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High-temperature structural phase transitions in perovskite (CaTiO₃)

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Abstract. High-temperature powder x-ray diffraction data are presented for CaTiO₃ perovskite between 293 and 1523 K. The temperature-dependence of superlattice intensities and cell parameters suggests a sequence of phase transitions from the room temperature orthorhombic (*Pbnm*) structure to a tetragonal (*I4/mcm*) polymorph at temperatures in the range 1373–1423 K, followed by transformation to the cubic (*Pm $\bar{3}m$*) aristotype at 1523 ± 10 K. The intensity of the diffuse background increases on transformation to the cubic structure and is associated with disorder (and anionic mobility) of the oxygen sub-lattice. The *I4/mcm*–*Pbnm* transition induces a large spontaneous strain, but the tetragonal spontaneous strain in the *I4/mcm* phase due to the *Pm $\bar{3}m$* –*I4/mcm* transition is small, below the resolution of this experiment. These results add weight to suggestions from recent computer simulations that orthorhombic MgSiO₃ may transform to a tetragonal (rather than a cubic) polymorph under the conditions of the Earth's mantle, in which case the effects on electrical conductivity would not be expected to be as great as for a transition to a cubic polymorph, although the consequences for elastic properties may be more significant.

1. Introduction

The high-temperature behaviour of perovskites is frequently employed as a textbook illustration of structural phase transitions. Generations of physicists have been introduced to phase transitions in crystalline solids by considering the structural instabilities of the MTiO₃ perovskites (where M is Ca, Sr or Ba) [1]. Phase transitions in perovskites have importance far beyond didactic exercises, however. Not only is this structural family technologically important in a range of materials applications in ferroelectric and optoelectric devices, it is also of geophysical importance because the Earth's lower mantle is thought to be composed largely of MgSiO₃ perovskite, which would make it by far the most abundant terrestrial silicate. Understanding the behaviour of perovskite as a function of pressure (*P*) and temperature (*T*) may, therefore, be of crucial importance in appreciating the geophysical properties of the lower mantle. Orthorhombic (*Pbnm*) MgSiO₃ is, however, highly metastable at room *P* and *T*, and the *in situ* experimental study of its potential high-*P/T* phase transitions to tetragonal or cubic polytypes of higher symmetry is technically difficult. Such data as do exist indicate that it becomes more distorted on increasing *P* and less so on increasing *T* [2–5], apparently transforming to a polymorph of higher symmetry at high *T* and 65 GPa [6]. Additionally, the ferro-elastic twinned microstructure of synthetic MgSiO₃ crystals is suggestive of a transformation from a paraphrase of higher symmetry. Computer simulations also indicate that one or more phase transitions, ultimately to cubic

symmetry, may occur at high P and T [7]; although no consensus has yet been reached on whether or not they are to be expected under the conditions of the Earth's lower mantle [8, 9].

In view of the experimental difficulties associated with the *in situ* study of MgSiO_3 , an alternative approach to understanding its behaviour has been to investigate the high- T behaviour of analogous phases which are more tractable experimentally [10, 11]. Of these, the type-mineral perovskite (CaTiO_3) is isostructural with MgSiO_3 , showing a similar distortion away from the cubic aristotype. It also shows the same twinned microstructures as those found in MgSiO_3 , thought to be associated with transitions from its $Pbnm$ room- T structure via a tetragonal intermediate to the high- T $Pm\bar{3}m$ phase [12, 13]. High- T calorimetric [14, 15], diffraction [16] and spectroscopic [17] studies of CaTiO_3 have not, however, arrived at an agreed position on whether or not such a sequence of phase transitions is observed on increasing T .

Previous x-ray diffraction experiments have shown that the orthorhombic distortion of CaTiO_3 decreases with increasing T , but have not taken perovskite to high enough T to observe a transition to cubic or tetragonal symmetry directly [18]. A recent high- T neutron diffraction study showed that CaTiO_3 is metrically and symmetrically cubic at 1600 K, and found no evidence for a tetragonal intermediate, but obtained only a limited number of structural analyses at lower T [19]. Here, the spontaneous strain of the low-symmetry orthorhombic phase and the superlattice reflections of the same phase are monitored as a function of T between room T and 1523 K at 50 K steps, and new evidence for the existence of a tetragonal phase intermediate between the orthorhombic and cubic structures is presented.

