Rheology and microstructure of (Ca$_{0.9}$,Sr$_{0.1}$)TiO$_3$ perovskite deformed in compression and torsion

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[1] Polycrystalline samples of (Ca$_{0.9}$,Sr$_{0.1}$)TiO$_3$ were synthesized from high-purity oxides yielding samples with <1% porosity and grain sizes between 10 and 100 $\mu$m. These samples were used to study the rheological properties of the tetragonal and cubic phases of (Ca,Sr)TiO$_3$. Data from compression experiments performed over a temperature range spanning the tetragonal to cubic phase transition show a change from a power law rheology at high stresses and large grain sizes to a linear-viscous rheology at low stresses and small grain sizes. The best fit flow law is $\dot{\varepsilon} = 10^{0.6} \sigma^{5.3} \exp(-521 \text{ kJ mol}^{-1}/RT) + 10^{8.4} (\sigma/z)^{1.4} \exp(-627 \text{ kJ mol}^{-1}/RT)$, where $z$ (m) is the grain size parameter which includes the median grain size and the standard deviation of the grain size distribution and $\sigma$ is in MPa. Microstructures from both torsion and compression experiments point to grain boundary and cooperative grain boundary sliding accommodating ~80% of the sample strain in both the power law and linear viscous fields. Misorientation axes align parallel to the kinematic axis of the imposed deformation in both compression and torsion tests. The crystallographic preferred orientations (CPO) are weak for both torsion and compression experiments but point to (100)$_{pc}$ as the dominant Burger’s vectors. We propose that our samples deform by grain boundary sliding accommodated by diffusion at low stresses and small grain sizes and grain boundary sliding accommodated by dislocation creep at high stresses and large grain sizes. Such deformation mechanisms will not lead to a significant CPO and hence would not create a substantial seismic anisotropy. Under the conditions investigated, little change in rheological behavior was observed across the tetragonal to cubic phase transformation of perovskite.

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1. Introduction

[2] (Mg,Fe)SiO$_3$ perovskite is considered to be the most abundant phase in the Earth’s lower mantle (~80% by volume), along with magnesiowüstite and other minor high-pressure phases [Hirose, 2002; Ringwood, 1968]. As the lower mantle is ~55% of the volume of the Earth, perovskite is likely to be the most abundant phase in the Earth. Therefore, knowledge of the rheological properties of (Mg, Fe)SiO$_3$ is crucial to the understanding of the rheology of the lower mantle and the dynamics of the Earth’s interior. Furthermore, ABO$_3$ perovskite structured ceramics can be manufactured with useful properties (e.g., high oxygen diffusivity) by A and/or B site doping and are used in solid oxide fuel cells and related technologies where they are used as proton and oxygen membranes [e.g., Salama et al., 2005]. Some high-pressure deformation experiments have been performed on (Mg,Fe)SiO$_3$ perovskite [e.g., Karato and Rubie, 1997]. However, deformation experiments yielding reliable rheological data cannot currently be performed within the stability field of (Mg,Fe)SiO$_3$ perovskite.

[3] Perovskite may be obtained using a wide variety of elements. (Ca,Sr)TiO$_3$ for example is stable at atmospheric pressure and can be used as an analog for (Mg,Fe)SiO$_3$ perovskite. It undergoes two structural phase transitions between 100 and 1600 K depending on the Ca:Sr ratio. Although there is still some debate, (Mg,Fe)SiO$_3$ perovskite is thought to be orthorhombic (space group $Pbnm$) in the lower mantle [Horiuchi et al., 1987]. (Ca,Sr)TiO$_3$ exhibits the same orthorhombic ($Pbnm \equiv Pnma$) structure at low temperature and transforms to the cubic ($Pm3m$) structure at high temperature via an intermediate tetragonal ($I4/mcm$) structure [Carpenter et al., 2001]. The (Ca,Sr)TiO$_3$ perovskite structure can be visualized as TiO$_6$ octahedra linked at the corners with the Ca and Sr atoms sitting in the gaps...
between eight octahedra (Figure 1). By studying the deformation behavior of (Ca,Sr)TiO₃, insight into the rheological properties of (Mg,Fe)SiO₃ perovskite can be gained. Ferré et al. [2009a] suggest that CaTiO₃ is a good isostructural analog for MgSiO₃ perovskite for dislocation glide. Throughout this paper when we refer to the orthorhombic structure we are referring to the Pbnm structure where a = 5.4671 Å, b = 5.4823 Å and c = 7.7461 Å. When we use miller indices in the pseudocubic setting, there will be “pc” subscript, in the orthorhombic setting we will use an “o” subscript, in the tetragonal setting we will use a “t” subscript, and in the cubic setting a “c” subscript.

2. Experimental Method

2.1. Starting Material

[4] The starting material was prepared by mixing high-purity (>99.9%) calcium carbonate, strontium carbonate and titanium (IV) oxide. Powders were first dried at 573 K to eliminate any adsorbed water and then weighed in the correct stoichiometric proportions (within 1000 ppm) to give a composition of (Ca₀.₉,Sr₀.₁)TiO₃ and mixed with a pestle and mortar in ethanol. After mixing the ethanol was evaporated under an infrared lamp. Powders were then decarbonated at 1373 K in air for 3 h and subsequently sintered at 1673 K in air for 12 h. The reacted product was ground to a fine powder (~10 μm) and fired again at 1673 K in air. This was repeated a further three times to ensure complete reaction. Powder X-ray diffraction was performed on the resulting material and only diffraction peaks for the (Ca,Sr)TiO₃ perovskite were observed, indicating greater than 98% purity. This composition was chosen in order to be able to study all three phases at a single composition within the temperature range of the apparatus. It was found however that at temperatures below 1400 K this material is very strong and deforms at very slow strain rates ~10⁻⁷ s⁻¹ at differential stresses less than 300 MPa. Therefore, it was not feasible to study the rheology of the orthorhombic phase.

