

Phase transitions in perovskite at elevated temperatures - a powder neutron diffraction study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 1479

(<http://iopscience.iop.org/0953-8984/11/6/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.214

The article was downloaded on 15/05/2010 at 06:58

Please note that [terms and conditions apply](#).

Phase transitions in perovskite at elevated temperatures—a powder neutron diffraction study

Brendan J Kennedy[†], Christopher J Howard^{†§} and Bryan C Chakoumakos[‡]

[†] School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

[‡] Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Received 6 October 1998

Abstract. The structure of CaTiO_3 has been studied at high temperatures by powder neutron diffraction methods. From inspection of the diffraction data two phase transitions are evident, with an intermediate tetragonal ($I4/mcm$) structure forming near 1500 K and a primitive cubic ($Pm\bar{3}m$) structure above 1580 K. Detailed Rietveld analyses of the data suggest there may also be a phase transition from the room temperature $Pbnm$ structure to an orthorhombic $Cmcm$ structure around 1380 K. A remarkable feature of the results is the regular variation in the out-of-phase octahedral tilt angle over the entire temperature range.

1. Introduction

An extraordinary number of oxides and fluorides of the general form ABX_3 are described as having a perovskite structure [1]. Only a handful of these have the ideal cubic symmetry under ambient conditions, most including the mineral perovskite CaTiO_3 itself, being distorted variants. The distortion usually arises from a mismatch in the size of the A and B type cations and its common manifestation involves rotations of the BX_6 octahedra [2, 3]. The tilting of the octahedra can result in significant oxygen or fluoride atom displacements, although the cation displacements as well as the distortion of the unit cell itself can be quite small. The determination of the precise symmetry of the distorted perovskite, therefore, generally relies on the analysis of weak superlattice reflections. For those perovskites containing heavy A or B type cations, and in which the distortion consists mostly of anion displacements, neutron diffraction methods are expected to offer advantages over the corresponding x-ray diffraction analysis.

Over the past decade there has been considerable interest in the structural transformations of CaTiO_3 [4–11] and other perovskite type oxides [4, 12–16], inasmuch as these serve as models for MgSiO_3 , which is thought to be the major mineral of the Earth's lower mantle [17]. CaTiO_3 is also an important component of Synroc, a synthetic rock form designed to immobilize radioactive waste [18].

Several perovskite type oxides exhibit orthorhombic, $Pbnm$, symmetry under ambient conditions [1]. The degree of the orthorhombic distortion typically decreases with increasing temperature and in a number of cases, such as SrZrO_3 , SrRuO_3 and CaGeO_3 , phase transitions to other perovskite type structures have been observed as the samples have been heated to high temperatures [12–16]. The precise behaviours of these oxides are however different.

§ On leave from Australian Nuclear Science and Technology Organisation, PMB 1 Menai, NSW 2234, Australia.

At room temperature SrRuO_3 is $Pbnm$ and has two tilts ($a^+b^-b^-$ in Glazer's notation [2]) and this transforms via a first order transformation to the one tilt ($a^0a^0c^-$) $I4/mcm$ structure and then via a possibly second order transformation to the zero tilt ($a^0a^0a^0$) cubic $Pm\bar{3}m$ structure [14, 15]. CaGeO_3 has been shown to transform upon heating from $Pbnm$ to a second orthorhombic structure, $Cmcm$, which is a two tilt ($a^0b^+c^-$) system [16]. SrZrO_3 transforms as follows: $Pbnm \rightarrow Cmcm \rightarrow I4/mcm \rightarrow Pm\bar{3}m$ [12, 13]. A similar sequence of structures has been reported in the solid solutions $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ at room temperature [19]. $Cmcm$ can undergo a second order transformation to $I4/mcm$ but must be derived from $Pbnm$ via a first order transformation. Howard and Stokes [20] have presented a detailed group theoretical analysis of the interconversions of the various tilted perovskites. A number of pathways exist by which an orthorhombic $Pbnm$ system can transform to a cubic $Pm\bar{3}m$ system, and it is therefore considered more likely that the transformation should proceed via a higher symmetry intermediate rather than directly. A similar conclusion can be drawn from the work of Woodward [21].

The situation for CaTiO_3 is not yet clear. Early high temperature x-ray diffraction studies demonstrated that the orthorhombic distortion decreases as the temperature increases [8, 22], but failed to reach high enough temperatures to directly observe a transition to a higher symmetry polymorph. Vogt and Schmahl [9], using neutron diffraction methods, reported that CaTiO_3 transforms directly to a cubic structure above 1550 K. These authors found no evidence for an intermediate tetragonal phase. Recently Redfern [10] presented new x-ray diffraction evidence for the existence, over a narrow temperature range, of a tetragonal phase intermediate between the orthorhombic and cubic structures, and suggested that because of its limited stability range it may have been missed in the work of Vogt and Schmahl [9]. Matsui *et al* have also presented x-ray evidence for an intermediate phase [11].