2. Experimental details

A synthetic sample of CaTiO_3 was prepared from analytical grade starting material which was sintered and annealed in air at 1723 K for 12 h, re-homogenized by thorough grinding, and then further annealed as a pressed pellet for a second period of 12 h at the same T . High-resolution synchrotron x-ray powder diffraction at lower-temperature showed the final material to be homogeneous single-phase orthorhombic perovskite. High- T x-ray powder diffraction patterns were obtained using the high- T diffractometer described by Salje *et al* [20], employing a curved 120° position-sensitive detector. Data were collected between 4° and 116° 2θ using strictly monochromatic $\text{Cu K}\alpha_1$ radiation at room T and then in T steps of 50 K from 323 to 1523 K. Powdered $\alpha\text{-Al}_2\text{O}_3$ was mixed with the sample to act as an internal standard, following the approach of Aldebert and Traverse [21].

3. Results

A restricted 2θ portion of the normalized data is shown in figure 1, in which the 022 and 202 reflections of the $Pbnm$ phase (at around $2\theta = 40.5^\circ$) can be seen to converge with T , indicating a transition to a higher symmetry polymorph. A reduction in the splitting of the 120_{Pbnm} and 210_{Pbnm} reflections, just below $2\theta = 37^\circ$, is similarly apparent. The splitting of the $\{121, 103, 211\}_{Pbnm}$ triplet at around $2\theta = 38.8^\circ$ is less well resolved but can still be detected. Upon heating, the intensities of this triplet and of the $\{120, 210\}_{Pbnm}$ doublet both decrease, although that of the $\{121, 103, 211\}_{Pbnm}$ triplet decreases almost continuously throughout the heating range, whereas the $\{120, 210\}_{Pbnm}$ doublet vanishes rapidly at around 1400 K upon converging to a single peak (as determined from the full

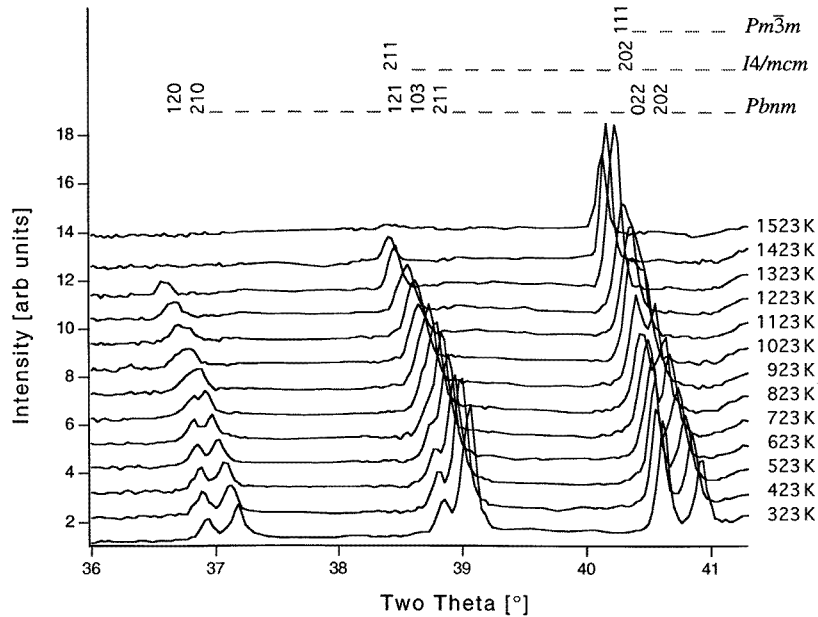


Figure 1. A portion of some of the high-temperature diffraction patterns of CaTiO_3 , showing the temperature-dependence of the splitting of the orthorhombic 022 and 202 reflections as well as the intensity variation of the groups of peaks near $2\theta = 37^\circ$ and 39° . At 1423 K the reflection near $2\theta = 37^\circ$ has vanished while that below $2\theta = 39^\circ$ remains present, which is indicative of $I4/mcm$ symmetry (as indicated by the indices positioned appropriately above the patterns). Successive diffraction patterns have been shifted parallel to the abscissa and peaks from the Al_2O_3 standard have been subtracted for clarity.