[5] The perovskite powder was then ground in an agate pestle and mortar and subsequently in a micronizing mill in ethanol to a grain size of ~10 μm. Pellets measuring 12 mm in diameter and 23 mm long were obtained by cold pressing at 200 MPa. These pellets were sintered at 1 atmosphere in air at 1773 K for 12 to 100 h resulting in grain sizes between 10 and 100 μm. Sintered pellets where ground and polished so that the ends of samples where parallel to better than 10 μm. Two such pellets were stacked together and encased in an iron jacket and were hot pressed at 300 MPa and 1500 K for 12 h in a gas-medium apparatus. This was done to aid further sintering and compaction of the samples and also to reset the defect chemistry to the lower oxygen fugacity (below the Fe-FeO buffer) within the deformation apparatus when compared to the one atmosphere furnace. This change in the defect chemistry could be assessed by an obvious change in color of the samples. After hot pressing the ends of the samples were reground to be parallel within 10 μm and were 9.75 mm in diameter and 20 to 25 mm long.

[6] At high oxygen fugacities the samples are colored pinkish orange while after hot pressing, they turned a dark gray color throughout the sample. Webb et al. [1999] use the weight change involved in the oxidization of a reduced sample of CaTiO₃ to estimate the amount of Ti³⁺ in the material, assuming that all the weight gain is due to the oxidation of Ti³⁺ to Ti⁴⁺. They found that in their samples, ~4% of the titanium was Ti³⁺. As their experiments were performed at conditions almost identical to ours, it is reasonable to expect a similar titanium oxidation state in our experiments. It is important that the point defect chemistry in the starting material is set to the conditions of the deformation experiments as diffusion in (Ca,Sr)TiO₃ is strongly dependent on the defect chemistry [Li et al., 2006; Webb et al., 1999].

2.2. Deformation Experiments

[7] Constant force and constant differential stress deformation experiments were performed in a Paterson deformation apparatus [Paterson, 1990; Paterson and Olgaard, 2000] at 300 MPa confining pressure and temperatures between 1350 and 1550 K. Constant differential stress is achieved by creating a force set point automatically to account for the change in cross-sectional area of the sample due to the axial shortening, assuming the sample deformation is isovolumetric. In this way the differential stress on the sample can be controlled to within 1 MPa of the desired value. Samples were deformed at differential stresses between 50 and 300 MPa using both stress stepping and temperature stepping tests. From the creep curves (Figure 2) quasi steady state regions were selected for each stress or temperature and a strain rate was then determined by calculating the slope of strain versus time data in this region. Apart from the lowest temperatures and stresses, where the strain rate measured was as low as 10⁻⁷ s⁻¹, each stress or temperature increment corresponded to ~1% natural strain. The force measured is corrected for the force supported by the iron jacket at the measured strain rate using iron flow laws [Frost and Ashby, 1982] and the cross-sectional area of the iron jacket.

2.3. Microstructure Measurement

[8] For microstructural analysis the compression samples were cut in half parallel to their axis and torsion samples...
were cut as close to the outer surface of the sample as possible parallel to the sample axis. Samples were then mounted in epoxy resin and polished (the final polishing was carried out using a colloidal silica solution).

2.3.1. Electron Backscatter Diffraction

[9] Microstructures and crystallographic orientations of the samples were quantified using electron backscatter diffraction (EBSD) in the scanning electron microscope (SEM) [e.g., Dingley, 1984] producing a map of lattice orientations in which the grains can be quantitatively identified and the microstructure studied in detail. From crystallographic preferred orientations (CPO) and microstructure analysis insight into the mechanisms that accommodated sample deformation during the experiments could be gained.

At ambient conditions perovskite [Carpenter et al., 2001]. However, the orthorhombic structure is only slightly distorted relative to the cubic and tetragonal high-temperature phases and it proved impossible to index the orthorhombic structure reliably in an automated SEM-EBSD orientation mapping. This is probably due to the extra reflections for the orthorhombic structure being lower intensity than the cubic reflections. The lattice strains between the orthorhombic and cubic structures are only small ($a = 3.824 \text{ Å}$ for the ideal cubic structure compared to $a/\sqrt{2} = 3.85 \text{ Å}$, $b/\sqrt{2} = 3.88 \text{ Å}$ and $c/2 = 3.822 \text{ Å}$ for the orthorhombic $Pbnm$ structure [Carpenter et al., 2001]). The EBSD technique is not sensitive enough to pick these small differences between the structures. Hence we used the cubic perovskite structure for indexing which yielded reliable results (>80% indexing). In using the cubic structure to index the diffraction patterns some crystallographic information was of course lost, but since at least some of the samples were deformed in the cubic stability field this information was not important for our study. In the case of samples deformed in the tetragonal stability field the partial loss of orientation information had to be considered (see below).

In order to investigate the microstructure of the deformed samples EBSD data were collected using step sizes between 0.25 and 1 µm, depending on the grain size. Nonindexed points reflected the presence of voids, due to sample preparation, or grain boundaries. Misindexed and nonindexed points were given average orientations of their neighbors being careful not to introduce errors using techniques discussed by Bestmann and Prior [2003] that minimize the introduction of artifacts to the data. Furthermore, grains with less than 5 pixels were excluded to avoid biases in the data. A minimum grain size of 2.2 times the step size used for mapping can thus be resolved.

2.3.2. Grain Size Analysis

[12] From the processed data sets grains are identified by grouping neighboring pixels with the same orientation to within 10° misorientation. Grain areas can then be calculated and from these, the diameter of a circle with the same area is obtained. A histogram of grain diameters for sample P0331, shown in Figure 3, shows a strong bias by the fine grain sizes (~5 µm). The large number of small grains represents only a small volume of the overall sample; therefore, a correction must be applied to obtain a volumetrically representative grain size. Heilbronner and Bruhn [1998] used the Schwartz-Saltykov method [e.g., Underwood, 1968] to correct grain diameter measurements made on a section for the artifact of not sectioning all grains at their maximum diameter. It assumes the grains are spherical in shape and works by progressively stripping the effect of coarser grain sizes on the grain size distribution measured for the finer grain sizes. This approach relies on being able to calculate the probability of different section diameters in a uniform distribution of spheres. This calculation is nontrivial for any 3-D space filling shape (e.g., tetrakiadekahedrons) and some systematic errors are introduced due to treating the 3-D shape of the grains as spheres; however, applying these corrections yields calculated distributions closer to a more representative grain size distribution. From the corrected
distributions a volumetrically averaged grain size can be calculated. Heilbronner and Bruhn [1998] showed that by using this approach to measure grain sizes they could explain differences in deformed microstructure and, therefore in rheology, that could not be explained by using the uncorrected average grain diameter. We have used the Johnson-Saltykov method [e.g., Underwood, 1968], which is essentially the same as the Schwartz-Saltykov method except that it uses a logarithmic scale, which has the advantage of more resolution at the low end of the grain size distribution. Figure 3b shows the grain size distribution in Figure 3a corrected as explained above. It can be seen that the volumetrically averaged grain size (48.9 μm) is much larger than the uncorrected average of 15.1 μm for this sample. The corrected volumetric distribution data are fit with a single lognormal distribution to get the mean and standard deviation of each distribution.