In this study we intended to (I) identify the phase(s) intermediate between $Pbnm$ and $Pm\bar{3}m$ in CaTiO_3 , (II) determine the structures of these phases and (III) determine the order parameters for the observed phase transitions. We have accomplished this using powder neutron diffraction measurements on CaTiO_3 between 293 and 1633 K.

2. Experiment

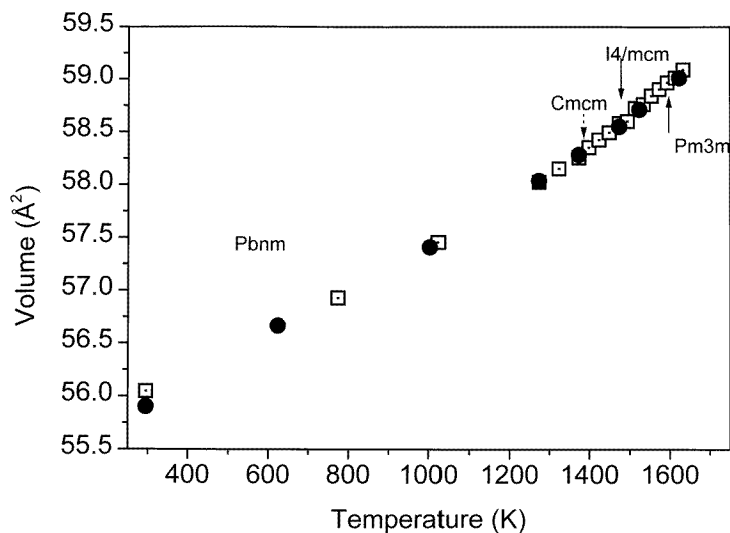
Two powder samples of synthetic CaTiO_3 were obtained, one from Aldrich chemicals (99%) and the other from Strem chemicals (99.995% lot No 128224-S). The Aldrich sample was pre-annealed at 1000 °C for 24 hours before use and the Strem sample was used as received. High resolution synchrotron diffraction patterns were recorded from the two samples at beamline 20B at the Photon Factory, Japan [23]. The lattice parameters of the two samples were slightly different, $a = 5.3812(2)$, $b = 5.4342(2)$ and $c = 7.6379(3)$ Å for the Strem sample and $a = 5.3766(1)$, $b = 5.4368(1)$ and $c = 7.6352(1)$ Å for the Aldrich sample. A small amount of an additional phase was observed in the Strem sample. The neutron powder diffraction patterns were recorded using neutrons of wavelength 1.5005 Å, in 0.05° steps over the range $11^\circ < 2\theta < 135^\circ$, on the powder diffractometer on HB4 at the High Flux Isotope Reactor, Oak Ridge National Laboratory [24]. Each sample was lightly ground and was contained in a thin-walled vanadium can which was in turn mounted in an ILL type vacuum furnace at a dynamic vacuum of around 10^{-6} Torr. The patterns were collected at room temperature and then at successively higher temperatures. The structural refinements were undertaken using the Rietveld program LHPM operating on a PC [25]. The background was defined by a third-order polynomial in 2θ and was refined simultaneously with the other profile parameters. The 2θ region near 38° affected by a peak from the Nb heating element of the furnace was excluded from the refinements.