width at half maximum). The intensity of the $\{121, 103, 211\}_{Pbnm}$ triplet persists to higher T than does that of the $\{120, 210\}_{Pbnm}$ doublet, as seen from the diffraction pattern at 1423 K, from which the $\{120, 210\}_{Pbnm}$ peak has vanished but the peaks at around $2\theta = 38.8^\circ$ still have measurable intensity, vanishing at the highest T of the experiment, some 1523 K. The differing behaviour of these three sets of reflections indicates the operation of more than one structural order parameter related to the phase transitions in the temperature region of the experiments and can be explained in terms of a transition from $Pm\bar{3}m$ through $I4/mcm$ to $Pbnm$ on cooling from more than 1523 K. Thus, on heating, the $\{121, 103, 211\}_{Pbnm}$ triplet converges to a single $211_{I4/mcm}$ reflection at around 1400 K. In the same temperature range the $\{120, 210\}_{Pbnm}$ doublet vanishes (with no corresponding superlattice reflection existing in $I4/mcm$). At 1523 K, the $211_{I4/mcm}$ reflection has also vanished and the diffraction pattern corresponds to that of a $Pm\bar{3}m$ structure.

4. Phase transitions in CaTiO_3 perovskite

Zhao *et al* [22] pointed out that the intensity of the $\{121, 103, 211\}_{Pbnm}$ reflections is related to the amplitude of the anti-phase tilting of the TiO_6 octahedra about the $[100]_{Pm\bar{3}m}$ and $[010]_{Pm\bar{3}m}$ axes of the cubic structure ($\phi_x^- = \phi_y^-$, where ϕ_x^- is the anti-phase octahedral tilting about $[100]_{Pm\bar{3}m}$ associated with the R_{25} point of the cubic Brillouin zone), which can be described as a single tilt, θ , about the $[110]_{Pm\bar{3}m}$ axis of the octahedron. On

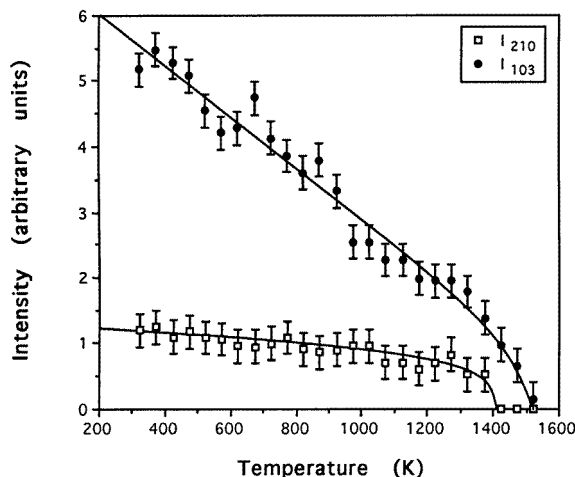


Figure 2. T -dependences of the intensities of the orthorhombic 210 and 103 reflections. The latter is zero for the $I4/mcm$ structure, whereas the former persists in the tetragonal phase but falls to zero at the transition to cubic. The quasi-linear behaviour of I_{210} indicates that the transition from tetragonal to cubic is of near second order, whereas that of I_{103} suggests a more abrupt transformation from orthorhombic to tetragonal.

the other hand, the intensity of the $\{120, 210\}_{Pbnm}$ peaks reflects the amplitude of the in-phase tilting, $\phi = \phi_z^+$ (ϕ_z^+ represents the in-phase tilting of successive layers about $[001]_{Pm\bar{3}m}$, corresponding to the M_3 point of the cubic Brillouin zone). Figure 2 shows the T -dependence of the peak intensities of the 210_{Pbnm} and 103_{Pbnm} (which becomes $211_{I4/mcm}$) reflections measured from the normalized diffraction patterns, demonstrating the difference in behaviour of these two groups of reflections. The rapid disappearance of the 210_{Pbnm} reflection between 1373 and 1423 K, with the persistence of 103_{Pbnm} (as $211_{I4/mcm}$) up to around 1523 K indicates the sequence of phase transitions:

$$T_c = 1373\text{--}1423 \text{ K} \quad T_c = 1523 \pm 10 \text{ K}$$

$$Pbnm \xleftrightarrow{M_3 \text{ point}} I4/mcm \xleftrightarrow{R_{25} \text{ point}} Pm\bar{3}m.$$