2.3.3. Strain Analysis

[13] In order to estimate the significance of grain boundary sliding on the sample bulk strain we have determined the strain recorded as shape change of the grains using the Fry technique [e.g., Erslev and Ge, 1990; Fry, 1979]. This technique plots the normalized distance between the nearest neighbor grains for each grain in the microstructure and the resulting point cloud describes the finite strain ellipse for the overall strain of the grains. We have used the enhanced normalized Fry routine proposed by Erslev and Ge [1990]. The Fry analysis is insensitive to deformation by the relative movement of grains past one another by, for example, grain boundary sliding and records only the strain accommodated by shape changes of the grains. Thus it can be used to assess the contribution of grain boundary sliding processes to accommodate sample strain [Walker et al., 1990]. For the compression experiments, the strain (ε) can be calculated from the axial ratio (R) of the finite strain ellipse fitted to the point cloud, assuming constant volume axisymmetric shortening, using

\[ \varepsilon = 1 - R^{-2/3} \]  

(1)

The error in the calculated strain was determined as the difference between the maximum and minimum values of the axial ratio that fit the Fry plot. This represents an overestimate, but the true error is difficult to calculate. For torsion experiments the shear strain (γ) can be calculated either from the axial ratio of the finite strain ellipse or from the angle between the long axis of the strain ellipse and the shear plane (φ), assuming simple shear, using

\[ \gamma = \frac{R - 1}{\sqrt{R}} \quad \gamma = \frac{2}{\tan(2\phi)} \]  

(2)

In order to estimate the error in the calculated shear strain we compared the value calculated using R and the value

Figure 3. (a) Probability density function of grain size for sample P0331 using the number of grains. (b) Probability density function of grain size using the volume of grains calculated from data in Figure 3a using the Johnson-Saltykov technique [Underwood, 1968]. The recrystallized grain size distribution (Rex) is shown in black, and the parent grain size distribution is shown in white. The recrystallized grains have been separated from the deformed grains using the mean misorientation threshold of 1.4°. (c) Probability density function of grain size using the volume of grains for starting material CST6 sintered at 1773 K for 48 h resulting in a volumetric mean grain size of 14 ± 7 μm.
Table 1. Experimental Data

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aDifferential stress MPa.
bError in differential stress in MPa.
cStrain rate in s$^{-1}$.
dError in strain rate in s$^{-1}$.
eTemperature in K.
fGrain size in $\mu$m.
gStandard deviation of the lognormal distribution in $\log_e \mu$m.
hFor torsion experiment the stress is shear stress, and the strain rate is a shear strain rate.
Figure 4. All stress stepping data plotted in log_{10} strain rate (s^{-1}) versus log_{10} stress (MPa). Four different temperatures are shown between 1350 and 1550 K. The best fit flow law of the form shown in equation (1) is also plotted for the different temperatures and grain sizes. The best fit flow equation is also shown, which was computed using the nonlinear least squares fitting routine. For comparison, the empirical flow laws from Li et al. [1996] for the diffusion creep of CaTiO_3 at 1500 K and 80 μm grain size (green dashed line) and from Wright et al. [1992] for dislocation creep of single crystals of CaTiO_3 orientated for easy slip on {100}pc at 1500 K (green dash-dotted line) are shown.

calculated using \( \phi \) to give a range of shear strains that would fit the Fry plot.

3. Mechanical Results

[14] Data for one representative stress step are shown in Figure 2. It can be seen that the transient creep portion of the curve is small and the sample response to the applied stress approaches steady state in a relatively small amount of strain. All values of stress, strain rate, temperature and grain size for all the samples deformed are shown in Table 1. Figure 4 shows that log strain rate versus log stress data cannot be represented by a single straight line for each temperature. This implies that sample deformation is not being accommodated by a single deformation mechanism; rather there is a transition from power law creep at high stresses to linear creep at low stresses [e.g., Bystricky and Mackwell, 2001; Dell’Angelo and Olgaard, 1995; Hirth and Kohlstedt, 1995a, 1995b]. The relative contribution of each mechanism is set by the stress, temperature and grain size. Power law creep is favored by high stresses and large grain sizes and linear creep is favored by low stresses and small grain sizes. As linear creep is commonly grain-size-dependent it is called grain-size-sensitive creep. In order to extract creep parameters from the experimental data we have fit the data to a flow law where the two creep mechanisms are independent from each other, the stress is constant for both mechanisms and the overall strain rate is given by the sum of the strain rates from the two mechanisms. This can be expressed by a creep equation of the form

\[
\dot{e} = A_p \sigma^n \exp \left( \frac{Q_{pl}}{RT} \right) + A_g sd^m \sigma \exp \left( \frac{Q_{gs}}{RT} \right)
\]  

where \( \dot{e} \) is the bulk strain rate (s^{-1}), \( \sigma = (\sigma_1 - \sigma_3) \) is the differential stress (MPa); \( T \) is the absolute temperature (K); \( d \) is the grain size (m); \( R \) is the gas constant; \( A_p, n, Q_{pl} \) are empirical parameters for the preexponential term, the stress exponent, and the activation energy for power law creep, respectively; and \( A_g, m, Q_{gs} \) are empirical parameters for the preexponential term, the grain size exponent, and the activation energy for grain-size-sensitive creep, respectively. Ter Heege et al. [2004] derived a grain-size-sensitive flow law for a material with a lognormal distribution of grain sizes where the grain size is replaced by

\[
z = d_{med} \exp \left[ \left( 3 + \frac{1}{2} m \right) S^2 \right]
\]