3. Results and discussion

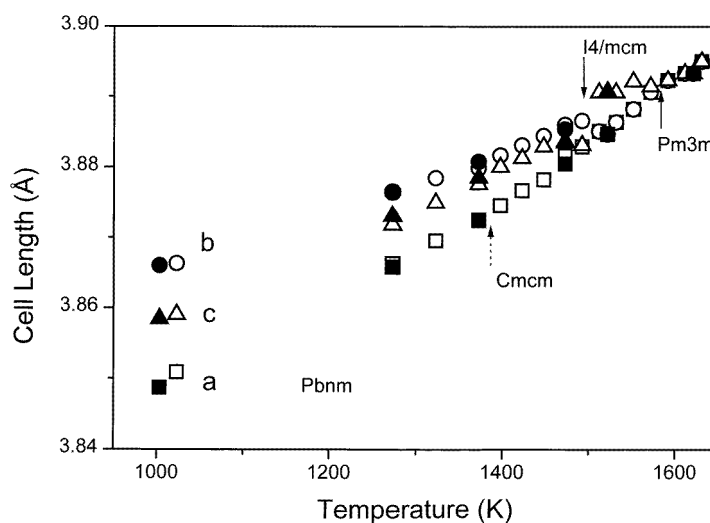
Powder neutron diffraction patterns were collected at eight and nineteen temperatures between ambient and 1633 K for the Aldrich and Strem samples, respectively. The temperature dependent structure of CaTiO_3 has attracted considerable attention and it is generally agreed that CaTiO_3 retains an orthorhombic $Pbnm$ structure up to at least 1300 K [8–11]. Accordingly in our study only a handful of patterns were collected at the lower temperatures, table 1 and figure 1. As found in previous powder x-ray diffraction studies the three cell edges increase in a nearly linear manner with temperature, with the rate of increase of the a axis being greater than that of the b axis [8,10]. Extrapolation of the cell parameters obtained below 1300 K suggests a transition to a tetragonal phase would occur near 1600 K. However careful examination of the patterns revealed that at least two phase transitions occurred, the first at significantly lower temperature, near 1500 K, and the second near 1580 K. The transition near 1500 K corresponds to the formation of an intermediate, tetragonal, phase that is stable over a limited temperature range, and the higher temperature transition is to a cubic phase.

Table 1. Cell parameters and space groups for the two samples of CaTiO_3 as a function of temperature. The numbers in parenthesis are the esd in the last significant figure.

Temp. (K)	Sample	a (Å)	b (Å)	c (Å)	Space group
295	Strem	5.3888(5)	5.4393(5)	7.6482(7)	$Pbnm$
295	Aldrich	5.3810(1)	5.4390(1)	7.6404(2)	$Pbnm$
623	Aldrich	5.4131(1)	5.4520(1)	7.6804(2)	$Pbnm$
773	Strem	5.4253(4)	5.4559(4)	7.6931(6)	$Pbnm$
1003	Aldrich	5.4429(2)	5.4674(2)	7.7169(3)	$Pbnm$
1023	Strem	5.4460(3)	5.4678(3)	7.7181(5)	$Pbnm$
1273	Strem	5.4678(6)	5.4821(6)	7.7436(10)	$Pbnm$
1273	Aldrich	5.4671(2)	5.4823(2)	7.7461(3)	$Pbnm$
1323	Strem	5.4724(6)	5.4850(6)	7.7499(9)	$Pbnm$
1373	Strem	5.4765(6)	5.4870(6)	7.7552(11)	$Pbnm$
1373	Aldrich	5.4766(2)	5.4883(2)	7.7570(2)	$Pbnm$
1398	Strem	5.4795(6)	5.4896(5)	7.7601(10)	$Pbnm$
		7.7545(10)	7.7597(10)	7.7601(10)	$Cmcm$
1423	Strem	5.4825(6)	5.4916(6)	7.7626(11)	$Pbnm$
		7.7582(12)	7.7614(11)	7.7639(9)	$Cmcm$
1448	Strem	5.4847(7)	5.4935(6)	7.7659(10)	$Pbnm$
		7.7621(8)	7.7641(9)	7.7674(8)	$Cmcm$
1473	Strem	5.4895(7)	5.4957(6)	7.7674(10)	$Pbnm$
		7.7659(9)	7.7698(8)	7.7683(8)	$Cmcm$
1473	Aldrich	5.4879(3)	5.4948(3)	7.7671(5)	$Pbnm$
		7.7642(6)	7.7674(4)	7.7667(4)	$Cmcm$
1493	Strem	5.4935(7)	5.4941(5)	7.7685(10)	$Pbnm$
		7.7662(8)	7.7756(9)	7.7693(9)	$Cmcm$
1513	Strem	5.4944(4)		7.7812(6)	$I4/mcm$
1523	Aldrich	5.4938(2)		7.7815(3)	$I4/mcm$
1533	Strem	5.4962(3)		7.7830(6)	$I4/mcm$
1553	Strem	5.4988(4)		7.7843(8)	$I4/mcm$
1573	Strem	5.5022(3)		7.7829(9)	$I4/mcm$
1593	Strem	3.8923(2)			$Pm\bar{3}m$
1613	Strem	3.8933(2)			$Pm\bar{3}m$
1623	Aldrich	3.8933(1)			$Pm\bar{3}m$
1633	Strem	3.8950(2)			$Pm\bar{3}m$



(a)



(b)

Figure 1. Temperature dependence of (a) the volume of the primitive cell and (b) the normalized lattice parameters for CaTiO_3 . The solid symbols correspond to values for the sample obtained from Aldrich Chemicals and the open symbols to that from Strem Chemicals. The values given below 1500 K are for the $Pbnm$ structure. See text for discussion.

