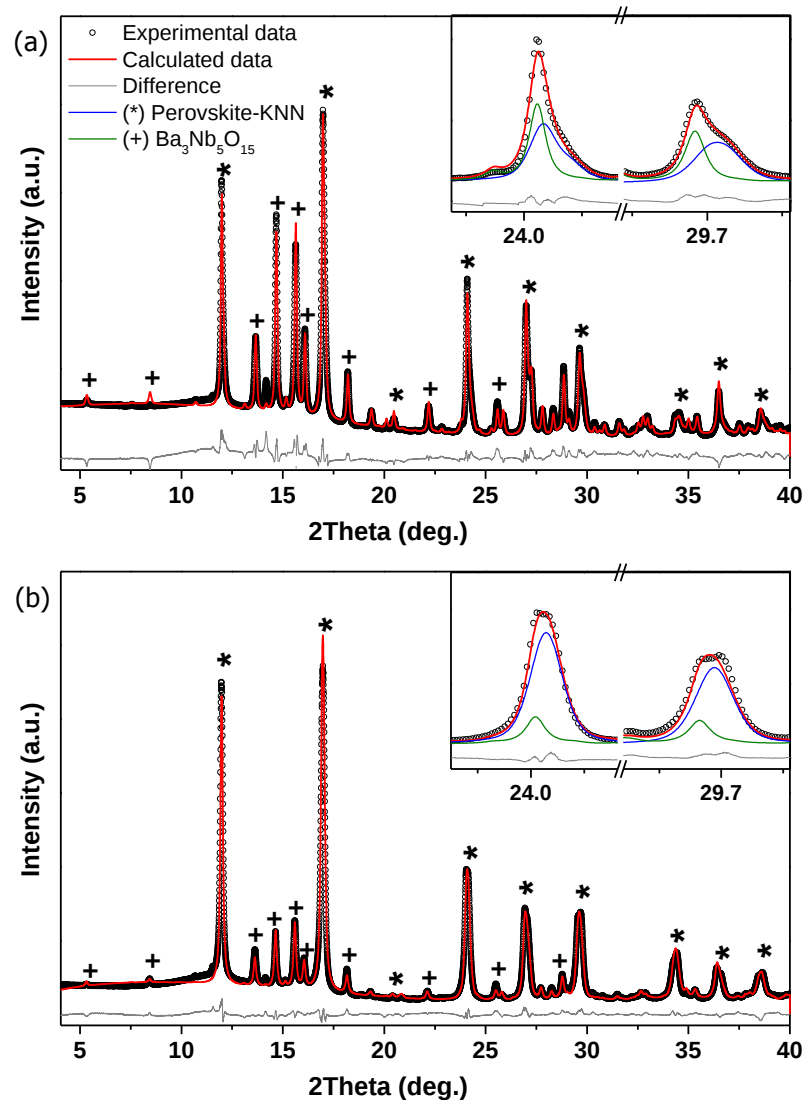


Figure 5.99 Full-pattern fitting for (a) K-50 and (b) K-80 glass-ceramic heated at 850 °C, showing the tetragonal perovskite-KNN phase (*), the second phase $\text{Ba}_3\text{Nb}_5\text{O}_{15}$ (+). The black circle is the experimental data, the red line is calculated results from refinement, and the grey line is the difference between experimental and calculated diffraction patterns. The shaded blue regions represent the perovskite-KNN phase and the green regions the second phase.

The temperature-dependent in-situ SXPD patterns for K-80 heat treated at 850 °C, shown in Figure 5.100, illustrate the changes in the perovskite {200} and {211} peak profiles on cooling from 500 to 60 °C. In the present case, the transition from tetragonal to the cubic structure was unclear due to the influence of particle size on tetragonality and peak broadening. A gradual reduction in c/a with increasing

temperature was evident, as shown in Figure 5.100 (b), which can be correlated generally with the broad peak in relative permittivity between 100 and 400 °C (Figure 5.88 above).

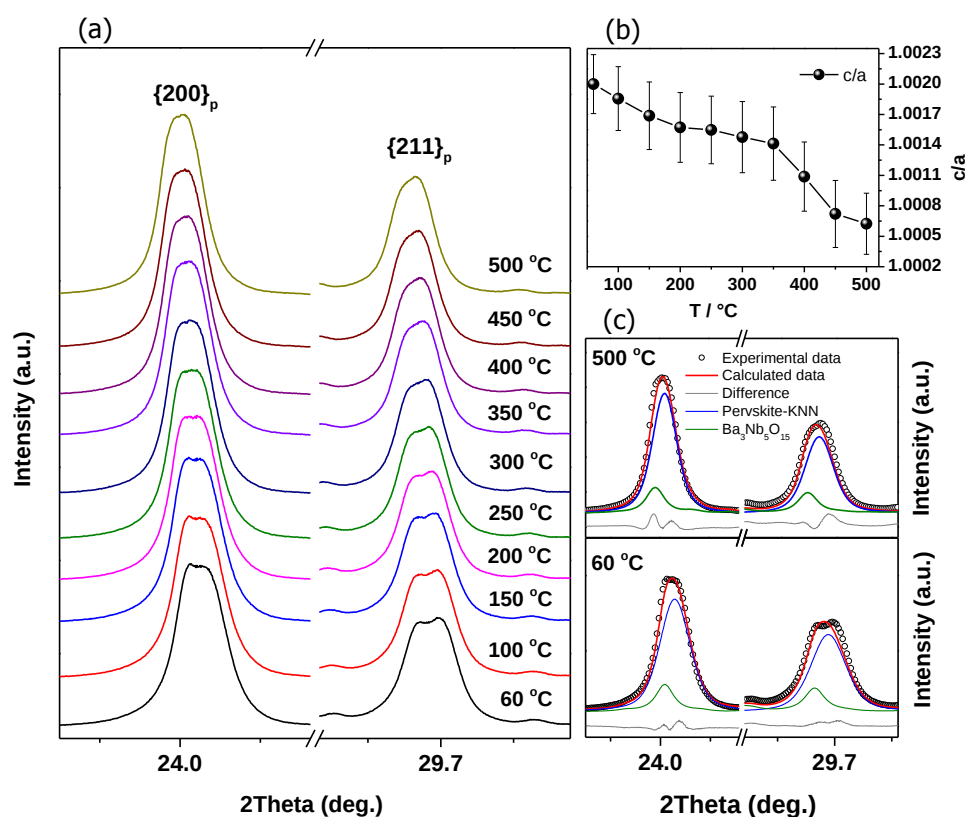


Figure 5.100 (a) In-situ SXPD profiles of $\{200\}_p$ and $\{211\}_p$ for K-80 during cooling, (b) changes in c/a ratio with temperature and (c) the measured, calculated and difference data obtained by full-pattern refinement at 500 and 60 °C, respectively, showing the phase transition from tetragonal to cubic for the perovskite KNN phase.

