Structures in the System CaTiO₃/SrTiO₃

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At room temperature the sequence of phases with increasing amounts of strontium in the system CaTiO₃/SrTiO₃ is orthorhombic (*Pnma*), orthorhombic (*Bmmb*), tetragonal (*I4/mcm*), and cubic (*Pm3m*). All phase boundaries shift toward smaller strontium contents with increase of temperature. Volume changes resulting from phase transformations are small for all compositions. Shape changes are greatest ($\sim 0.3\%$) for the *Bmmb/I4/mcm* transition, but would probably be accommodated by microtwinning and so are unlikely to affect the mechanical integrity of a specimen. © 1998 Academic Press

INTRODUCTION

Perovskite, $CaTiO_3$, is one of the major phases of Synroc, a titanate ceramic designed for immobilization of high-level radioactive waste (1). It is the major host phase for strontium, an important radwaste element, and will also incorporate significant amounts of the actinides. Obviously, the limits of solubility of strontium and other waste elements, and the phases formed when these limits are exceeded, are of interest. It is known that $CaTiO_3$ and $SrTiO_3$ are completely miscible and cubic at high temperatures, but the temperatures of transformation to the less symmetrical lowtemperature phases, and any volumetric and shape changes associated with such phase changes during cooling from the temperature of formation, are not known. There is even some uncertainty as to what the room temperature phases are.

The ternary system BaTiO₃/SrTiO₃/CaTiO₃ is of considerable technological importance on account of the ferroelectric behavior of many of its compositions. While most attention has been given to Ba-rich compounds, the $Ca_{1-x}Sr_xTiO_3$ binary system has been studied by several groups of workers. Gränicher and Jakits (2) reported the existence of orthorhombic, rhombohedral, "nearly cubic," tetragonal, and cubic structures with increasing proportions of SrTiO₃, at room temperature, but they did not measure found only orthorhombic, tetragonal, and cubic phases. By extrapolation of the cell parameters of the orthorhombic phase he placed the orthorhombic/tetragonal phase boundarv at x = 0.55 at room temperature, which is close to the "nearly cubic"/tetragonal boundary reported by Gränicher and Jakits. McQuarrie also found that the phase boundaries shifted to lower strontium contents at higher temperatures, though at room temperature the rate of change of composition with temperature for both phase boundaries was small. Mitsui and Westphal (4) investigated only the strontiumrich end of the phase diagram ($x \ge 0.8$). They confirmed the existence of the tetragonal phase, and put the tetragonal/cubic phase boundary at x = 0.9 at room temperature. A sample with x = 0.8 changed from tetragonal to a different structure, which appeared to be the "nearly cubic" structure of Gränicher and Jakits, near 110K. More recently Ceh et al. (5) questioned the existence of the tetragonal phase. They reported cell parameters for the orthorhombic phase for $0 \le x \le 0.9$, though they also stated that for x = 0.6 only lines characteristic of a cubic structure were present.

the cell parameters for any of these phases. McQuarrie (3)

Because of the importance of this system, and the lack of agreement between previous workers, we have reexamined the phases in the (Ca/Sr) TiO_3 system. In this we have been greatly helped by the excellent resolution obtainable with synchrotron radiation.

EXPERIMENTAL

Materials of composition $Ca_{1-x}Sr_xTiO_3$, with x = 0 and 0.10 up to 1.0 in steps of 0.05, were prepared by first hydrolyzing a known quantity of Ti-isopropoxide with an aqueous Sr-nitrate solution. An appropriate amount of CaCO₃ was slurried with water and converted to Ca-nitrate solution by addition of HNO₃, before being added to the other precursors. The sample was then stir dried and calcined at 600°C for 1 h. The resulting powder was pelleted and sintered at 1400°C for 96 h in air. The sintered pellet was ground to < 0.1 mm, repelleted, and refired at 1550°C for 85 h before final grinding.

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XRD measurements at room temperature were made with Debye-Scherrer geometry on rod-shaped specimens of diameter ~ 0.2 mm, using the X-ray diffractometer installed at the Australian National Beamline Facility at the Photon Factory in Tsukuba, Japan (6). Wavelengths of ~ 1 Å were used. Elevated temperature measurements (up to 500° C) were made in the same diffractometer, but using a thin layer of powder on the flat end of an electrically heated hot finger. Resolution was maximized by narrowing the incident beam to a ribbon of width ~ 0.1 mm, and the number of grains contributing to a reflection was increased by rocking the specimen through 1° during the exposure. This arrangement was not entirely satisfactory. The diffraction arcs were spotty in appearance, so although the splitting of lines could be clearly seen, the intensities of the lines were greatly affected by particle statistics and any attempt at Rietveld analysis of the patterns would have been pointless. The hot finger stage did have the merit of being cheap and easily assembled.