Portions of the powder diffraction profiles, and their associated Rietveld fits, are shown in figure 2. At higher temperatures the departures of the lattice from cubic and/or tetragonal symmetry are sufficiently small to make identification of the phase transitions problematic. The weak superlattice reflections due to tilting of the octahedra are however diagnostic. Accordingly the identification of the symmetry appropriate at each temperature was based on analysis of the superlattice reflections and was confirmed by a satisfactory Rietveld analysis.

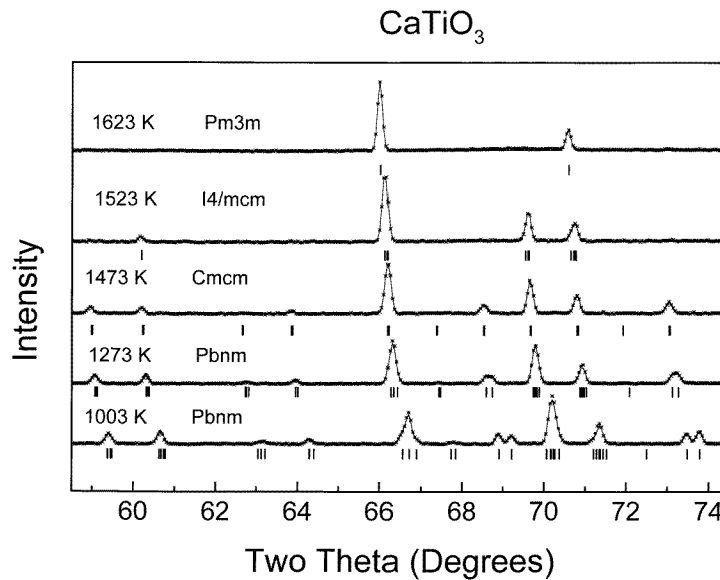


Figure 2. Part of the powder neutron-diffraction profiles ($\lambda = 1.5005 \text{ \AA}$) showing the temperature dependence of some of the superlattice reflections associated with the tilted octahedra. The shift of peaks to lower angle with increasing temperature is a result of lattice expansion. In each case the solid line is that calculated by the Rietveld refinement and small vertical markers show the positions of all the allowed Bragg reflections.

The transition temperatures noted above are in reasonable, but not excellent agreement with the two specific heat anomalies observed by Guyot *et al* (1384 and 1530 K) [6]. This variation may be a result of small differences in the composition and/or the atmosphere used to study the sample, although we note that the high temperature structural properties of the two samples studied here are essentially identical. Guyot *et al* [6] have proposed that the first anomaly in their specific heat measurements at 1384 K, is due to an orthorhombic (*Pbnm*) \rightarrow orthorhombic (*Cmcm*) transition. These two structures are very closely related in perovskite type oxides. In the absence of a clear splitting of the 022–202 type reflections in *Pbnm*, and of observable intensity of the peaks diagnostic of *Cmcm*, 110, 112, 330, 114 and 332, it is extremely difficult to distinguish between these two possibilities in powder diffraction studies [8, 16, 19]. As is illustrated in figure 3 at temperatures up to 1373 K there is a measurable splitting of the 044–404 reflections so the space group is definitely *Pbnm*. Above this, for example at 1473 K, the splitting is no longer observed allowing the possibility of *Cmcm*. Between 1398 and 1493 K the qualities of the fits obtained in Rietveld analyses were comparable and could not be used to distinguish between the two models.

Refinements in either space group resulted in small anomalies in the temperature dependence of the cell and structural parameters for the Strem sample between 1373 and 1398 K. For example the cell volumes calculated for both models show a discontinuity, as do the octahedral tilt angles. The temperature of these structural anomalies is in excellent agreement with that of the first anomaly in the heat capacity observed by Guyot and co-workers [6]. It appears that a *Pbnm* to *Cmcm* transformation may occur near 1385 K and we have analysed the data accordingly.