An additional experiment was undertaken in order to quantify the relative fractions of the KNN perovskite, barium niobate and amorphous glassy phases in the K-50 and K-80 glass-ceramics heat treated at a temperature of 850 °C. An additional 20 wt% of standard alumina powder (corundum, NIST SRM676a) was mixed with the glass-ceramic powder and the SXPD patterns recorded at 20 °C. Due to experimental constraints, a higher photon energy of 25 keV was employed, corresponding to an x-ray wavelength of 0.494216 Å. The results of full-pattern fitting for the mixed powder are illustrated in Figure 5.101. It is apparent that the diffractions peaks corresponding to the standard alumina powder have a narrow peak profile and do not overlap strongly with the main peaks associated with the crystalline phases in the glass-ceramic. Therefore, the results obtained by this procedure are considered as reliable.

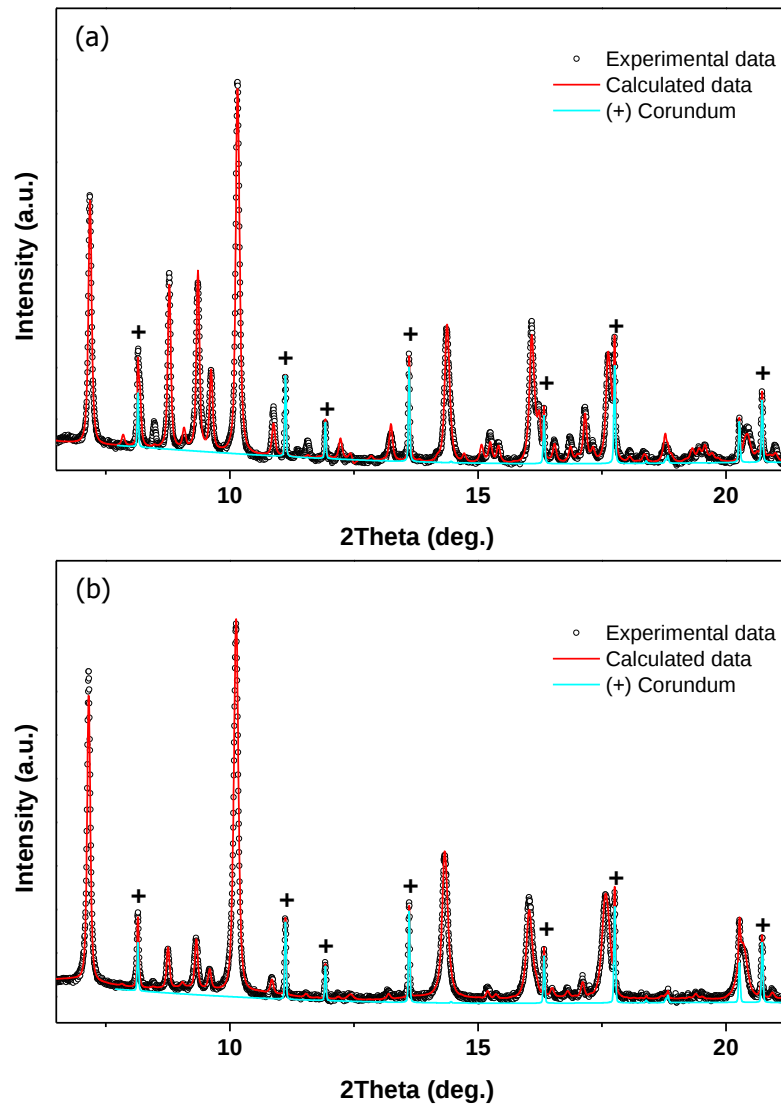


Figure 5.101 Full-pattern fitting for (a) K-50 and (b) K-80 glass-ceramic heated at 850 °C, showing the 20 %wt corundum phase added. The black circle is the experimental data; the red line is calculated results, and the cyan line (+) is the corundum phase.

The results obtained for the crystalline and amorphous phase fractions are summarised in Table 5.9. Firstly, the relative phase fractions of the 3 crystalline phases in the powder mixture (denoted *Cryst wt%*) were determined directly from the full pattern fit. Next, all of the crystalline phase fractions were multiplied by the appropriate factor (e.g. 0.2/0.256 for K-50) to yield the known wt% of the standard alumina powder in the mixture, assuming the remainder to comprise the amorphous glassy component (denoted *Mix. wt%*). Finally, the phase fractions of crystalline and amorphous components were determined by dividing by the known wt% of glass-ceramic i.e. 0.8 (denoted *Total wt%*). It is worth noting that the increase in KNN content within the quenched amorphous glass, from 50 to 80 %, gave rise to doubling of the perovskite KNN phase fraction in the heat-treated glass-ceramic, from 35 % to 71 %. This was

accompanied by reductions in the barium niobate and amorphous phase fractions, from approximately 37 to 11 % and 28 to 19 %, respectively.

Table 5.9 Crystal-amorphous phase fractions, calculated from full-pattern fitting for K-50 and K-80 glass-ceramic heated at 850 °C. Numbers in parentheses are statistical standard deviations of the last significant digit(s).