where \( d_{med} \) is the median volumetric grain size and \( S \) is the standard deviation of the log normal distribution; this takes into account the effect of the average grain size as well as the tightness of the grain size distribution on the rheology. [15] All the data shown in Table 1 were fit to equation (3) using a nonlinear least squares fitting routine [Bevington, 1969], with \( d \) substituted by \( z \) from equation (4). All the data for temperatures of 1350, 1400, 1500 and 1550 K are shown in Figure 4 with lines for the best fit flow law at constant temperature for an average grain size and standard deviation. The best fit flow law is

\[
\dot{e} = 10^{0.6 \pm 1.4} \sigma^{5.3 \pm 0.6} \exp \left( \frac{\sigma \pm 30}{RT} \right) - 10^{8.5 \pm 2.0} \sigma^{2.4 \pm 0.2} \exp \left( \frac{-627 \pm 65}{RT} \right)
\]  

where the activation energies are given in kJ mol^{-1}, stresses are in MPa and \( z \) is in m. The best fit flow law parameters are given in Table 2 along with flow law parameters for

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_p ) (s^{-1} MPa^{-n})</th>
<th>( n )</th>
<th>( Q_{pl} ) (kJ mol^{-1})</th>
<th>( A_g ) (s^{-1} MPa m^{-n})</th>
<th>( m )</th>
<th>( Q_{gs} ) (kJ mol^{-1})</th>
</tr>
</thead>
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<td>(Ca_{0.9}Sr_{0.1})TiO_3 this study</td>
<td>10^{0.6 \pm 1.4}</td>
<td>5.3 \pm 0.6</td>
<td>-521 \pm 30</td>
<td>10^{8.5 \pm 2.0}</td>
<td>-1.4 \pm 0.2</td>
<td>-627 \pm 65</td>
</tr>
<tr>
<td>Wright et al. [1992] [110] SC-CaTiO_3</td>
<td>10^{1.1 \pm 0.2}</td>
<td>3.0 \pm 0.5</td>
<td>-444 \pm 57</td>
<td>2.5 \pm 0.5</td>
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<td>10^{11.9 \pm 9}</td>
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<td>-620 \pm 30</td>
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<td>Wang et al. [1993] [100] SC-SrTiO_3</td>
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<td>-748 \pm 30</td>
<td>10^{11.9 \pm 9}</td>
<td>3.6 \pm 0.3</td>
<td>-620 \pm 30</td>
</tr>
<tr>
<td>Wang et al. [1993] [110] SC-SrTiO_3</td>
<td>10^{11.9 \pm 9}</td>
<td>3.6 \pm 0.3</td>
<td>-620 \pm 30</td>
<td>10^{10}</td>
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Table 2. Best Fit Values and Errors of the Parameters in the Nonlinear Least Squares Fit of the Data to Equation (1)^{a}

^a Root mean variance for fit was 0.19. Empirical parameters are from the literature for CaTiO_3 and SrTiO_3 single crystals and polycrystalline aggregates.
perovskite from the literature. The overall quality of the fit can be judged from the root mean variance of the measured strain rate from that predicted by the flow law. For the creep equation above the root mean variance was 0.19. This indicates that the creep equation (5) above is a good fit to the data. Some specific aspects of the fitting routine are discussed below. The fitting routine minimizes the sum of the residuals squared:

\[ \chi^2 = \sum (y - y_{\text{fit}})^2 \]  

The best estimate of the error for each empirical parameters in equation (5) is equivalent to the change in the parameter required to double \( \chi^2 \) [Bevington, 1969].

Figure 5 shows strain rate versus inverse temperature for all data at a single grain size (14 μm) in the power law creep regime; the data for all stresses were corrected to the mean stress values using the stress exponent calculated from the fit (n = 5.3). It can be seen that the activation energy predicted from these data alone is higher than that obtained from the best fit in equation (3). The minimum root mean variance is obtained when all 6 empirical parameters \( (A_{\text{dis}}, n, Q_{\text{dis}}, A_{\text{gss}}, m, Q_{\text{gss}}) \) were allowed to vary during the fit. It can be seen in Figure 5 that the two data points at temperatures in the cubic stability field deviate slightly from the trend of the rest of the data, suggesting that the magnitude of the activation energy is slightly higher in the cubic stability field.

Figure 6. (a) Plot of \( \log_{10} \) strain rate (s\(^{-1}\)) versus \( \log_{10} \) grain size (μm) for data in low-stress (n = 1) regime. The data are extrapolated to the mean stress (120 MPa) of the data set using a linear relationship between strain rate and stress. Linear fits of the data for each temperature are plotted, which give grain size exponents of between \(-1.53\) and \(-0.8\). Also the nonlinear least squares fit of the whole data set is shown with the dashed line for each temperature. (b) Plot of \( \log_{10} \) strain rate (s\(^{-1}\)) versus \( \log_{10} \) grain size (μm) for data in high-stress power law creep (n = 5.3) regime. The data are extrapolated to a stress of 226 MPa using a power law relationship between strain rate and stress with a stress exponent of n = 5.3. Linear fits of the data for each temperature are plotted which give grain size exponents between \(-1.05\) and \(-0.51\). Also the nonlinear least squares fit of the whole data set is shown with the dashed line for each temperature.
Figure 6a shows how the strain rate varies with grain size at constant temperature (1500 K) and constant stress (120 MPa) for the data showing a linear strain rate versus stress relationship at low stress. It can be seen that the grain size exponent calculated from a linear regression of the data in Figure 6a is within error the same as the value calculated in the global fit using equation (5). The exponent of $-1.4$ is higher than the values predicted for Coble and Nabbarro-Herring creep of $-3$ and $-2$, respectively. Figure 6b shows that there is little to no grain size dependence of the strain rate for the data showing a power law relationship between stress and strain rate at high stress. This slight grain size dependence is due to all our deformation experiments being carried out close to the transition between power law and linear creep.

4. Microstructural Results

The microstructures of the deformed samples were investigated with EBSD in the SEM. Up to 1500 K the samples underwent little or no grain growth during the deformation stage as they had been previously sintered at 1773 K for up to 100 h. This is in agreement with the work of Li et al. [1996], who observed little grain growth of CaTiO$_3$ below 1490 K after 10 h in air at 1 atmosphere, but significant grain growth between 1490 and 1530 K after 10 h. Our experiment at 1550 K showed a small amount of grain growth during the deformation stage.