Cell parameters were refined from the measured peak positions of Bragg reflections assuming the space groups listed above using a nonlinear least-squares routine [23]. Peak splitting for the $Pbnm$ structure could be resolved at all T up to the transition to $I4/mcm$, but at higher T the splitting of tetragonal peaks in the $I4/mcm$ structure could not be resolved. The lattice parameters for samples at 1423 K and above were, therefore, refined as cubic, since the tetragonal phase appears metrically cubic within the resolution of the diffractometer. Cell parameters, written in terms of the cubic parent structure ($Z = 1$), are given in table 1 and shown as a function of T in figure 3. The orthorhombic cell edge lengths increase anisotropically in a quasi-linear manner with T up to 1173 K (with mean linear expansivities $\alpha_a = 1.58 \times 10^{-5}$, $\alpha_b = 6.37 \times 10^{-6}$, $\alpha_c = 1.22 \times 10^{-5}$ and $\alpha_{vol} = 3.416 \times 10^{-5}$, $298 \leq T \leq 1173$ K) and then begin to converge more rapidly as the phase transition to tetragonal is approached. This results in a λ -shaped anomaly in the volume thermal expansion at the $Pbnm$ – $I4/mcm$ transition (figure 4). The anisotropy of thermal expansion in CaTiO_3 has previously been associated with structural microstresses in Synroc-related materials (ceramic matrices designed to immobilize radionuclides in high-

level nuclear waste) [24]. It is clear that the phase transition to higher symmetry introduces volume strains over and above this effect, which will further compromise the mechanical properties of such perovskite-containing ceramics. The position of the phase transition and the nature of the critical behaviour of α_{vol} are nearly identical to those observed by Guyot *et al* [14] from heat capacity measurements (placing T_c at 1384 K). This implies that the transition they observed is the $Pbnm-I4/mcm$ transition seen here and that their C_p anomaly at higher T (1520 K) is associated with the transition from $I4/mcm$ to $Pm\bar{3}m$ shown for here the first time by x-ray diffraction measurements.

Table 1. Cell parameters of CaTiO_3 perovskite as a function of temperature. Numbers in parentheses are 1σ . Orthorhombic cell parameters have been expressed in terms of the cubic prototype and tetragonal cell parameters above 1373 K were refined as cubic since the tetragonal strain was below the resolution of the diffractometer.

| T (K) | $a/\sqrt{2}$ (Å) | $b/\sqrt{2}$ (Å) | $c/2$ (Å) | a_{cubic} (Å) | Primitive cell V (Å ³) |
|---------|------------------|------------------|------------|-----------------|--------------------------------------|
| 293 | 3.8083(13) | 3.8507(12) | 3.8230(16) | | 56.062(25) |
| 323 | 3.8107(13) | 3.8515(11) | 3.8245(15) | | 56.131(24) |
| 373 | 3.8136(11) | 3.8525(10) | 3.8266(14) | | 56.219(22) |
| 423 | 3.8167(11) | 3.8534(10) | 3.8289(14) | | 56.313(21) |
| 473 | 3.8189(11) | 3.8544(10) | 3.8311(14) | | 56.393(21) |
| 523 | 3.8218(11) | 3.8554(09) | 3.8334(14) | | 56.484(20) |
| 573 | 3.8243(10) | 3.8563(08) | 3.8362(12) | | 56.576(19) |
| 623 | 3.8376(10) | 3.8577(08) | 3.8380(12) | | 56.671(19) |
| 673 | 3.8308(10) | 3.8589(08) | 3.8406(12) | | 56.775(19) |
| 723 | 3.8330(11) | 3.8599(09) | 3.8426(13) | | 56.851(20) |
| 773 | 3.8361(11) | 3.8612(09) | 3.8448(14) | | 56.949(21) |
| 823 | 3.8385(11) | 3.8625(09) | 3.8469(14) | | 57.036(21) |
| 873 | 3.8411(11) | 3.8636(10) | 3.8492(14) | | 57.125(22) |
| 923 | 3.8440(11) | 3.8648(10) | 3.8516(14) | | 57.222(22) |
| 973 | 3.8469(11) | 3.8662(10) | 3.8540(14) | | 57.319(21) |
| 1023 | 3.8501(11) | 3.8675(09) | 3.8565(13) | | 57.424(20) |
| 1073 | 3.8541(11) | 3.8691(10) | 3.8596(14) | | 57.554(21) |
| 1123 | 3.8571(10) | 3.8708(08) | 3.8614(12) | | 57.650(19) |
| 1173 | 3.8604(11) | 3.8721(09) | 3.8641(13) | | 57.761(20) |
| 1223 | 3.8653(11) | 3.8735(09) | 3.8665(14) | | 57.863(21) |
| 1273 | 3.8677(12) | 3.8759(11) | 3.8696(15) | | 58.010(23) |
| 1323 | 3.8755(15) | 3.8804(13) | 3.8723(18) | | 58.233(29) |
| 1373 | 3.8807(15) | 3.8836(13) | 3.8747(19) | | 58.397(30) |
| 1423 | | | | 3.8837(5) | 58.578(24) |
| 1473 | | | | 3.8859(5) | 58.675(25) |
| 1523 | | | | 3.8881(5) | 58.777(23) |