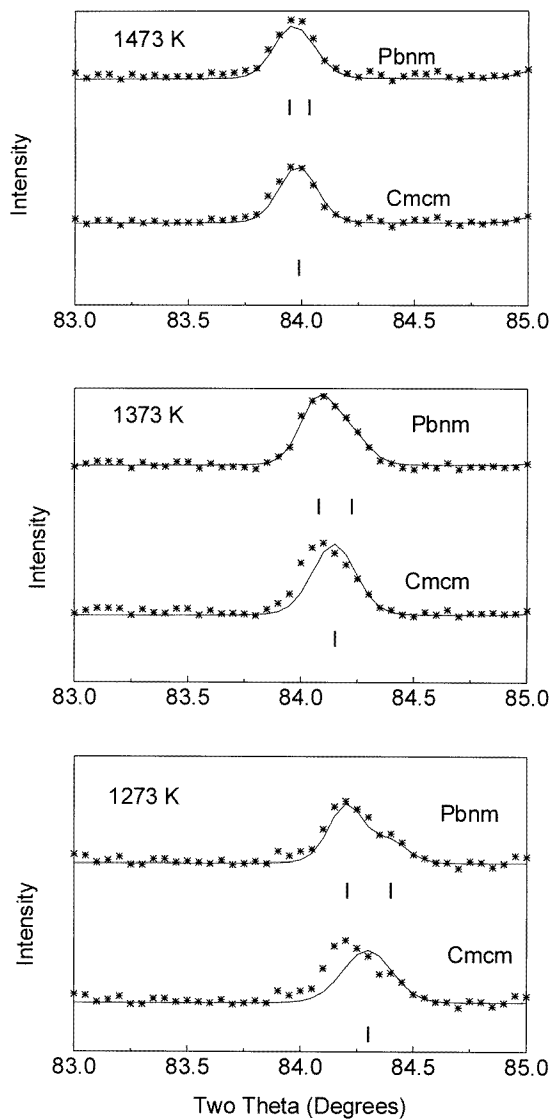


Figure 3. Comparison of part of the observed and calculated neutron diffraction profiles for CaTiO_3 . The calculated profiles were obtained by Rietveld refinements in space groups $Pbnm$ and $Cmcm$. In $Pbnm$ two reflections, the 044 and 404, are expected in the illustrated region whereas in $Cmcm$ only a single 444 reflection is expected. Note the gradual coalescence of the $Pbnm$ 044 and 404 reflections upon heating the sample.

3.1. Orthorhombic structures

The structure of CaTiO_3 between ambient temperature and 1493 K was refined in the orthorhombic space group $Pbnm$. The refined structural parameters for the two samples are in good agreement with previous studies [26], including the room temperature single crystal x-ray diffraction study of Sasaki *et al* [27]. The results from a typical refinement, at 1273 K, are given in table 2. Two points of note from the study are:

Table 2. Representative structural parameters for the four phases of CaTiO₃.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
<i>Pbnm</i> 1273 K <i>a</i> = 5.4671(2) <i>b</i> = 5.4823(2) <i>c</i> = 7.7461(3) Å					
Ca	4c	0.003(1)	0.519(1)	$\frac{1}{4}$	3.0(3)
Ti	4a	0	0	0	1.4(3)
O1	4c	-0.055(1)	-0.008(1)	$\frac{1}{4}$	2.7(2)
O2	8d	0.2177(5)	0.2802(5)	0.0286(4)	2.4(1)
<i>Cmcm</i> 1473 K <i>a</i> = 7.7642(6) <i>b</i> = 7.7674(4) <i>c</i> = 7.7667(4) Å					
Ca1	4c	0	-0.019(4)	$\frac{1}{4}$	3.8(12)
Ca2	4c	0	0.505(5)	$\frac{1}{4}$	3.9(12)
Ti	8d	$\frac{1}{4}$	$\frac{1}{4}$	0	2.3(9)
O1	8e	0.278(2)	0	0	4.1(6)
O2	8f	0	0.226(2)	0.032(1)	2.9(5)
O3	8g	0.280(2)	0.251(2)	$\frac{1}{4}$	3.0(6)
<i>I4/mcm</i> 1523 K <i>a</i> = <i>b</i> = 5.4938(2) <i>c</i> = 7.7815(3) Å					
Ca	4b	0	$\frac{1}{2}$	$\frac{1}{4}$	3.9(2)
Ti	4c	0	0	0	1.8(2)
O1	4a	0	0	$\frac{1}{4}$	5.1(4)
O2	8h	0.2783(5)	0.7783(5)	0	4.2(2)
<i>Pm3m</i> 1623 K <i>a</i> = <i>b</i> = <i>c</i> = 3.8933(1) Å					
Ca	1b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.8(1)
Ti	1a	0	0	0	1.9(1)
O	3d	$\frac{1}{2}$	0	0	5.2(1)

The standard *R* factors for the four structural refinements are:

1273 K *Pbnm* *R_B* 5.89 *R_p* 7.74 *R_{wp}* 9.67 *R_{exp}* 7.19%.

1473 K *Cmcm* *R_B* 1.36 *R_p* 6.21 *R_{wp}* 7.81 *R_{exp}* 6.68%.

1523 K *I4/mcm* *R_B* 1.78 *R_p* 7.00 *R_{wp}* 8.86 *R_{exp}* 6.01%.

1473 K *Pm3m* *R_B* 1.78 *R_p* 6.78 *R_{wp}* 8.65 *R_{exp}* 4.25%.

(1) The TiO₆ octahedra are not rigid. Under ambient conditions the two different Ti–O(2) distances are approximately equal and these are marginally longer than the Ti–O(1) distance so that the TiO₆ octahedra are axially compressed.