DATA ANALYSIS

The simplest structure in the (Ca/Sr) TiO₃ system is that of SrTiO₃, which is cubic with cell parameter $a \approx 3.905$ Å. The structure consists of TiO_6 octahedra with Sr ions between them. Other structures can be derived from that of SrTiO₃ by small distortions of this cubic cell. As discussed by Glazer (7, 8), these distortions consist of (i) tilts of the octahedra, (ii) displacements of the cations, and (iii) distortions of the octahedra. The tilts of the octahedra lead to splitting of the X-ray diffraction lines of the simple cubic structure and the appearance of additional (superlattice) reflections with half-integral indices when referred to the cubic cell. These reflections indicate that the true unit cell is a multiple of the pseudocubic subcell. As shown by Glazer (8) the nature of the tilts, and hence the space group, can be deduced by examining the superlattice reflections from a single crystal, but the problem is more difficult with a powder pattern since the superlattice reflections are always very weak and difficult to locate precisely, and therefore, given that the departure from the cubic cell is small, almost impossible to index unambiguously. The lattice type, however, can be determined by inspection of the strong lines, and once this is known the possible space groups consistent with tilts of regular octahedra are quite restricted. Since in may cases the tilts are very small, the resultant splitting of the strong lines is also very small and may only be apparent in some of the lines. In these cases it helps to know where to look.

A tetragonal structure is obtained by expansion (or contraction) along [001] (all indices are based on the pseudocubic subcell, unless otherwise stated). The greatest splitting in this case is of the h00 lines, which split into two components with intensities approximately in the ratio 2:1. The

clearest splitting is of the 400 line, since higher-order lines (visible with $\lambda = 1$ Å) are overlapped by other lines. Unfortunately this is a relatively weak line; another indication that the structure is not cubic is provided by the 310 complex, since although the 310 and 301 lines are overlapped, they are clearly separated from the 103 line. A change of dimension along two (or three) $\langle 100 \rangle$ directions gives rise to an orthorhombic structure. For these cases *hhh* lines are not split, but again may be overlapped by lines that are. We have examined the 222 and 444 lines. An orthorhombic structure can also be obtained by a [100] (010) shear (or variant thereof), with or without a change of dimension along [010]. The shear leads to splitting of hhh lines, into two approximately equal components, and the change along [010] leads to splitting of h00 lines, as for the tetragonal structure.

It is important to notice the difference between the two ways of developing an orthorhombic structure. In the first case the axes of the subcell remain orthogonal so the subcell also has orthorhombic symmetry and *hhh* lines are not split. In the second case the angle between two of the subcell axes is changed by the angle of shear, leading to monoclinic symmetry for the subcell. It is because these two axes remain equal in length that the overall symmetry becomes orthorhombic, but *hhh* lines are split, by an amount proportional to the angle of shear.

A rhombohedral structure [reported by Granicher and Jakits (2)] is obtained by a change of dimension along [111]. In this case the h00 lines are not split but the *hhh* lines are, into two components with intensities approximately in the ratio 3:1.

By profile fitting of *h*00 and *hhh* lines [using the program XFIT (9)], we have been able to determine the lattice type in all cases and hence to deduce the likely space group. This has been confirmed and cell parameters obtained by Rietveld analysis, using the program LHPM [Howard and Hill (10)].

RESULTS

At room temperature, $\operatorname{Ca}_{1-x}\operatorname{Sr}_x\operatorname{TiO}_3$ with $0 \le x \le 0.40$ is orthorhombic, with space group # 62. The cell parameters in the setting *Pnma* and the angle of shear of the pseudocubic subcell vary with composition as shown in Figs. 1 and 2, respectively. The variation of the shear angle with x suggests transformation to another phase between x = 0.45and x = 0.5, but this is very uncertain for two reasons: (i) there is significant curvature in the plot, making a linear extrapolation from any short section of the plot highly subjective, and (ii) there is no reason to suppose that the angle of shear differs only infinitesimally from zero at the transformation.