		KNN	BN	Al₂O₃	Glass	Cryst.
	Cryst. wt%	36.1	38.2	25.1	--	--
<u>K-50</u>	Mix. wt%	28.2	29.1	20	22.1	78.1
	Total wt%	35.1(4)	37.3(4)	--	27.6(1.2)	72.4(1.2)
	Cryst. wt%	66.2	09.1	23.1	--	--
<u>K-80</u>	Mix. wt%	56.3	08.4	20	15.1	84.9
	Total wt%	70.6(3)	10.5(4)	--	18.9(1.1)	81.1(1.1)

5.7 Dielectric energy storage characteristics

The stored (recoverable) energy densities, U_{rec} , of the sintered ceramics and heat-treated glass-ceramics were calculated from high field P-E hysteresis loops in terms of the area between the P-E hysteresis curve and the polarisation axis, as described in section 4.6.6.2 [20]. The calculations were performed by a simple numerical integration method in Microsoft Excel using the trapezoidal method. The results of the analysis are summarised in this chapter to provide an overview of the energy storage characteristics of the different materials produced during the project.

5.7.1 BaTiO₃ ceramics

The P-E hysteresis loops for pure BT (1300 °C) and the BT-2G1 ceramic (1100 °C) are presented in Figure 5.102. The resulting changes in U_{rec} as a function of the electric field, also including the results for BT-2G2, shown in Figure 5.102 (b), show a slightly sub-linear increase in the energy density as a function of E, with a slight tendency for saturation. The U_{rec} - E_{Max} relationships demonstrate a strong departure from the parabolic relationship that would be predicted for a linear dielectric, according to

$$U_{rec} = \frac{1}{2} \epsilon_0 \epsilon_r E_{Max}^2 \quad 5-4$$

In this case, both the dielectric nonlinearity (saturation in P) and the hysteresis loss associated with ferroelectric domain switching act to reduce the recoverable energy density relative to that of a linear, high relative permittivity. Generally, the presence of the glasses leads to an increase in the recoverable energy density of BT ceramics, which is primarily a result of the increase in P_s due to higher density.

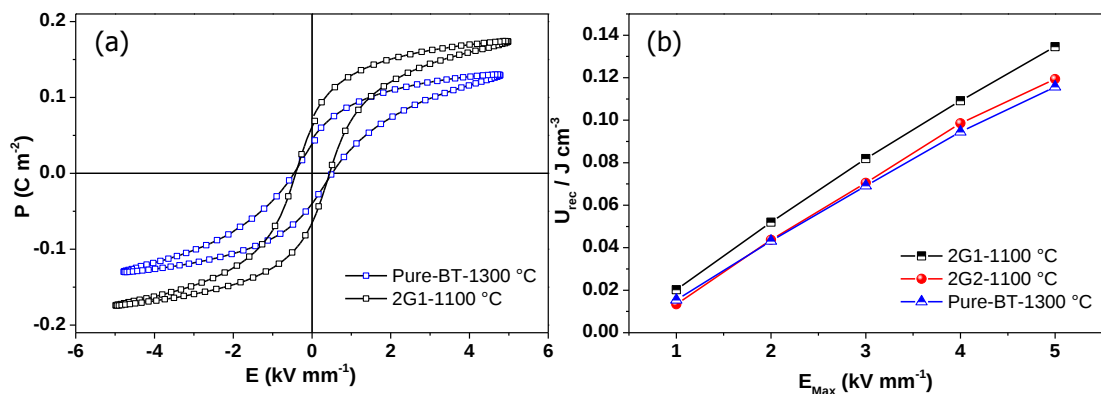


Figure 5.102 (a) P-E hysteresis loops obtained for pure BT and BT-2G1 (b) the recoverable energy density of pure BT, BT-2G1 and BT-2G2 as a function of the maximum electric field.

5.7.2 BCZT ceramics

The P-E loops and U_{rec} values obtained for the pure and glass-modified BCZT ceramics are shown in Figure 5.103. The most noticeable effect is the significant reduction in P_s for the BCZT-2G2 ceramic, which reduces the recoverable energy density dramatically. On the other hand, the U_{rec} values for pure BCZT and the BCZT-2G1 ceramics are similar, despite the reduction in P_s for the latter (from 0.187 to 0.102 C m⁻²). This effect is attributed to the concomitant reduction in P_r (from 0.096 to 0.035 C m⁻²). The BCZT samples show a sub-linear $U_{\text{rec}}-E_{\text{Max}}$ relationship, similar to that of pure BT, although the U_{rec} values are approximately 30 % lower. This result can be explained in terms of the better-saturated P-E loops and higher P_r values for BCZT in comparison with BaTiO₃.

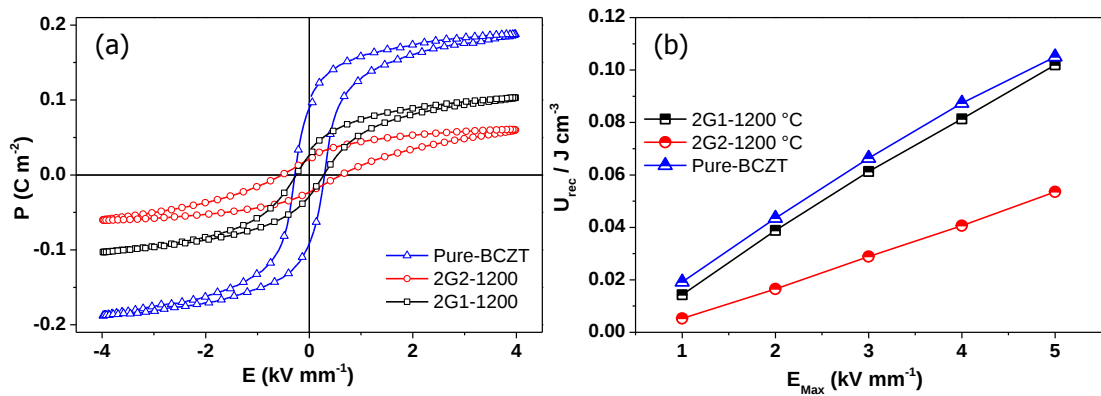


Figure 5.103 (a) P-E hysteresis loops obtained for pure BCZT and BCZT-2(G1,G2) measured at a frequency of 2 Hz. (b) the energy density of pure BCZT, BCZT-2G1 and BCZT-2G2 sintered at temperatures of 1400 and 1200 °C as a function of the electric field.