(2) The interoctahedral Ti–O–Ti angles both gradually increase as the temperature is increased and the slight difference between them becomes progressively smaller indicative of a more regular structure at higher temperatures.

Though it would be possible to estimate the magnitudes of the tilts for *rigid* TiO₆ octahedra in *Pbnm* using the lattice parameters, $\cos \psi = a/b$ and $\cos \varphi = 2^{1/2}a/c$, our results clearly demonstrate that the octahedra are not rigid. The tilt angles are therefore better estimated from the atomic coordinates. In *Pbnm* the octahedral tilt angles can be obtained from the displacement of the O2 oxygen atoms from $(\frac{1}{4}, \frac{1}{4}, 0)$ to $(\frac{1}{4} - u, \frac{1}{4} + v, w)$. The in-phase tilting occurs about the *c*-axis and, if rigid, would have $u = v$. We estimate the tilt angle by $\tan \psi = 4\delta$, where δ is taken as the average shift, $(u + v)/2$. The tilt about the diad axis is given by $\tan \varphi = 4\sqrt{2}w$. By ignoring the distortion of the TiO₆ octahedra and calculating from the lattice parameters alone the tilt angles are underestimated by around 2°. The two tilt angles decrease progressively as the temperature is increased, figure 4, showing the structure to be less distorted at higher temperatures.

The refinements of the structure in *Cmcm* were in general problematic. As discussed in more detail for the isostructural SrZrO₃ case [13] there are four equivalent solutions to the refinements in this space group. This, coupled with the weakness of the superlattice reflections

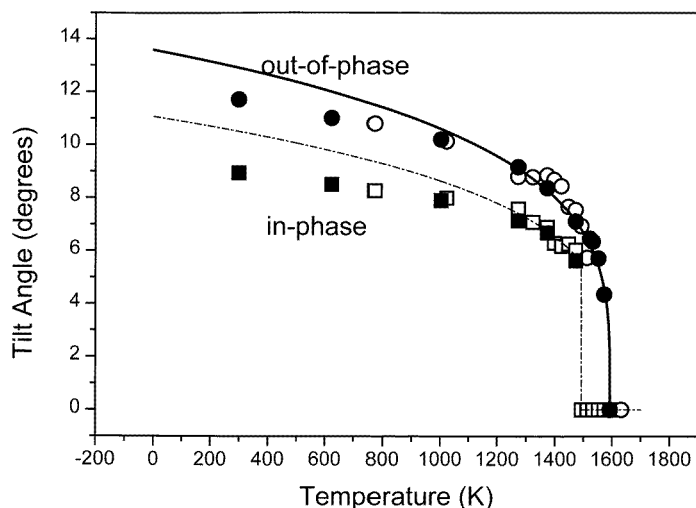


Figure 4. Temperature dependence of the octahedral tilt angles. The solid symbols correspond to values for the sample obtained from Aldrich Chemicals and the open symbols to that from Strem Chemicals. The solid line through the out-of-phase tilts is given by $\varphi = A(T_c - T)^{1/4}$, with $A = 2.15$ and $T_c = 1593$ K. The dashed line, with $A = 1.75$, through the in-phase tilts suggests a similar temperature dependence up to the transition to the tetragonal phase.

and unresolved splitting of the peaks, resulted in some instability in the refinements, and this has resulted in larger than usual uncertainties in the refined positional parameters. The results of a typical refinement are given in table 2. The tilt system in *Cmcm* comprises out-of-phase tilting of the oxygen octahedra around the *b*-axis and in-phase tilting around the *c*-axis. The coordinates of the oxygen atoms can be written as O1 ($\frac{1}{4} + u_1, 0, 0$) O2 ($0, \frac{1}{4} - v_2, w_2$) and O3 ($\frac{1}{4} + u_3, \frac{1}{4} + v_3, \frac{1}{4}$) where u, v and w are small and the tilt angles can be estimated using $\tan \varphi = 2(u_3 + w_2)$ and $\tan \psi = 2(u_1 + v_2)$.