The transitions from $I4/mcm$ to $Pm\bar{3}m$ and for $Pbnm$ to $I4/mcm$ are associated with two separate critical points on the Brillouin zone, although both are zone-boundary phase transitions. The tetragonal and orthorhombic spontaneous strains, which are measures of the distortion of the unit cell away from the $Pm\bar{3}m$ prototype structure, behave as the squares of the order parameters for the transitions. In each case the magnitude of the spontaneous strain can simply be derived as a scalar quantity in terms of the root mean square of the elements of the spontaneous strain tensor: $\varepsilon_S = \sqrt{\varepsilon_{ij}^2}$ [25]. There are three spontaneous strains of interest, arising from potential cubic–orthorhombic, cubic–tetragonal and tetragonal–orthorhombic transitions. We see (figure 5) that the strain arising from the $Pbnm-I4/mcm$ transition goes to zero at the same point as that of which the 210_{Pbnm}

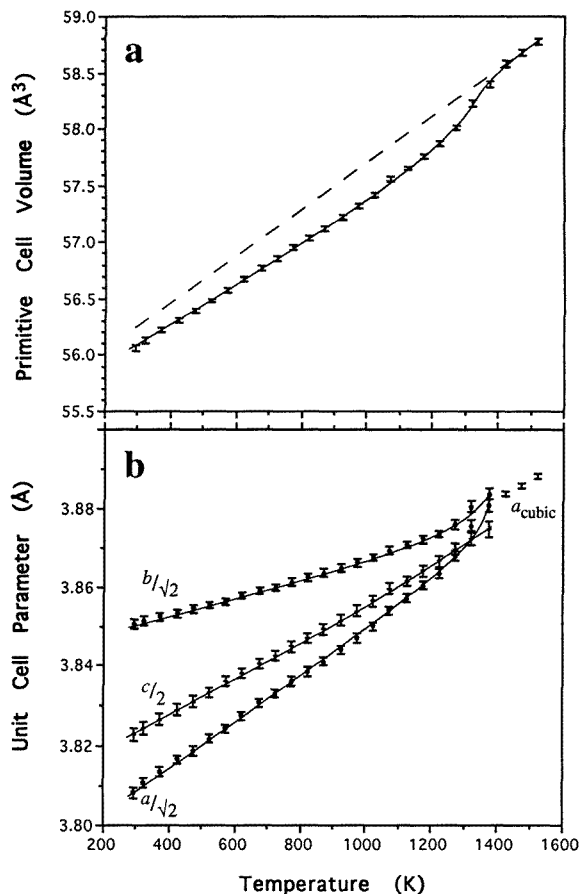


Figure 3. T -dependences of (a) the cell volume and (b) the cell edges of CaTiO_3 , shown in terms of the primitive cell containing one formula unit. In (a) the broken line is the extrapolation to low temperatures of the behaviour of the cubic paraphase. In (b) the tetragonal diffraction patterns above 1373 K have been refined as cubic, since the strain is below the resolution of the experiment.

superlattice reflection disappears and that the behaviour of this strain is analogous to that of the superlattice intensity, indicative of a transition which is near second order (but possibly with a small first-order discontinuity). On the other hand, the orthorhombic- and tetragonal-type distortions of the cell, with respect to a cubic prototype, both extrapolate to zero at around 1520 K, the same T as that determined from the behaviour of the 103_{Pbnm} (and $211_{I4/mcm}$) superlattice intensity. The linear dependence of the cubic \rightarrow orthorhombic and cubic \rightarrow tetragonal strains on T implies second-order behaviour of the ferro-elastic order parameter for the transition to cubic, η , with critical exponent $\beta = \frac{1}{2}$, where $\eta = (T - T_c)^\beta$ and $T_c \approx 1520$ K.