At x = 0.5 the 222 line (Fig. 3a) shows no splitting, indicating a zero angle of shear and therefore a space group other



FIG. 1. Unit cell parameters of *Pnma* phase of (Ca,Sr) TiO₃. +, *a*; \bigcirc , *b*/ $\sqrt{2}$; ×, *c*.

than *Pnma*. The 400 line (Fig. 3b), however, is split, suggesting a tetragonal structure with c/a < 1. Tilt system No. 16 of Glazer's (8) classification gives rise to such a structure but the space group (*I*4/*mmm*) is not consistent with the

observed superlattice lines. Figure 4 shows the portion of the pattern between the lines 222 and 321, indexed on the subcell and on a unit cell with all axes double those of the subcell. The presence of lines with $h^2 + k^2 + l^2 \neq 2n$ shows



FIG. 2. Angle of shear, ϕ , of pseudocubic subcell of *Pnma* phase of (Ca,Sr) TiO₃.



FIG. 3. (a) 222 and (b) 400 X-ray diffraction lines of $Ca_{0.5}Sr_{0.5}TiO_3$ ($\lambda \approx 1.00$ Å).

that the lattice is not body-centred. The most likely alternatives are Glazer's (8) tilt system Nos. 17 and 18, both of which give rise to an orthorhombic structure with space group No. 63 (*Bmmb*). These tilt systems differ in that No. 18 leads to equality of the *b* and *c* parameters, whereas No. 17 does not. Neither of these tilt systems will account for all of the observed superlattice reflections, but the space group allows for *A*-cation displacements from their positions in the cubic subcell and for distortion of the TiO₆ octahedra, which will account for the extra lines. The structure refined satisfactorily in space group *Bmmb* with the results shown in Fig. 5 and Table 1, confirming that this is the correct space group and that the tilt system is No. 17.

It is difficult to determine the composition of the boundary between the two orthorhombic phases. As noted above, extrapolation of the angle of shear in the *Pnma* phase suggests transformation between x = 0.45 and x = 0.5, but the 222 line for a specimen with x = 0.45 (Fig. 6a) shows no evidence of splitting, indicating that the space group is the same as for x = 0.5, i.e., *Bmmb*. The 400 line (Fig. 6b) confirms this. The 222 and 400 lines for x = 0.4 are shown in Figs. 6c and 6d. Splitting is not obvious but the 222 line is significantly wider than the 222 line for x = 0.45 and the shape of the peak is consistent with splitting into two nearly equal components, suggesting that the space group is *Pnma*. In principle it is possible to distinguish between the phases by observing (or not, as the case may be) the reflections 121 and 323 in Bmmb (indexed on the true unit cell), which would be the reflections (120,021) and (320,023), but are forbidden, in Pnma. These reflections arise from cation displacements, not tilts of the octahedra. However, with the parameters of Table 1 the intensities of these lines are less than 1% of the intensities of other superlattice lines, which themselves are less than 1% of the intensities of the main (subcell) lines, so the fact that they were not observed is not very informative. Refinement in *Pnma* of the X-ray pattern from the sample with x = 0.4 gave the data shown in Figs. 1 and 2, which are close to the values predicted by extrapolation of the data for lower values of x, confirming that this is the correct space group for x = 0.4. We conclude from this that the structure is orthorhombic with space group *Pnma* unless the splitting of h00 lines suggests a tetragonal structure with c/a < 1, in which case the structure is actually orthorhombic with space group Bmmb.

For $0.65 \le x \le 0.9$ the structure is tetragonal with c/a > 1. The superlattice lines are consistent only with tilt system No. 22 giving rise to space group No. 140, I4/mcm, which is the space group of SrTiO₃ below 90 K (4) and of CaTiO₃ above 1100°C (11). For $x \ge 0.95$ the structure is cubic (*Pm3m*).

FIG. 4. Portion of X-ray diffraction pattern of $Ca_{0.5}Sr_{0.5}TiO_3$. Values of $h^2 + k^2 + l^2$ are shown for the lines when indexed on the pseudocubic subcell and on the super cell with all parameters double those of the subcell ($\lambda \approx 1.00$ Å).





FIG. 5. Observed (...), calculated (—), and difference X-ray diffraction patterns from Ca_{0.5}Sr_{0.5}TiO₃ at room temperature ($\lambda \approx 1.00$ Å).