5.7.3 Glass-modified KNN ceramics

The pure KNN ceramics prepared in the present study exhibited lossy P-E loops with low breakdown fields and therefore were not included in this analysis. The glass-modified KNN materials were found to show almost linear but lossy P-E loops, with relatively low saturation and remanent polarisation values, in comparison with the BaTiO₃ and BCZT ceramics, as shown in Figure 5.104. Consequently, the $U_{\text{rec}}-E_{\text{Max}}$ relationships displayed a super-linear trend, approaching the levels attained by the BT-based materials at the highest electric field used in the present study.

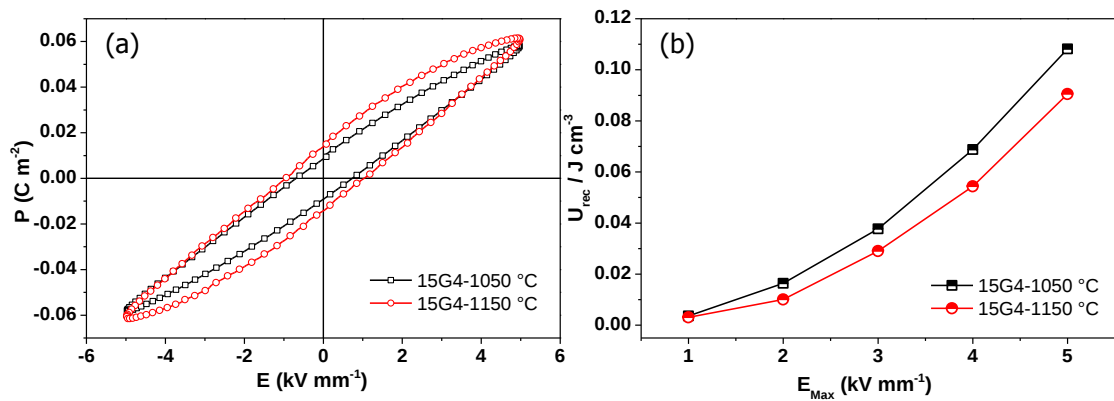


Figure 5.104 (a) P-E hysteresis loops and (b) the energy density as a function of the electric field obtained for KNN-15G4 ceramics sintered at of 1050 and 1150 °C and measured at a frequency of 2 Hz.

5.7.4 Glass-modified KBN ceramics

The P-E loops of the glass-modified KBN ceramics were similar to those of the glass-modified KNN ceramics, although with slightly lower P_s and P_r values, as shown in Figure 5.105. The super-linear $U_{\text{rec}}-E_{\text{Max}}$ relationship was also apparent in these results, with slightly lower U_{rec} values. However, it is worth noting that the hysteresis loss for KBN-15G4 was significantly lower than that of the other KNN-based ceramics, yielding an improved energy storage efficiency. This point is discussed further below.

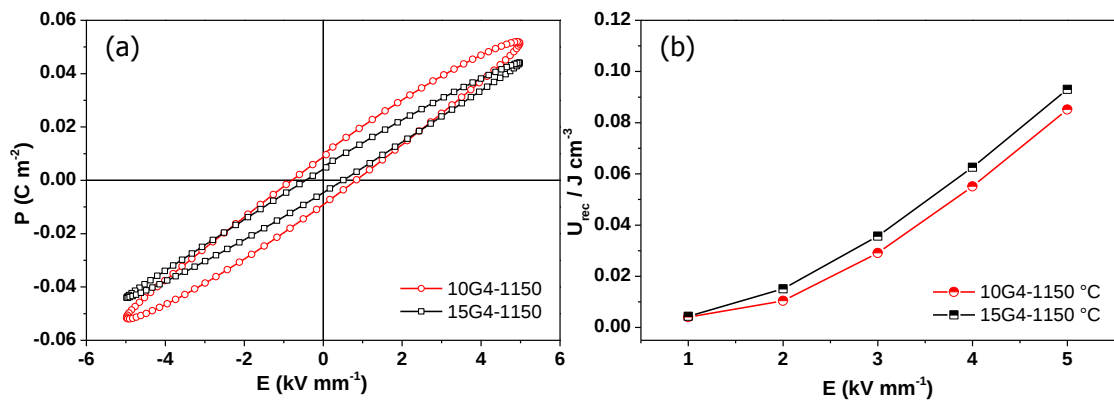


Figure 5.105 (a) P-E hysteresis loops and (b) the energy density as a function of the electric field obtained for KBN-10G4 and KBN-15G4 ceramics sintered at 1150 °C and measured at a frequency of 2 Hz.

5.7.5 KNN glass-ceramics

The energy density as a function of the electric field for K-50 and K-80 glass-ceramics heat treated at different temperatures is shown Figure 5.106. Clearly, both samples show a super-linear increase in the energy density as the heat treatment temperature and electric field increased. Generally, K-80 exhibits an energy density much higher than that of K-50. The forms of the $U_{\text{rec}}-E_{\text{max}}$ curves are super-linear, similar to those of the pure and glass-modified KNN ceramics.