One further feature of the high- T behaviour of CaTiO_3 becomes apparent upon closer inspection of the diffraction patterns. Above the $Pbnm$ - $I4/mcm$ transition the intensity of the background begins to rise (figure 6). This transition and the further symmetry change $I4/mcm$ - $Pm\bar{3}m$ correspond to rotations of the TiO_6 octahedra. Dynamic disorder

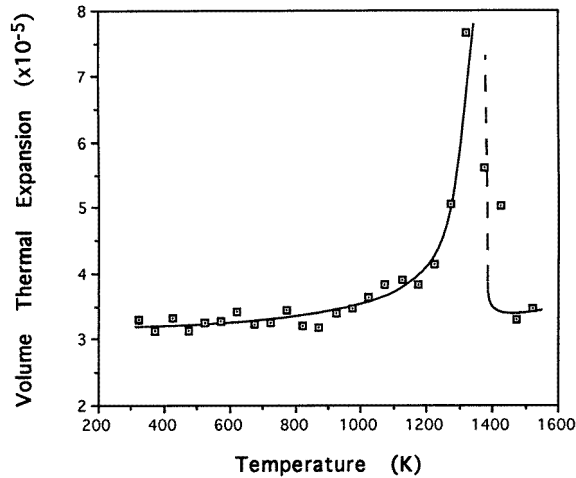


Figure 4. The T -dependence of the volume thermal expansion of CaTiO_3 , which shows a λ -anomaly at the tetragonal–orthorhombic transition between 1373 and 1423 K.

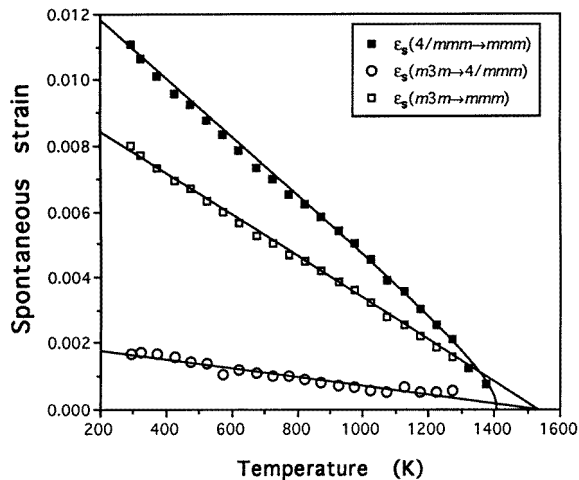


Figure 5. The T evolution of the tetragonal distortion from cubic symmetry (open circles: proportional to $(c - a)/a_0$) as well as of the orthorhombic distortions from tetragonal (full squares: proportional to $(b - a)/a_0$) and from cubic (open squares: proportional to $[2(a^2 + b^2 + c^2 - ab - bc - ca)/(3a_0^2)]^{1/2}$). In each case the cell parameters are those for the $Z = 1$ pseudo-cubic cell and a_0 is approximated as their mean. The orthorhombic distortion from tetragonal falls to zero upon transformation to $I4/mcm$ and both the orthorhombic and the tetragonal distortions from cubic extrapolate to zero, indicating the transition to a cubic phase at 1523 ± 10 K, as suggested also by I_{210} .

of these octahedra in the high-symmetry $Pm\bar{3}m$ structure would account for the increased diffuse background on transformation to the highest-symmetry polytypes. Similar diffuse intensity was observed in the neutron experiments of Vogt and Schmahl [19], suggesting the likelihood of enhanced anionic mobility in the cubic structure, as has been observed