The starting material for the deformation experiments shows a dense equilibrated microstructure (Figure 7). Densities greater than 97% of the theoretical density were achieved after sintering and to better than 99% after hot isostatic pressing. The grains have straight grain boundaries. For a sample sintered for 48 h at 1773 K the volumetric mean grain diameter is 14 ± 7 μm (Figure 7a) and for a sample sintered for 110 h the volumetric mean grain diameter is 102 ± 42 μm. Some clusters of small grains seem not to grow during the sintering process. From the distribution of misorientations between random pairs of data points it can be seen that the CPO of the starting material is effectively random; furthermore, the pole figures do not show any clustering (Figure 7). In the starting material there are some low-angle grain boundaries shown by the peak in the neighbor pair misorientation distribution at low angles.
Figure 8. EBSD map of sample P0300 deformed to a strain of 0.19 at 1550 K. The image is colored according to the inverse pole figure for the compression direction. Sinuous grain boundaries, subgrains, and recrystallized grains can be seen. Many grains are lozenge shaped, and grain boundaries can be seen to line up in conjugate microshears at \(\sim 50^\circ\) to the compression direction. Compression direction is vertical in this image.

Figure 9. EBSD image of a tangential section of torsion sample P0318 taken close to the outer surface of the sample. In this section the deformation approximates to simple shear [Paterson and Olgaard, 2000]. The sample has been deformed with a top to the right sense of shear with the shear plane horizontal to a shear strain of 4.9 at 1500 K. Each grain is given a random color not related to its orientation. The pole figures for the same data are shown in Figure 13.
These are most likely formed during grain growth when a grain boundary migrates and leaves behind a low-angle grain boundary [see Bestmann et al., 2005; Piazolo et al., 2006].

4.1. Deformation Microstructures

[19] Large grains (>20 μm) in all samples show lattice distortion picked out by internal gradients in crystallographic orientation (Figure 8) with the development of substructure and subgrains. Also grain boundaries can be seen to be sinuous in shape with some incipient dynamic recrystallization probably by grain boundary bulging. Recrystallized grains have little or no internal strain and straight grain boundaries (Figure 8). These grains can be easily identified using the mean misorientation calculated for each grain during processing of the EBSD map [Cho et al., 2005]. As the strain within a recrystallized grain is low its mean misorientation should be low, whereas the parent grains will be internally strained and hence have a high mean misorientation. Care must be taken when using this approach because, at constant grain size, the mean misorientation calculated will be inversely proportional to the step size used for EBSD mapping and systematically lower in smaller grains. With this in mind a semiquantitative approach can be used to identify the recrystallized grains whereby a mean misorientation is chosen that distinguishes satisfactorily the deformed grains from the recrystallized grains. By assuming that the area fraction of the recrystallized grains is equal to the volume fraction (a common assumption in stereology [e.g., Underwood, 1968]), the volumetric grain size distributions of both the recrystallized and the deformed grains can be calculated (Figure 3). The recrystallized grain size is thus ~7 μm.

[20] It can be seen from both the torsion and compression experiments that grain boundaries are mostly aligned in conjugate sets (Figures 8 and 9). This is thought to be due to sliding of grain boundaries over lengths scales greater than the grain size and is often termed cooperative grain boundary sliding (CGBS) [Kaibyshev, 2002; Zelin and Mukherjee, 1995]. Bons and Jessels [1999] observed such a phenomenon in situ in octachloropropane (OCP) with a petrological microscope and called them microshears. In the torsion experiments the microshears are orientated approximately parallel to the shear plane and at 45° to the shear plane.
plane in a direction opposing the shear (Figure 9). In compression experiments these microshears are aligned at \( \sim 50° \) to the compression direction (Figure 8). Also, where these microshears intersect a grain there is an increase in internal distortion of the grain and these zones are also sites of recrystallization (see Figures 8 and 9). Many of the grains are lozenge shaped. The microstructures described above indicate that grain boundary sliding is occurring in both fine and coarse-grained (\( \sim 100 \mu m \)) samples.

4.2. Fry Analysis

[21] The mean misorientation has been used to perform the Fry analysis on the deformed grains only (i.e., grains with mean misorientation >2°). The Fry analysis shows that the strain recorded by the shape of the grains (grain strain) is consistently lower than the bulk strain imposed on the sample (Figure 10).

[23] In the axially symmetric shortening experiments the grain strain is simply of lower magnitude than the bulk strain. As shown in equation (2) the shear strain in simple shear can be calculated from either the axial ratio of the finite strain ellipse (\( R \)) or from the angle between the long axis of the strain ellipse and the shear plane. In the torsion experiment the value of shear strain calculated from \( R \) is lower than the shear strain calculated from \( \phi \) and both are lower than the bulk strain of the sample (Figure 10). The fact that the shear strain calculated from \( R \) is different from that calculated from \( \phi \) implies that the grain strain is not a simple shear with the same shear plane as the bulk strain. Hence for torsion, it is not possible to get a unique solution for the strain accommodated by grain boundary sliding as it becomes necessary to make assumptions about the geometry of the deformation for both grain strain and grain boundary sliding. A relatively good match could be made if one distorts the grain strain ellipse to the shape of the bulk strain just by simple shear with the shear plane parallel to the bulk shear; this gives a grain boundary sliding shear strain of 4.3 when compared to the bulk imposed strain of 4.9. It can be seen from Figure 11 that the grain strain is consistently \( \sim 20\% \) of the total strain for all samples.

[23] This variance of grain strain from bulk strain could be due to one or both of the following mechanisms: (1) grain boundary migration will tend to make the grains less elliptical to minimize their surface energy and hence, as often observed in mylonitic rocks, the grain shapes do not reflect the bulk finite strain ellipse [e.g., Lister and Snoke, 1984]; and (2) some component of sample deformation is accommodated by the relative movement of grains along grain boundaries. At the temperatures used in this study grain boundary migration is relatively slow; it can therefore be assumed that it plays a minor role so that the difference between the bulk applied strain and the grain strain gives an upper estimate of the strain accommodated by grain boundary sliding.