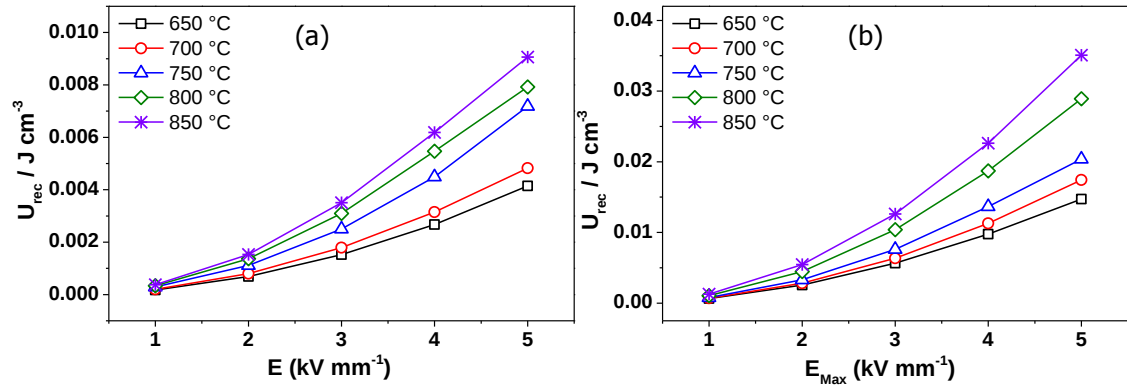


Figure 5.106 Influence of the heat treatment crystallisation temperature on the energy density of (a) K-50 and (b) K-80 glass-ceramics as a function of electric field.

The changes in energy density, measured at a maximum electric field of 5 kV mm^{-1} , as functions of KNN content and heat treatment temperature, are shown in Figure 5.107. It can be seen that the energy density increases due to an increase in both KNN content and heat treatment temperature. These results are in good agreement with the XRD patterns, which show how the content of the high- relative permittivity crystalline perovskite phase is improved with higher heat treatment temperature or KNN content. Furthermore, evidence was found to show improvements in connectivity between the crystalline clusters, which help to achieve higher average relative permittivity values.

Here, the average of the increase in the energy density due to the effect of heat treatment from 650 to 850 °C is about 53 % for K-50 and 60 % for K-80. It was shown above that the perovskite phase contents achieved after crystallisation at 850 °C were 35 % and 71 % for K-50 and K-80, respectively. The lower fraction of the low- relative permittivity glassy phase in K-80 (18 % compared with 27 %) is also significant in view of its influence on the connectivity between crystalline regions.

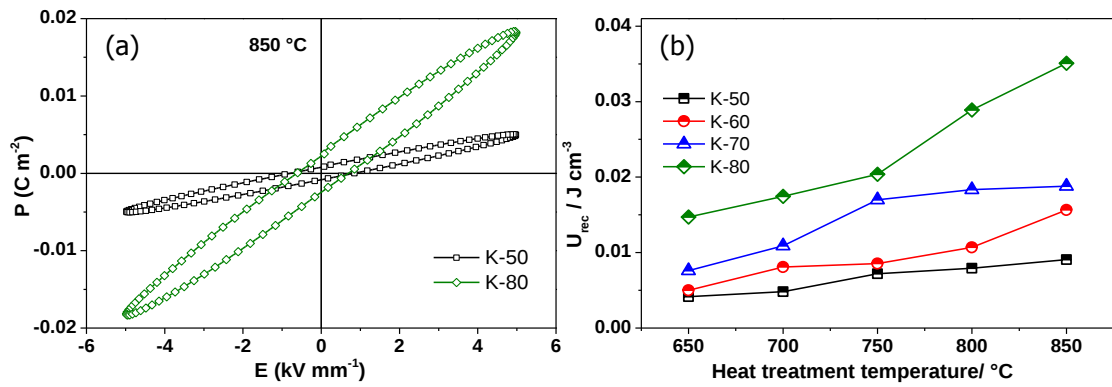


Figure 5.107 (a) P-E hysteresis loops for K-50 and K-80 heat treated at temperatures of 850 °C and (b) the energy density of glass-ceramics as a function of heat treatment temperature with different KNN content, measured at an electric field of 5kV mm⁻¹.

5.7.6 Comparison of Energy Storage Characteristics

The departure from linear dielectric behaviour can be described most simply in terms of a modification to equation 5-4, as follows:

$$U_{rec} = \frac{1}{2} \epsilon_0 \epsilon_r E_{Max}^n \quad 5-5$$

The value of n would be equal to 2 for a linear dielectric. According to this approach, the tendency for saturation in the P-E relationship causes a reduction in the effective relative permittivity at high fields and consequently $n < 2$. On the other hand, an increase in relative permittivity (such as that described by the Rayleigh Law) would result in $n > 2$. The $\log(U_{rec})$ - $\log(E_{Max})$ plots presented in Figure 5.108 illustrate the differences between the BT and KNN-based materials. Firstly, the BT-based materials exhibit higher U_{rec} values at low fields as a result of the higher polarisation values. However, the gradient of the log-log plot for BT-2G1 was determined as 0.97, which indicates the strong tendency for saturation.

On the other hand, both the glass-modified KNN and the KNN glass-ceramic exhibited higher gradients in the log-log plots (2.06 and 2.05, respectively) (as shown in Table 5.10), and therefore U_{rec} increased more rapidly with increasing field. The fact that $n > 2$ for these two materials is consistent with the weak nonlinearity and Rayleigh behaviour described in sections 5.4.2 and 5.6.6. On the basis of the projected U_{rec} - E_{max} relationships (illustrated below in Figure 5.110, labelled as points 'A' and 'B'), it is predicted that U_{rec} for the glass-modified KNN-15G4 would exceed that of BT-2G1 at 6.1 kV mm⁻¹, while the crossover point for the K-80 glass-ceramic should occur around 18.5 kV mm⁻¹. Clearly, the glass-modified KNN materials should be favoured for energy storage applications at high electric field levels, although the ultimate fields achievable

have yet to be determined, for example by measurements of breakdown strength. The glass-ceramic could also be useful as an energy storage dielectric, provided that higher breakdown fields could be achieved due to the uniform and dense nanostructure. Further discussion of the extrapolated 'high-field' energy storage characteristics and comparison with values reported in the literature are given below.