The relations between the phases can best be seen by comparing the parameters of the subcells which, except for the phase *Pnma*, have the symmetry of the true unit cell. The subcell parameters for specimens with $x \ge 0.45$ are shown in Fig. 7. For the phase *Bmmb* the true cell parameters are twice the subcell parameters, for the phase *I4/mcm* the relation is $a = \sqrt{2}a_p$, $c = 2c_p$, where a_p and c_p are the subcell parameters, and for the cubic phase the subcell is the true unit cell. For the phase *Pnma* the subcell is of monoclinic symmetry, but with $a_p = c_p$.

Extrapolation of the parameters for the phase I4/mcm suggests that the boundary with the cubic phase is at $x \sim 0.925$ at room temperature, in agreement with our ob-

 TABLE 1

 Structural Parameters in Ca_{0.5}Sr_{0.5}TiO₃, Space Group Bmmb^a

| Atom | | и | v | w | $B~(\mathrm{\AA}^2)$ |
|----------|------------|-------------------------|---------------|-------------------------|----------------------|
| (Ca,Sr)1 | 4 <i>c</i> | 0 | $\frac{1}{4}$ | -0.007_{1} | 1.0215 |
| (Ca,Sr)2 | 4c | 0 | $\frac{1}{4}$ | $\frac{1}{2} - 0.006_1$ | 0.9815 |
| Ti | 8d | $\frac{1}{4}$ | 0 | $\frac{1}{4}$ | 0.6010 |
| O1 | 8 <i>e</i> | $\frac{1}{4} + 0.018_4$ | 0 | 0 | 2.05_{40} |
| O2 | 8 <i>f</i> | 0 | 0.0342 | $\frac{1}{4} - 0.019_3$ | 0.6720 |
| O3 | 8g | $\frac{1}{4} + 0.028_3$ | $\frac{1}{4}$ | $\frac{1}{4} - 0.000_1$ | 0.7230 |

^{*a*} Decimal fractions show displacements of atoms from positions in cubic aristotype. Estimated standard errors (suffixes) apply to least significant figure of parameter. $a = 7.7378_1$ Å, $b = 7.7440_3$ Å, $c = 7.7446_3$ Å, Bragg *R* factor = 1.7.

servation that samples with $x \ge 0.95$ were cubic, but, as for the transformation between the two orthorhombic phases, extrapolation may not be a valid procedure. The boundary between the phases *Bmmb* and *I4/mcm* cannot be obtained by extrapolation since there is a discontinuity in the parameters at the boundary. However, we observed a small amount of the phase *Bmmb* in the sample with x = 0.65,



FIG. 6. X-Ray diffraction lines from $Ca_{1-x}Sr_xTiO_3$: (a, b) x = 0.45, $\lambda \approx 1.00$ Å; (c, d) x = 0.4, $\lambda \approx 1.05$ Å; (a, c) line 222; (b, d) line 400.



FIG. 7. Cell parameters of pseudocubic subcell in Ca_{1-x}Sr_xTiO₃. Phase *Bmmb*: +, *a*; \bigcirc , *b*; ×, *c*. Phase *I*4/*mcm*: \oplus , *a*; \otimes , *c*. Phase *Pm*3*m*: \bullet , *a*.

possibly due to compositional inhomogeneity or to hysteresis in the transformation, which shows that the boundary is very close to this composition. diffraction patterns. We have estimated the temperature of the transformation between the two orthorhombic phases for a sample with x = 0.35 by extrapolating the splitting of the 222 line to zero, although as mentioned above, this may not be a valid procedure. The data are shown in Fig. 8.

Determination of the phase boundaries at elevated temperatures is difficult, because of the poorer quality of the



FIG. 8. Ca_{0.65}Sr_{0.35}TiO₃: angular separation of lines 440_{Pnma} and 044_{Pnma} ($\lambda \approx 1.05$ Å).



FIG. 9. $Ca_{0.35}Sr_{0.65}TiO_3$: splitting of pseudocubic subcell line 400 ($\lambda \approx 1.05$ Å).

Close to the transformation temperature we could not detect splitting of either the h00 or hhh lines. The boundary between the tetragonal and cubic phases could also be obtained by extrapolation, in this case of the splitting of the 400 line. Data for the sample with x = 0.65 are shown in Fig. 9. We have tried to bracket the temperature of the boundary between the *Bmmb* and *I4/mcm* phases but have found that both phases are present at some temperatures. This could have been due to compositional inhomogeneity, but temperature variation within the specimen may also have been significant. We take the transformation temperature as the temperature at which there are about equal amounts of the two phases.