4.3. Crystallographic preferred orientation

[24] As described in section 2.3, we were able to index only the cubic crystal structure of perovskite using EBSD.

![Figure 11](image1.png)

**Figure 11.** Equivalent grain strain calculated from the Fry analysis versus equivalent sample strain. It can be seen that the grain strain is consistently 20% of the total sample strain. The shear strain from the torsion experiment was divided by \( \sqrt{3} \) to give an equivalent Von Mises strain that could be compared with the compression data [e.g., Paterson and Olgaard, 2000].

![Figure 12](image2.png)

**Figure 12.** (a) Upper hemisphere equal-area projections of [100], [111], and [110] contours of multiples of a uniform distribution for sample P0331 deformed in compression at 1400 to 1500 K to a strain of 0.21. The compression axis is vertical. (b) Upper hemisphere projection of compression axis in crystal coordinates contours of multiples of a uniform distribution.
sliding (GBS) to diffusion accommodated GBS. Below we believe we are observing a change in deformation mechanism from dislocation creep [e.g., Hirth and Kohlstedt, 1995a, 1995b]. From the microstructures and CPOs we attribute to a change in deformation mechanism from diffusion creep to dislocation creep [e.g., Salama et al., 2005]. This kind of behavior in many minerals (e.g., olivine) is other perovskite structure minerals [e.g., Wright et al., 1996; Salama et al., 2005]. The misorientation angle data in Figures 14a and 14d in both compression and torsion show that the misorientation axes have a weak preferred orientation parallel to [001] for low misorientation angles which is partly inherited from the starting material, whereas there is a stronger preferred orientation of the misorientation axes in sample coordinates (Figures 14b and 14e). In compression the misorientation axes form a girdle perpendicular to the compression axis and in torsion they form a maximum perpendicular to the shear direction in the shear plane. In both cases these are the kinematic axes for the respective deformation geometry. The misorientation angle data in Figures 14c and 14f supports the evidence from the pole and inverse figures that CPO in these samples is weak as the random pair distribution is very close to the distribution expected for a set of randomly orientated crystals (theoretical random pair distribution).

5. Discussion

The mechanical results show a transition between power law creep and linear viscous grain-size-sensitive creep at a stress of about 100 MPa at 1500 K. This transition from linear viscous to power law creep has been observed in other perovskite structure minerals [Salama et al., 2005]. This kind of behavior in many minerals (e.g., olivine) is attributed to a change in deformation mechanism from diffusion creep to dislocation creep [e.g., Hirth and Kohlstedt, 1995a, 1995b]. From the microstructures and CPOs we believe we are observing a change in deformation mechanism from dislocation creep accommodated grain boundary sliding (GBS) to diffusion accommodated GBS. Below we will discuss (1) the details of the empirical flow law and how it fits with previous work, (2) the implied deformation mechanism, (3) the CPO and likely slip systems and (4) the implications for seismic anisotropy of the Earth’s lower mantle.

[25] It can be seen from Figure 3 that our data in the grain-size-sensitive field are in agreement with published flow laws for the grain-size-sensitive creep of fine-grained (~10 μm) CaTiO₃ [Karato and Li, 1992; Li et al., 1996; Webb et al., 1999]. Karato and Li [1992] proposed a deformation mechanism of diffusion accommodated grain boundary sliding. Their activation energy of 750 kJ mol⁻¹ is higher than our 627 kJ mol⁻¹ and their grain size exponent of −2 is just lower than our −1.4. These differences may occur because we are close to the power law creep field and both diffusion accommodated grain boundary sliding and dislocation creep accommodated grain boundary sliding are contributing to sample deformation. If we use the flow law parameters of Li et al. [1996] in our flow law and only vary the power law creep terms, we obtain a stress exponent of 4.3 ± 0.3 and an activation energy of 501 ± 23 kJ mol⁻¹. This regression function is overall less robust than allowing all 6 creep parameters in equation (3) to vary independently. It can be seen in Figure 4 that our best fit flow law overestimates the strain rate at 1350 K. This could be due to the effect of the tetragonal to orthorhombic phase transition on the observed behavior for the experiments at 1350 K. In Figure 5 the temperatures of the two phase transformations that occur in perovskite at atmospheric pressure are shown [Carpenter et al., 2001]. The transformation temperatures are likely to be higher at 300 MPa when compared to atmospheric pressure data due to pressure having the effect of stabilizing the low-temperature phase. Therefore, our low-temperature data may be closer to the orthorhombic to tetragonal phase transformation than indicated in Figure 5 and this proximity to the phase transformation may be affecting the creep behavior of the sample. Furthermore, there is a slight increase in the clog Ɛ/ (∂/∂T) data at temperatures >1500 K, which could be due to the transformation from the tetragonal to the cubic phase. However, as outlined above, the transition temperature may be higher due to the pressure of our experiments and hence our
experiments may be barely inside the cubic field. As the high-temperature phases are not quenchable we cannot be certain of the phase field of the samples during deformation.

[27] It also can be seen that our data in the power law creep field fits well with published flow laws for climb accommodated dislocation creep with slip on \{100\}pc for CaTiO$_3$ single crystals [Wright et al., 1992]. Wright et al. [1992] found that slip on \{100\}pc was 100 times weaker than slip on \{110\}pc. In SrTiO$_3$, slip on \{100\}c is \sim 10 times weaker than slip on \{110\}c [Wang et al., 1993]. It is interesting to note that our rheology for polycrystalline (Ca$_{0.9}$Sr$_{0.1}$)TiO$_3$ is similar to the rheology of the weak slip system in perovskite. This suggests that the hard slip systems are not being activated. As the slip system \langle010\rangle_c on \{100\}_c has only three independent strain components, it cannot accommodate a general strain state [Von Mises, 1928; Wang et al., 1993]. This suggests that another strain accumulation mechanism must be active in the power law creep field. We propose that it is grain boundary sliding accommodated by dislocation creep. As grain boundary sliding can relax the Von Mises criterion, only the weakest slip system may need to be active [e.g., Hirth and Kohlstedt, 1995a, 1995b; Mecklenburgh et al., 2006; Zhang et al., 2000].