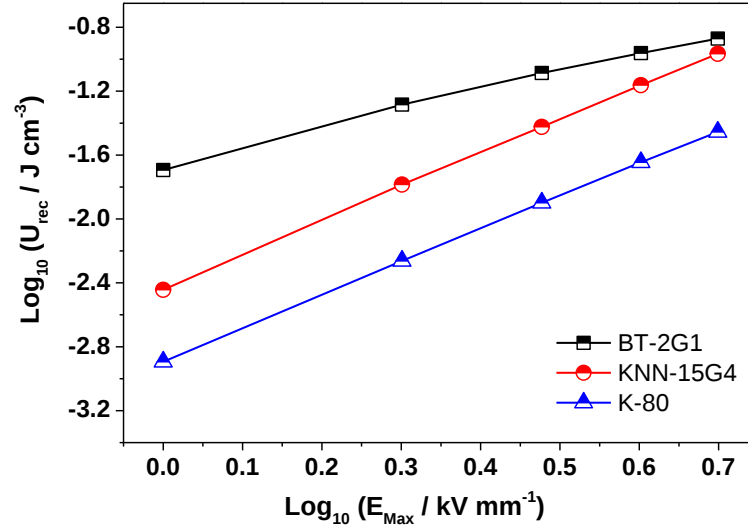


Figure 5.108 Comparison of the energy storage density-dependent of the electric field for BT-2G1/1100 °C, KNN-15G4/1050 °C and K-80/850 °C.

Another important aspect to consider is the dielectric loss, U_{loss} , which is clearly evident in many of the ferroelectric hysteresis measurements as the area enclosed within the P-E loop. This leads to the definition of the energy storage efficiency, η , as

$$\eta = \frac{U_{rec}}{U_{rec} + U_{loss}} \quad 5-6$$

While the U_{rec} values are highest for the barium titanate-based ceramics, the hysteresis losses are also largely due to the strongly hysteretic P-E loops and therefore the energy storage efficiencies are relatively low (50-60 %). Both the glass-modified KNN ceramics and K-80 glass-ceramic materials exhibit higher energy storage efficiencies ≈ 70 %, as shown in Table 5.10, consistent with the slimmer hysteresis loops and more linear dielectric behaviour. Although the U_{rec} values for these materials should improve remarkably at higher field levels, it seems unlikely that the efficiency would change significantly since increased relative permittivity values would also be accompanied by increased losses i.e. both ϵ_r' and ϵ_r'' increase with E_{Max} . This effect is illustrated by the $\epsilon_r'-\epsilon_r''$ relationships plotted in Figure 5.109. The relationship between ϵ_r'' and U_{loss} is

given in equation 5-7, which is similar to the expression for U_H given in equation 4-6, since U_H is equal to $2 \times U_{loss}$ [208].

$$2U_{loss} = \pi \epsilon_0 \epsilon_r'' E_0^2 \quad 5-7$$

Table 5.10 Comparison of U_{rec} , U_{loss} , power exponent (n) and energy storage efficiency (η) for different materials, measured at 5 kV mm^{-1} . Numbers in parentheses are estimated uncertainties in the last significant digit(s).

Samples	$U_{rec} / \text{J cm}^{-3}$	$U_{loss} / \text{J cm}^{-3}$	n	$\eta / \%$
BT-2G1-1100 °C	0.134(4)	0.150(3)	0.97(5)	48(3)
BCZT-2G1-1200 °C	0.103(5)	0.089(3)	0.99(3)	59(1)
KNN-15G4-1050 °C	0.108(1)	0.053(1)	2.06(2)	67(2)
KBN-15G4-1150 °C	0.093(2)	0.034(2)	1.88(2)	73(1)
K-80-850 °C	0.035(2)	0.015(2)	2.05(1)	69(2)

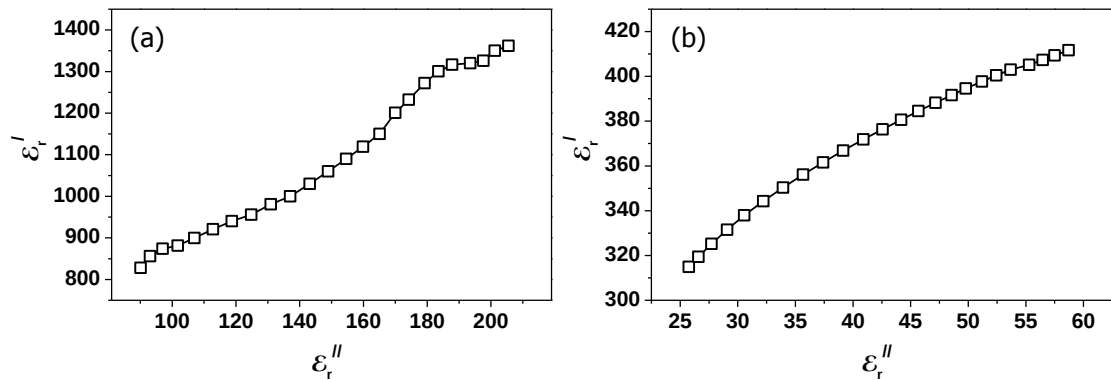


Figure 5.109 The relationship between real and imaginary parts of relative permittivity calculated from P-E hysteresis loops for (a) KNN-15G4 and (b) K-80.

Among the materials investigated in the present study, the glass-modified BT ceramics appear to provide the highest energy storage densities, with $U_{rec} \approx 0.13 \text{ J cm}^{-3}$ for BT-2G1 at an electric field level of 5 kV mm^{-1} . However, these materials show a clear tendency for saturation and relatively high hysteresis loss in the P-E relationship, giving a limited performance and poor storage efficiency. The glass-modified KNN and KBN ceramics yielded slightly lower U_{rec} values, but with much-improved linearity and storage efficiency. These materials, with effective ϵ_r values in the region of 1000, have good potential to withstand higher electric field levels due to the influence of the glass on densification and grain size.

The extrapolated values of U_{rec} for KNN-15G4, shown in Figure 5.110, are 1.9 and 4.3 J cm⁻³ at electric field levels of 20 and 30 kV mm⁻¹, corresponding to $\log_{10}(E_{Max}/\text{kV mm}^{-1}) = 1.3$ and 1.47, respectively. These predicted results compare favourably with the U_{rec} values of 1.1 J cm⁻³ (at 28 kV mm⁻¹) and 0.89 J cm⁻³ (at 20 kV mm⁻¹) for BCZT and BST ceramic-glass composites respectively, as illustrated in Table 5.11 and Figure 5.110 [24, 35]. At a higher electric field of 40 kV mm⁻¹, the predicted U_{rec} value for KNN-15G4 increases to 7.9 J cm⁻³, which is higher than those reported for KNN-based ceramics (3.67 J cm⁻³) and glass-ceramics (1.89 J cm⁻³) [129, 209].