The positions of the phase boundaries found in this work are shown in Fig. 10. Also shown are the results of Mitsui and Westphal (4) for Sr-rich materials at low temperatures and some of the phase boundaries reported by Gränicher and Jakits (2).

DISCUSSION

Our results are in good agreement with the results of Mitsui and Westphal (4). From the positions of the phase boundaries we can conclude that the "nearly cubic" phase reported by Granicher and Jakits (2) is the phase *Bmmb*, but we find no evidence of a trigonal-rhombohedral phase. Instead, the phase *Pnma* persists up to the boundary with *Bmmb*. The boundaries of the tetragonal phase reported by McQuarrie (3) agree less well with our results, and he did not identify the phase *Bmmb*.

The sequence of phases that we find with increasing strontium at room temperature is exactly the same as the sequence of phases in SrZrO₃ with increasing temperature observed by Carlsson (12). He found a few very faint lines indicative of an enlarged unit cell, but he did not determine the structures of the two phases intermediate between the room temperature orthorhombic and high-temperature cubic phases, which he described as tetragonal with c/a < 1 and c/a > 1. Ahtee *et al.* (13) determined the structures and showed that the phases were orthorhombic (*Bmmb*) and tetragonal (*I4/mcm*), as we have found in the (Ca,Sr) TiO₃ system. They explained this sequence of phases by considering the sequence of tilting which, in Glazer's (7) notation, is

with condensation of soft modes, which consist of oscillations of the octahedra, at each transformation on cooling from the cubic phase.

With this interpretation of the phase transitions we might expect to find the same sequence of phases on heating CaTiO₃. Vogt and Schmahl (14) found no intermediate phases between the room-temperature orthorhombic and high-temperature cubic phases, but Redfern (11) has found the tetragonal phase with space group I4/mcm between 1400



FIG. 10. Variation with temperature of phase boundaries in the system CaTiO₃/SrTiO₃: •, *Pnma/Bmmb*; +, *Bmmb/I4/mcm*; ×, *I4/mcm/Pm3m*; \oplus , \otimes , data of Mitsui and Westphal (4); lines, data of Granicher and Jakits (2).

and ~ 1500 K; he did not find the phase *Bmmb*. Matsui et al. (15) have also examined CaTiO₃ at high temperatures. Their XRD patterns are very similar to those of Redfern, but they identified the intermediate phase as Cmcm (an alternative setting of Bmmb). They based this identification on the continued presence of the unresolved group of lines 121. 103, and 211 (indexed on the low-temperature orthorhombic phase, in the setting Pbnm), which are the lines 311, 131, and 113 when indexed on the supercell with all axes twice those of the pseudocubic subcell, but the only alternative space group they considered was P4/mbm, which results from the tilt system $a^0a^0c^+$. It is true that none of the 311 group of lines would appear in P4/mbm, but 311 and 131 would appear in I4/mcm (supercell space group F4/mmc). *Cmcm* can be distinguished from *I4/mcm* through the presence, or otherwise, of the lines 120_{Pbnm} and 210_{Pbnm} . When indexed on the supercell these are the lines 310 and 130, which should appear in *Cmcm* but not in F4/mmc (I4/mcm). The fact that these lines are not seen in the temperature range of the intermediate phase suggests that it is I4/mcm and not Cmcm.

This is not to say that *Bmmb* does not occur at lower temperatures. As we have noted, it is very difficult to distinguish between the phases *Pnma* and *Bmmb*, and inspection of the superlattice lines is of little use since, structurally, the phases differ only through the presence of tilts of the octahedra about the subcell x axis in *Pnma*, but not in *Bmmb*, and, possibly, through cation displacements and distortions

of the octahedra. The tilt about the x axis produces reflections which (indexed on the supercell) have all indices odd and $k \neq l$. Reflections with all indices odd and $h \neq k$ will also be present, on account of the tilts about the z axis, as they are in Bmmb. Consequently, for example, the line with $h^2 + k^2 + l^2 = 51$ in Fig. 4 would be a superposition of the lines 515, 155, 711, and 171 in Bmmb, and of the same lines plus 551 and 117, but with all lines split, in Pnma (indexed on the monoclinic supercell). However, lines 551 and 117, present in Pnma but not in Bmmb, would be exactly superimposed on 155 and 711, respectively, since in the monoclinic supercell a = c. The difficulty of distinguishing between these cases is apparent and reduces to the problem of resolving the splitting, as for the main lines. Redfern (11) reported that peak splitting could be resolved at all temperatures up to the transition to I4/mcm, but that splitting of peaks in the I4/mcm structure could not be resolved. Our experience with varying strontium content at room temperature was that splitting in the low-Sr I4/mcm structure was greater than in the high-Sr Pnma and Bmmb structures. Near to the boundary with the cubic phase, of course, the splitting approached zero. It is possible that the temperature range of stability of *Bmmb* fell entirely between temperatures investigated by Redfern. It is also possible that Bmmb does not form at all in CaTiO₃, which would be the case if the b^+ tilt in *Pnma* disappeared at the same temperature as the a^- tilt, with one a consequence of the other. We can think of no compelling reason