[28] From our Fry analysis we concluded that grain boundary sliding must be accommodating a maximum of \sim 80% of the total imposed deformation. Furthermore, the lozenge shaped grains and the presence of conjugate

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**Figure 14.** (a) Upper hemisphere equal-area projections of misorientation axes plotted in crystal coordinates for sample P0331 deformed in compression to a strain of 0.21. (b) Upper hemisphere equal-area projections of misorientation axes plotted in sample coordinates for sample P0331. (c) Histograms of misorientation angles neighbor pair misorientations and random pair distributions are shown also the theoretical distribution for a set randomly orientated crystals with cubic (Pm$\overline{3}$m) symmetry for sample P0331. (d, e, and f) are the same as Figures 14a, 14b, and 14c but for sample P0318 deformed in torsion to a shear strain of 4.9.
microshears points to GBS and CGBS being responsible for a considerable proportion of sample deformation. GBS and CGBS are occurring both in the linear grain-size-sensitive field and in the power law creep field, shown by the microstructures of the torsion sample P0318 (Figure 8) deformed completely in the power law creep field. Hence we observe in our data a transition from diffusion accommodated GBS at low stresses and small grain sizes to dislocation creep accommodated GBS at large grain sizes and high stresses. The stress $\sigma_t$ at which the transition between diffusion accommodated and dislocation creep accommodated GBS occurs, can be calculated by setting the two flow laws in equation (3) equal to each other and rearranging to get a relationship between $\sigma_t$, grain size ($d$) and temperature ($T$):

$$\sigma_t = \left[\frac{A_{gov}}{A_{pl}} \cdot d^n \exp \left(\frac{Q_{gov} - Q_{pl}}{R} \right)\right]^{1/n}.$$  \hspace{1cm} (7)

From equation (7) and the empirical flow law equation (5) one can create a deformation mechanism map as shown in Figure 15. Li et al. [1996] show a similar diagram where they normalize the stress with the shear modulus and the temperature with melting temperature in order to extrapolate their data to MgSiO$_3$ perovskite deforming in the Earth’s lower mantle. As there is a large uncertainty in the shear modulus and melting temperature of MgSiO$_3$ perovskite it is difficult to use this approach to extrapolate our flow law in this way. However, it can be pointed out that at high temperatures and low stresses as would be expected in the Earth’s lower mantle MgSiO$_3$ perovskite could be deforming by a combination of diffusion accommodated and dislocation creep accommodated grain boundary sliding. We

**Figure 15.** Deformation mechanism map for perovskite showing the transition from diffusion accommodated grain boundary sliding (Diff. GBS) to dislocation creep accommodated grain boundary sliding (Dis. GBS) in log stress versus log grain size space at 1300, 1400, and 1500 K, which corresponds to homologous temperatures in the range 0.6 to 0.7. Dotted lines are strain rate contours at 1400 K with labels in $s^{-1}$. The graph is calculated using the empirical flow law given in equation (5).

**Figure 16.** Crystal structure of perovskite CaTiO$_3$. (a) Cubic ($Pm\bar{3}m$) structure viewed along the [001] showing the unit cell $(a_c = 3.8933\text{Å})$. (b) Tetragonal ($I4/mcm$) structure viewed along [001], with the tetragonal unit cell shown also the pseudocubic cell is shown $(a_t = b_t = 5.4938\text{Å}, c_t = 7.7815\text{Å})$. (c) Orthorhombic ($Pbnm$) structure viewed along [001], with the orthorhombic and pseudocubic unit cells shown $(a_o = 5.4671\text{Å}, b_o = 5.4823\text{Å}, c_o = 7.7461\text{Å})$ [Kennedy et al., 1999].
find that GBS is decoupling the local strain field from the bulk strain field in the torsion samples. This has implications for using CPO data to interpret the orientation of shear and also the measurement of strain in rocks where GBS is playing a role, even in the dislocation creep regime.

[25] From the CPO data we can try to deduce the active slip system during sample deformation. Figure 16 shows the relationship between the cubic, pseudocubic, orthorhombic and tetragonal phases. The fact that there is a preferred orientation of [100]pc parallel to the shear direction in the torsion experiments suggests that the Burgers vector of the most common dislocations is [100]pc. From our CPO data alone we cannot constrain the dislocation slip plane [Wenk et al., 2009]; therefore, we use TEM data from the literature and experiments on oriented single crystals to estimate what the most likely slip plane is in our samples. As our mechanical data in the power law creep field plot so close to the single-crystal data for crystals orientated for slip on [001]pc, the most likely slip plane is {001}pc. This is consistent with CPO data although all of our CPOs are very weak. Besson et al. [1996] showed with careful TEM that all the dislocations found in deformed CaTiO3 single crystals were of screw type. They found a number of dislocation microstructures: (1) [100]pc and [011]pc Burgers vectors disassociated on the (01T)pc plane and (2) [101]pc and [011]pc on (010)pc react to form twist walls producing an [002]pc Burgers vector that decomposes into two perfect [001]pc dislocations.

[30] As CPO data only sees the net effect of many dislocations and dislocation interactions and not the distortion of individual dislocations, in this study it is not possible to differentiate between these slip systems from CPO data alone. However, in agreement with our results, the data of Besson et al. [1996] suggest that [001]pc Burgers vectors would be most common. Therefore, the most likely slip system consistent with our data and the literature is (100)pc on [001]pc.