The K-80 glass-ceramic yielded lower U_{rec} values than those of glass-modified KNN and KBN ceramics, but significant improvements are possible due to the potential for higher breakdown fields. The predicted U_{rec} value at 40 kV mm⁻¹ was 2.26 J cm⁻³, which is higher than 1.89 J cm⁻³ as reported previously for a KNN-based glass-ceramic [129]. In fact, most of the high U_{rec} values quoted in the literature demand the use of very high electric field levels, as shown in Table 5.11 and Figure 5.110; it has yet to be proven that reliable operation can be achieved in practical applications under such operating conditions. Improved processing procedures (for better uniformity) and preparation of materials in thin and thick forms will be key considerations for future pulsed power device applications.

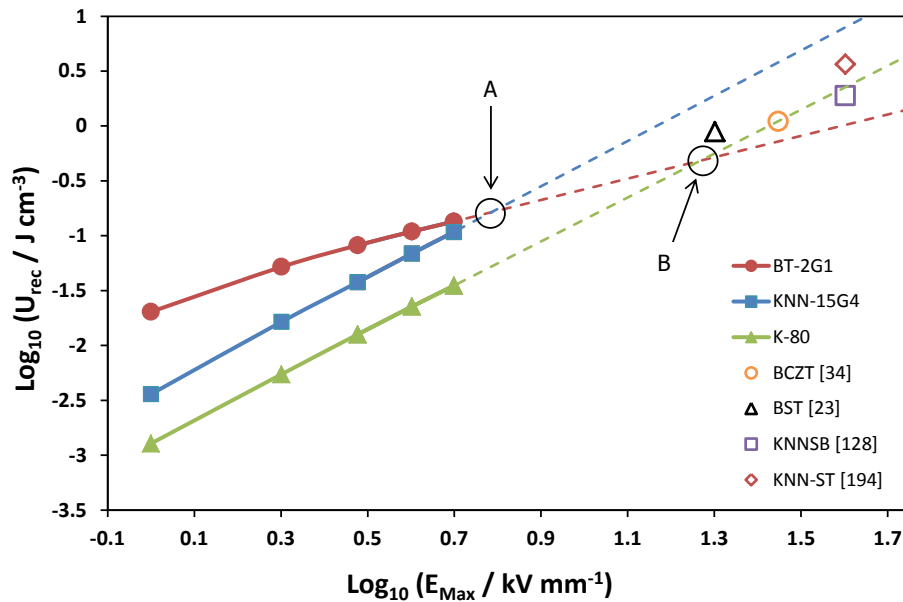


Figure 5.110. The extrapolated values of U_{rec} for BT and KNN-based materials compared with those from previous reports for BCZT [35], BST [24], KNNSB [129] and KNN-ST [209]. The dashed lines are the trendlines used in order to extrapolate the U_{rec} values at high electric field levels. 'A' and 'B' denote the crossover points for KNN-15G4 and K-80, at which the U_{rec} values are predicted to exceed that of BT-2G1.

Table 5.11 Comparison of reported U_{rec} , E_{max} and ϵ_r values for different materials.

Material	$U_{rec} / \text{J cm}^{-3}$	$E_{max} / \text{kV mm}^{-1}$	ϵ_r	Reference
$\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ +5% BBS ceramic (BST)	0.89	20	750	[24]
BCZT-BBZ glass-ceramic/composite (BCZT)	1.1	28	378	[35]
0.8KNN–0.2ST/ ceramic (KNN-ST)	3.67	40	1000	[209]
Na_2O - BaO - Nb_2O_5 - SiO_2 +2mol% Li_2O_3 glass-ceramic	1.2	28	500	[210]
PbSr - Nb_2O_6 - NaNbO_3 - SiO_2 glass-ceramic	2.27	35	600	[211]
K_2O - Na_2O - Nb_2O_5 - SiO_2 - B_2O_3 glass-ceramic (KNNSB)	1.89	40	190	[129]
BaTiO_3 -PVDF nanocomposite	3.54	200	25	[212]
Poly (vinylidene fluoride)–(PVDF)	14	500		[213]

6. Conclusions and Future work

6.1 Conclusions

Several different barium borosilicates (BBS)-based glass systems were prepared successfully using a conventional melting and quenching method. The glass types G1 and G2 were added into BT/BCZT ceramics as sintering aids, while G3 and G4 were added into KNN/KBN ceramics, resulting in much improved densification behaviour at reduced sintering temperatures.

A strong dependence of relative permittivity on grain size was observed for the glass-modified BT ceramics; BT-10G1 sintered at 1100 °C displayed a high relative permittivity ≈ 4000 but also exhibited strong frequency-dependent behaviour, which was attributed to an interfacial polarisation mechanism associated with relatively high electrical conductivity. The ferroelectric switching behaviour was enhanced due to the improved densification at low glass contents; for example, the saturation polarisation values at 5 kV mm⁻¹ were determined as 0.131 and 0.175 C m⁻² for pure BT ceramic sintered at 1300 °C and BT-2G1 at 1100 °C, respectively. These values reduced at higher glass contents due to the low relative permittivity of the glass phases.

Similar effects on densification and dielectric/ferroelectric properties were observed when the glass additives were employed as sintering aids for BCZT ceramics, helping to reduce the required sintering temperature from very high levels (typically 1500 °C) to only 1200 °C. Furthermore, it was found that the presence of the glasses in BCZT led to the occurrence of two additional phase transitions, identified as inflections in the ϵ_r -T curves for the glass-modified BCZT ceramics. The ϵ_r -T curves exhibited a clear shoulder at 40-60 °C, associated with the O-T transformation and another inflection at a higher temperature of 120 °C; these transitions were not evident in the dielectric results for pure BCZT with this composition. The additional phase transitions were explained in terms of the redistribution of Ca and Zr ions between the crystalline and glassy phases, resulting in the formation of some Ca- and Zr-depleted BaTiO₃ grains. The structural nature of the phase transformations was supported by the results of in-situ temperature-dependent SXPD measurements, which were evaluated by full-pattern fitting.