3.2. Tetragonal structure

The existence of a number of weak superlattice reflections due to tilting of the TiO_6 octahedra show that the phase between 1500 and 1580 K is not yet cubic but rather is tetragonal. From the work of Howard and Stokes [20] we identified two probable space groups for the tetragonal phase, *P4/mbm* and *I4/mcm*, both of which can be obtained from *Cmcm* by a second order phase transition. Analysis of the data rapidly indicated that *P4/mbm* was inappropriate, as was also concluded by Matsui *et al* [11] in their x-ray diffraction study. It appears that the high temperature tetragonal phase of CaTiO_3 , adopts the same *I4/mcm* structure as is observed in SrZrO_3 , SrRuO_3 and SrTiO_3 [12–15, 28]. This is in agreement with the recent x-ray study of Redfern [10] and the re-interpretation of the x-ray data of Matsui *et al* [11] by Ball and co-workers [19]. The identification of the tetragonal phase has previously been problematic, leading Redfern [10] to suggest that the stability of this phase is dependent on composition and/or preparation method. We have clearly demonstrated the occurrence of this phase at similar temperatures in both samples studied.

Satisfactory refinements of structure between 1500 and 1580 K were obtained in space group *I4/mcm*, table 2. As found for the isostructural phases of SrRuO_3 [15] and SrZrO_3 [13] the use of anisotropic atomic displacement parameters resulted in a significantly better

agreement between the observed and calculated profiles than when isotropic values were used.

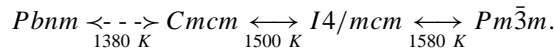
In the tetragonal phase the TiO_6 octahedra are tetragonally compressed with the axial Ti–O(1) bonds being about 0.01 Å shorter than the basal Ti–O(2) bonds, 1.945 versus 1.955(3) Å. The degree of this distortion is less than observed in SrZrO_3 [13] and consequently there is a very small change in the distortion as the temperature is increased. The observed transition temperature to $I4/mcm$, 1500 K, is in reasonable agreement with the results reported by Redfern [10] (1423 K) and falls within the range of the second feature observed in the heat capacity measurements of Guyot *et al* [6]. As stressed by Guyot this second feature is less well defined than the feature at 1384 K and may have resulted from two overlapping phase transitions occurring at different temperatures. In the tetragonal structure the O2 atom is at $(\frac{1}{4} + u, \frac{3}{4} + u, 0)$ and the angle of the out-of-phase rotation is given by $\tan \varphi = 4u$.

3.3. Cubic structure

Above 1580 K the superlattice reflections indicative of tilted octahedra were absent and the peaks could be indexed on the basis of a primitive cubic cell with $a \approx 3.9$ Å. The structure was refined in the cubic space group $Pm\bar{3}m$, table 2. The atomic displacement parameters of the oxygen atoms are highly anisotropic and they have their largest displacement amplitudes perpendicular to the linear Ti–O–Ti groups. This displacement is observed to decrease in magnitude above the transition temperature as expected for a soft-mode transition to the tetragonal phase. We note the development of diffuse scattering in the high temperature patterns possibly indicative of oxygen disorder [9, 10].

4. Phase transitions

The above results demonstrate that CaTiO_3 undergoes at least two phase transitions upon heating. There is weaker evidence for the existence of a third phase transition that has previously been identified in heat capacity measurements. A possible sequence of transitions is as follows:



This sequence is the same as is reported for SrZrO_3 [12, 13] and CaGeO_3 is also reported to form a $Cmcm$ intermediate phase [16]. The first of these transformations must be first order and the cell volume shows a slight discontinuity near 1380 K that we have taken as evidence for the $Pbnm$ – $Cmcm$ transition. As noted above we are unable to unequivocally identify the temperature at which the $Cmcm$ phase forms although the weight of evidence suggests its onset may be between 1373 and 1398 K. The observation of superlattice reflections at 1513 K clearly demonstrates that the structure is tetragonal at this temperature, even though no splitting of the strong reflections is resolved. At higher temperatures these superlattice reflections vanish as the cubic, $Pm\bar{3}m$, structure is formed.

Orthorhombic perovskites in space group $Pbnm$ have two tilts ($a^-a^-c^+$), an in-phase tilt about the tetrad axis and a tilt about the diad axis of the oxygen octahedron. The latter is equivalent to two equal out-of-phase tilts about the tetrad axes. In transforming to $Cmcm$ ($a^0b^-c^+$), one of the out-of-phase tilts is removed and by arguments given previously [13, 16, 20] the transition is necessarily first order. In $I4/mcm$ there is a single out-of-phase tilt about the tetrad axis ($a^0a^0c^-$). Of course, a direct transition from $Pbnm$ to $I4/mcm$ would also be first order since this would involve a change in an axis of tilt from the diad to the tetrad axis of the octahedron as well as loss of the in-phase rotation.