FIG. 11. Angle of tilt, α , of a^- tilts in *Pnma* phase of Ca_{1-x}Sr_xTiO₃ at room temperature.

why this should not happen. The heat capacity measurements of Guyot *et al.* (16) on CaTiO₃ and of Nagarajan *et al.* (17) on Ca_{0.85}Nd_{0.15}TiO₃ identified transitions at ~1380 and ~1520 K, in agreement with the XRD data of Redfern (11) and Matsui *et al.* (15), but showed no sign of a transition at a lower temperature. However, this is not conclusive evidence that no such transition occurs, since it would not necessarily be accompanied by a measurable heat capacity anomaly: for instance, the heat capacity measurements of Naylor and Cook (18) on CaTiO₃ showed no evidence of the transition at ~1380 K.

The variation of shear angle ϕ with composition in the phase Pnma was shown in Fig. 2. A more fundamental quantity is the angle of tilt, α , of the octahedra about the x and z axes. Since successive octahedra along both of these axes are tilted in opposite senses (- tilts, in Glazer's notation) the axes are inclined to one another, as Glazer (8) has shown. For the tilt system resulting in the phase Pnma the magnitudes of the tilts about the two axes are the same, and it can be shown that $\sin \phi = \sin^2 \alpha$. The variation of α with composition is shown in Fig. 11. No particular significance is attached to the approximately linear variation of α with x, but it is apparent that α , and therefore ϕ , differs from zero by a significant amount at the transformation to *Bmmb*, which at room temperature, as we have shown, occurs between x = 0.4 and x = 0.45. Of course, a discontinuous change in at least one of the tilts was inevitable, since tilts about one of these axes persist in phase Bmmb. Another way of looking at the transformation is to note that equal tilts about the x and z axes are equivalent to a single tilt about [101], and at the transformation the axis of tilt changes to [001].

The variation of the volume of a subcell with composition at room temperature is shown in Fig. 12. The fact that the subcell volumes are closely the same on either side of a phase boundary at room temperature does not prove that there is a negligible volume change in a given material when it undergoes a transformation at some other temperature, but that is probably the case. There is certainly no evidence to the contrary. Unfortunately our high-temperature data were not sufficiently precise to enable a worthwhile comparison of volumes to be made.

Although there is little change in volume on transformation there is a change of shape, particularly in the transformation from *Bmmb* to *I4/mcm*. By extrapolating the parameters found in the phase *Bmmb* to a strontium content of x = 0.65 and comparing with the parameters of the phase *I4/mcm* at that composition, we find that the biggest change of dimension when *Bmmb* transforms to *I4/mcm* is an expansion of 0.31% along the *c* axis, with contractions of 0.04 and 0.23% along *a* and *b*, respectively. These changes are calculated on the assumption that the *c* axis in *Bmmb* becomes the *c* axis in *I4/mcm*. In practice it is likely that microtwinning will occur which will greatly reduce long-range stresses, so mechanical integrity of a specimen is unlikely to be affected.



FIG. 12. Volume of pseudocubic subcell in $Ca_{1-x}Sr_xTiO_3$ at room temperature. •, phase *Pnma*, +, phase *Bmmb*; •, phase *I4/mcm*; ×, phase *Pm3m*.

CONCLUSIONS

At room temperature the phases in the system Ca_{1-x} Sr_xTiO₃ are *Pnma* for $0 \le x \le 0.4$; *Bmmb* for $0.45 \le x \le 0.6$; *I4/mcm* for $0.65 \le x \le 0.9$; and *Pm3m* for $x \ge 0.95$.

Volume changes resulting from transformations between phases are small.

The largest shape changes occur for the *Bmmb/I4/mcm* transformation, but at most are ~ 0.3% and would probably be accommodated by microtwinning, so the mechanical integrity of a specimen is unlikely to be affected by phase transformations during cooling from the temperature of formation.

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