The use of BBS glass as a sintering aid in KNN ceramics was also investigated, although it was found that further modifications to the glass composition were necessary to provide lower melting temperatures, compatible with the lower melting temperature of KNN in comparison with BT. Relative density values of greater than

90 % were achieved for G4-modified KNN at a sintering temperature of 1050 °C. The dielectric property measurements indicated generally high relative permittivity values ($\epsilon_r \approx 740$ at room temperature), although slim P-E loops with relatively low polarisation values were obtained for the G4-modified material sintered at temperatures of 1050 and 1150 °C.

Improvements in density were observed for the glass-modified KBN ceramics, with a relative density of approximately 95 % being obtained for KBN-15G4 sintered at 1050 °C. In common with the glass-modified BCZT ceramics, the dielectric properties of KBN were affected significantly by the presence of the glass additives. Two additional transitions were clearly evident in the ϵ_r -T curves, which corresponded closely with those of the phase transformations in pure KNN ceramics. It is proposed that a similar mechanism, involving the heterogeneous dissolution of dopant elements into the glass phase, is responsible for this behaviour.

Amorphous BBS-KNN glasses were prepared successfully using a conventional melt-quenching method. These were transformed into nanocrystalline glass-ceramics by subsequent heat treatment at temperatures up to 850 °C. Different microstructures were obtained by varying the composition and heat treatment temperatures. Crystallisation of several intermediate phases was initiated at temperatures around 600 °C; these phases subsequently transformed into a mixture of the perovskite KNN phase and barium niobate ($\text{Ba}_3\text{Nb}_5\text{O}_{15}$) by 800 °C. The maximum particle size, obtained from particle size-broadening effects in the XRD results, was approximately 25 nm; this compares with a typical crystallite size of around 40 nm in the TEM images.

Quantitative phase analysis of the heat-treated glass-ceramics was achieved by analysis of the SXPD results using an internal alumina standard. These results indicated that the perovskite KNN phase contents of the K-50 and K-80 glass-ceramics were 35 and 71 wt%, respectively, while the amorphous glassy phase contents were ≈ 28 and 19 wt%. The electrical studies indicate that the materials exhibit promising dielectric properties, with ϵ_r values up to 350, although relatively high dielectric losses were evident. Near-linear ferroelectric P-E loops were obtained, with a Rayleigh coefficient of $28 \times 10^{-6} \text{ m V}^{-1}$ for K-80 heat treated at 850 °C.

The highest dielectric energy storage density achieved was $U_{\text{rec}} \approx 0.13 \text{ J cm}^{-3}$ for BT-2G1 at an electric field level of 5 kV mm^{-1} . However, all of the BT-based materials demonstrated a tendency for saturation at high field levels and poor storage efficiency (≈ 50 to 60%). Therefore, they are considered to have the poor potential for use as

energy storage dielectrics. On the other hand, both the glass-modified KNN ceramics and K-80 glass-ceramic materials exhibit higher energy storage efficiencies ($\approx 70\%$) and, although possessing lower energy densities at 5 kV mm^{-1} , $U_{\text{rec}} \approx 0.11$ and 0.035 J cm^{-3} , respectively, the extrapolated values of U_{rec} for KNN-15G4 increase to 1.9 and 4.3 J cm^{-3} at electric field levels of 20 and 30 kV mm^{-1} , respectively. Clearly, further work is required to establish whether such levels of recoverable energy density can be demonstrated in practical devices, as noted below.

6.2 Future Work

The results of the present study indicate a number of areas that could be useful as topics for further research, addressing both fundamental issues and practical applications.

Studies of the electrical breakdown strength of both the sintered ceramic-glass composites and recrystallized glass-ceramics are needed to establish the feasibility of increasing the electric field levels to improve energy storage density. The fabrication of thick film coatings by methods such as tape casting or electrophoretic deposition would also enable the effects of much higher field strengths to be evaluated, since it is well-known that the breakdown field strengths of thin and thick films are often substantially higher than those of bulk ceramics due to improvements in microstructural homogeneity.

The relatively high dielectric losses observed in some of the results in the present work are attributed to electrical conduction effects in the glass phases. Further research should be undertaken to investigate the conduction mechanisms and to determine whether improvements in resistivity can be obtained by compositional modifications. For example, it was shown by Zhou that addition of Gd_2O_3 to ferroelectric glass-ceramics is highly effective at improving resistivity and electrical breakdown strength [214]. Reactions between the crystalline and glassy components during sintering should also be investigated in order to confirm the origins of the unusual changes in dielectric behaviour that were observed in the present work. Micro-chemical analysis using wavelength-dispersive x-ray spectroscopy (WDS) could be employed to evaluate the chemical interactions between the phases.

In terms of dielectric energy storage characteristics, it was found that the KNN-based materials show greater potential for improvement than the BT- or BCZT-based

ceramics. There was only a limited variation of KNN composition within the present study. Therefore, it would be of great interest to investigate the influence of the K/Na ratio on the properties of both KNN-glass composites and KNN glass ceramics. Na-rich compositions could be of particular interest since the antiferroelectric nature of NaNbO_3 could lead to benefits in energy storage parameters.

High resolution TEM studies of the glass-ceramics after heat treatment over a range of temperatures are needed to identify the intermediate phases that were observed in the in-situ SXPD results. The initial stages of crystal nucleation and growth, as well as the mechanism of conversion to the perovskite KNN phase, are also of great interest. It is likely that the use of more refined glass-making procedures could result in more chemically homogeneous glasses, which might allow the formation of the perovskite phase at lower temperatures. The *incorporation* method described by Yongsiri [77] is one such approach that could be investigated. The use of additives to enhance nucleation could also be a useful means to improving crystallisation behaviour.

7. References

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