The variation in the tilt angles with temperature, calculated from the refinements in the *Pbnm* model to 1493 K and *I4/mcm* above this, is illustrated in figure 4. The temperature dependence of the in-phase tilt shows a sharp discontinuity above 1493 K indicative of a first order transformation to the tetragonal phase. We note that when the structure is refined in *Cmcm* there is a discontinuity at the *Pbnm*–*Cmcm* transition point and the transformation to the tetragonal phase is less abrupt. The magnitude of the out-of-phase tilt varies in a smooth manner over the entire temperature range, a remarkable result in view of the fact that one of the phase transitions must be first order. Within the tetragonal phase it is possible to reproduce its the variation with temperature by the expression $\varphi \propto (T_c - T)^{1/4}$, where T_c is the cubic transition temperature. This behaviour, which was also seen in SrZrO₃ [13] and certain other perovskites [17], is typical of tricritical phase transitions.

Acknowledgments

Support from the Access to Major Facilities Program to carry out the work at the Oak Ridge National Laboratory and the Australian Synchrotron Research Program is gratefully acknowledged. Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation for the US Department of Energy under contract number DE-AC05-96OR22464.

References

- [1] Woodward P M 1997 *Acta Crystallogr. B* **53** 44
- [2] Glazer A M 1972 *Acta Crystallogr. B* **28** 3384
- [3] Megaw H 1973 *Crystal Structures: a Working Approach* (Philadelphia, PA: Saunders)
- [4] Wang Y, Guyot F and Liebermann R C 1992 *J. Geophys. Res.* **97** 12 327
- [5] Zhao Y, Weidner D J, Parise J B and Cox D E 1993 *Phys. Earth Planet Int.* **76** 1
- [6] Guyot F, Richet P, Courtial Ph and Gillet Ph 1993 *Phys. Chem. Miner.* **20** 141
- [7] Gillet P, Guyot F, Price G D, Tournier B and Le Cleach A 1993 *Phys. Chem. Miner.* **20** 159
- [8] Liu X and Liebermann R C 1993 *Phys. Chem. Miner.* **20** 171
- [9] Vogt T and Schmahl W W 1993 *Europhys. Lett.* **24** 281
- [10] Redfern S A T 1996 *J. Phys.: Condens. Matter* **8** 8267
- [11] Matsui T, Shigematsu H, Arita Y, Hanajiri Y, Nakamitsu N and Nagaskai T 1997 *J. Nucl. Mater.* **247** 72
- [12] Ahtee M, Glazer A M and Hewat A W 1978 *Acta Crystallogr. B* **34** 752
- [13] Kennedy B J, Howard C J and Chakoumakos B C 1998 *Phys. Rev. B* **5**
- [14] Chakoumakos B C, Nagler S E, Misture S T and Christen H M 1997 *Physica B* **241–243** 358
- [15] Kennedy B J and Hunter B A 1998 *Phys. Rev. B* **58** 653
- [16] Liu X, Wang Y, Liebermann R C, Maniar P D and Navrotsky A 1991 *Phys. Chem. Miner.* **18** 224
- [17] Carpenter M A and Salje E K H 1998 *Eur. J. Miner.* **10** 693
- [18] Ringwood A E, Kesson S E, Reeve K D, Levins D M and Ramm E J 1988 *Radioactive Waste Forms for the Future* ed W Lutze and R C Ewing (Amsterdam: Elsevier) p 233
- [19] Ball C J, Begg B D, Cookson D J, Thorogood G J and Vance E R 1998 *J. Solid State Chem.* **139** 238
- [20] Howard C J and Stokes H T 1998 *Acta Crystallogr. B* **54** 782
- [21] Woodward P M 1997 *Acta Crystallogr. B* **53** 32
- [22] Kay H F and Bailey P C 1957 *Acta Crystallogr.* **10** 219
- [23] Garrett R F, Cookson D J, Foran G J, Sabine T M, Kennedy B J and Wilkins S W 1995 *Rev. Sci. Instrum.* **66** 1351
- [24] Chakoumakos B C 1997 *Physica B* **241–243** 361
- [25] Hill R J and Howard C J 1986 *Australian Atomic Energy Commission* (now ANSTO) Report M112
- [26] Koopmans H J A, Van de Velde G M H and Gellings P J 1983 *Acta Crystallogr. C* **39** 1323
- [27] Sasaki S, Prewitt C T and Bass J D 1987 *Acta Crystallogr. C* **43** 1668
- [28] Shirane G, and Yamada Y, 1969 *Phys. Rev.* **177** 858