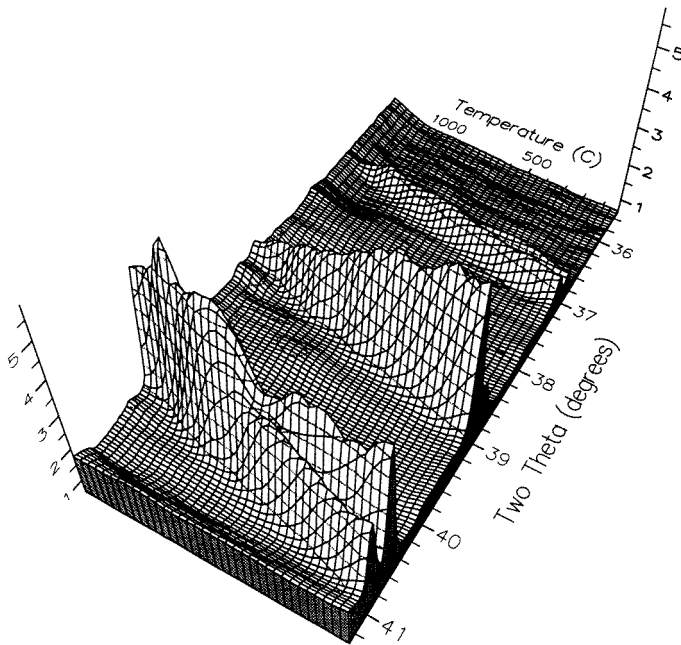


Figure 6. A three-dimensional plot of a portion of the diffraction data, illustrating the rise in the background intensity at the same temperature as the disappearance of first the 103 reflection near $2\theta = 37^\circ$ (on transformation to tetragonal) and secondly the 210 reflection near $2\theta = 39^\circ$ (on transformation to cubic). This increased background is associated with the increased mobility of the oxygen sub-lattice in the high-symmetry phases, in particular the cubic phase.

in high- T measurements of oxygen self-diffusion in CaTiO_3 [26] and indeed predicted for high-symmetry phases of MgSiO_3 from molecular dynamics simulations [27].

How do the results from this study compare with those of previous investigations on CaTiO_3 ? They are in good agreement with the drop calorimetric study by Guyot *et al*: the $Pbnm$ - $I4/mcm$ transition at 1373–1423 K corresponds to their 1384 K specific heat anomaly and the $I4/mcm$ - $Pm\bar{3}m$ transition at 1523 ± 10 K corresponds to their second anomaly at 1520 K, which was put at 1530 K by Naylor and Cook [14, 15]. The heat capacity remains anomalously high in the cubic phase, most probably as a result of the pronounced disorder of the oxygen sub-lattice also indicated here. The observed sequence of phase transitions would also account for the twin microstructures of quenched natural CaTiO_3 observed in the electron-microscopical study of Wang and Liebermann, which indicated the existence of an intermediate tetragonal phase between the room- T orthorhombic structure and the cubic prototype. The measured thermal expansivities between 273 and 1173 K are close to those of the previous lower T studies [16, 18, 24]. Vogt and Schmahl [19] found no evidence for an intermediate tetragonal phase, inferring a direct transition from orthorhombic to cubic between 1550 and 1600 K (although their DTA data place the transition at 1511 K). The discrepancies between these studies may arise from small differences in chemical composition between the samples studied, or even from differences in the preparation of the synthetic samples. This would imply that the tetragonal $I4/mcm$ phase has only marginal stability compared with the $Pbnm$ and $Pm\bar{3}m$ structures which flank it in T -space. None the less, the picture emerges that natural CaTiO_3 undergoes a sequence of phase transitions

$Pbnm-14/mcm-Pm\bar{3}m$ incorporating the tetragonal intermediate and that the high- T cubic structure shows the propensity for anionic disorder of the oxygen sub-lattice resulting in enhanced anionic conductivity.

The relationship of the observed behaviour of CaTiO_3 to the likely behaviour of MgSiO_3 in the mantle remains hard to judge. The latest *ab initio* computer simulations [7] consider phonon dispersion at high P and T , suggesting that MgSiO_3 transforms to cubic via an intermediate tetragonal phase at very high T with the tetragonal phase possibly being accessible under lower mantle conditions (although it appears that the cubic phase would not be). The $14/mcm$ tetragonal polymorph was indeed identified as the most likely stable tetragonal phase (amongst other potential candidates), with energies intermediate between those of the orthorhombic and cubic structures. The results for CaTiO_3 indicate that the tetragonal strain away from cubic is small, but its transformation to cubic and the accompanying anion disorder induce the greatest heat effect. Note also, however, that the largest effect on spontaneous strain is the $Pbnm-14/mcm$ transition; hence it is expected that this would have a significant effect on the elastic properties of a perovskite undergoing such a transformation. Furthermore, the influence both of major and of minor element chemistry on the transformation behaviour of perovskites is likely to be significant, and these results suggest that an orthorhombic–tetragonal phase transition in MgSiO_3 may be strongly dependent not only on T and P , but also on thermal history and chemistry. Such a tetragonal intermediate would not be expected to show as high an anionic conductivity as has been postulated for the cubic prototype, however.

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