[31] Recently, Ferré et al. [2007, 2008, 2009a, 2009b] used ab initio simulations of dislocations in MgSiO3, SrTiO3, CaSiO3 and CaTiO3, respectively, to investigate the transition to glide of slip systems in perovskite structured minerals. Ferré et al. [2009a] found [Ti0]pc on (001)pc to be the weakest slip system in CaTiO3 (it should be noted that these are given in the orthorhombic Pbnm cell and hence have an o subscript) which is consistent with our predicted weakest slip of (100)pc on (010)pc for the pseudocubic structure. In MgSiO3 perovskite they found that all the slip systems investigated had Peierls stresses in the range 7–68 GPa. Ferré et al. [2007] find the weakest two slip systems to be [100]pc on (010)pc and [010]pc on (100)pc which correspond to [T10]pc on (110)pc and [110]pc on (10T)pc, respectively, in the pseudocubic lattice. Furthermore, they found [001]pc on (100)pc and [010]pc on (010)pc to be the hardest slip systems equivalent to [001]pc on (110)pc and [010]pc on (110)pc in the pseudocubic lattice, respectively. The family of slip systems we propose (100)pc on {010}pc for our samples is equivalent to the following slip systems in the orthorhombic structure [001]pc on (T10)pc, [T10]pc on (010)pc, and [110]pc on (T10)pc. Ferré et al. [2007] find that these slip systems are dissociated, which fits with the observations of Besson et al. [1996], who found dissociation of (110)pc and (001)pc on {110}pc planes. All these ab initio simulations are performed for 0 K where dislocations cannot climb out of their glide plane. However, at high temperatures, dislocations gain the ability to climb to overcome obstacles by diffusive mass transport. From creep data on CaTiO3 perovskite single crystals, Wright et al. [1992] found the rheology fitted a dislocation climb–accommodated creep. Also the stress exponent and activation energy from our experiments indicates that dislocation climb was controlling dislocation motion. For most materials climb-controlled dislocation creep is favored by high temperatures and low stresses whereas at high stresses and low temperatures, creep is controlled by the glide of dislocations [e.g., Poirier, 1985]. Therefore, the high-temperature creep of perovskite type minerals is most likely not controlled by the resistance to glide but by the rate of climb.

[32] There is a paucity of direct measurements of diffusivities of different species in the (Ca,Sr)TiO3 system. Paladino et al. [1965] measured oxygen diffusion in SrTiO3 and determined activation energies of 116 to 123 kJ mol−1, Gautason and Muehlenbachs [1993] estimated an activation energy of 313 kJ mol−1 for oxygen diffusion in CaTiO3. Li et al. [1996] estimated the calcium diffusion rates in CaTiO3 from the Ca–Sr interdiffusion from polycrystalline CaTiO3/SrTiO3 diffusion experiments [Butler et al., 1991] and found an activation energy of 250 kJ mol−1. Wright and Price [1993] used molecular simulations to predict diffusivities of the different ions in perovskites and found activation energies for intrinsic oxygen diffusion to be dependent on crystal direction and ranged from 247 to 479 kJ mol−1. For intrinsic calcium diffusion these authors found an activation energy of 550 kJ mol−1 and for intrinsic diffusion of titanium an activation energy of 895 kJ mol−1. Wright and Price [1993] explain the differences in the activation energy, measured in single-crystal creep experiments by Wright et al. [1992], in different directions by diffusion of oxygen to and from the climb plane as the rate controlling process. Li et al. [1996] postulate that the high activation energies for diffusion–accommodated GBS may be due to diffusion of titanium being rate controlling. Webb et al. [1999], from microtorsion and forced oscillation experiments on CaTiO3, concluded that grain boundary impurities enhanced grain boundary diffusion and hence controlled the diffusivity of the slowest diffusing species. From the activation energies alone it is difficult to assess what diffusing species is controlling deformation rate in both the power law and grain-size-sensitive creep fields in this study. In most perovskite structured minerals oxygen diffusion is faster than cation diffusion [e.g., Dobson et al., 2008; Gautason and Muehlenbachs, 1993]. The high activation energy from simulations [e.g., Wright and Price, 1993] and the lack of a direct migration path between two neighboring sites, suggests that the octahedrally coordinated cation (Ti in our case) is the least mobile species and hence rate controlling in creep of perovskite type minerals [Salama et al., 2005]. The rate of titanium diffusion may be aided by the reduction of Ti4+ to Ti3+, which would be charge balanced by oxygen vacancies [Webb et al., 1999].
during deformation of (Ca,Sr)TiO$_3$ no strong CPOs are developed even in the power law creep field, as the majority of sample deformation is being accommodated by GBS. Therefore, the lack of seismic anisotropy in the Earth’s lower mantle cannot be simply attributed to diffusion accommodated GBS but may be due to the fact that perovskite type minerals deform by GBS and CGBS in both diffusion and power law creep fields. Mainprice et al. [2008] show using a viscoplastic self-consistent model that only weak CPOs would develop in MgSiO$_3$ perovskite deforming by dislocation glide where the relative strength of the different slip systems was defined by the results of ab initio simulations of dislocation glide in MgSiO$_3$ perovskite [Ferré et al., 2007]. However, at elevated temperatures within the lower mantle it would be expected that climb-controlled dislocation creep be more important than glide, which would have a profound affect on the relative strength of the different slip systems. Furthermore, the relative strength of slip systems is often dependent on temperature [Gumbsch et al., 2001], and therefore, the ab initio simulations of Ferré et al. [2007] at 0 K should be applied to the Earth’s lower mantle with caution.

6. Conclusions

The microstructures in our samples show clear evidence of grain boundary and cooperative grain boundary sliding with lozenge shaped grains and the alignment of grain boundaries. From the Fry analysis we estimate that grain boundary sliding accommodated ~80% of the sample strain and that the local grain strain is partially decoupled from the bulk sample strain. The stronger alignment of misorientation axes in sample coordinates parallel to the kinematic axis compared to the weaker alignment of misorientation axes in crystal coordinates is also indicative of grain boundary sliding. Perovskite deforms by diffusion accommodated grain boundary sliding at low stresses and small grains sizes, and by grain boundary sliding accommodated by dislocation creep at higher stresses and larger grain sizes. From our data the tetragonal to cubic phase transformation has little affect on the rheology of (Ca$_{0.9}$, Sr$_{0.1}$)TiO$_3$. The CPO data indicates that the most likely slip systems in our samples are [100]$_{pc}$ on [001]$_{pc}$ which is consistent with previous TEM observations. The fact that our data in the power law creep field show similar strength to single crystals deformed with slip on the weakest slip planes [100]$_{pc}$ suggests that the grain boundary sliding is relaxing the Von Mises criterion allowing sample strain to be accommodated by grain boundary sliding and slip on the weakest slip system. If (Mg,Fe)$_3$SiO$_3$ perovskite deforms by a similar mechanism in the lower mantle only a very weak CPO would be developed, which would not lead to any significant seismic anisotropy, as is observed in the Earth’s lower mantle.

References


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