Space-group symmetry for the perovskite $Ca_{0.3}Sr_{0.7}TiO_3$

LETTER TO THE EDITOR

Space-group symmetry for the perovskite Ca$_{0.3}$Sr$_{0.7}$TiO$_3$

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Abstract

It is shown, using synchrotron x-ray powder diffraction at room temperature and above, by invoking geometrical and symmetry arguments, and most directly by electron diffraction, that the perovskite Ca$_{0.3}$Sr$_{0.7}$TiO$_3$ at room temperature is tetragonal with space-group symmetry $I4/mcm$. This is in accord with the common view (Ball *et al* 1998 *J. Solid State Chem.* **139** 238–47). The proposition that the compound adopts a metrically tetragonal orthorhombic structure in space group $Imma$ (Ranjan and Pandey 1999 *J. Phys.: Condens. Matter* **11** 2247–58) cannot be sustained.

Crystal structures across the perovskite system Ca$_{1-x}$Sr$_x$TiO$_3$ have been the subject of a number of studies, but the results remain in dispute. The end members CaTiO$_3$ and SrTiO$_3$ are known to adopt at room temperature orthorhombic (in space group $Pnma$) and the ideal cubic ($Pm\bar{3}m$) structures respectively. Upon heating, the CaTiO$_3$ end member transforms to a tetragonal structure ($I4/mcm$) at 1500 K, and to the cubic structure ($Pm\bar{3}m$) at 1580 K [1, 2]. There was some suggestion of a structure in $Cmcm$ just preceding the transition to the tetragonal phase [2], but it was realized subsequently, after consideration of the expected nature of the transitions involved, that such an intermediate structure would be unlikely [4].

It might be expected that the substitution of Sr for Ca as in Ca$_{1-x}$Sr$_x$TiO$_3$ would produce the same structural sequence as obtained on heating CaTiO$_3$. Ball *et al* [5] undertook a careful synchrotron x-ray powder diffraction study of the room-temperature structures, and reported orthorhombic structures in $Pnma$ for $0 \leqslant x \leqslant 0.4$, a metrically tetragonal structure in $Cmcm$ for $0.45 \leqslant x \leqslant 0.6$, the tetragonal structure in $I4/mcm$ for $0.65 \leqslant x \leqslant 0.9$, and the ideal cubic ($Pm\bar{3}m$) for $x \geqslant 0.95$. In re-examination of the $x = 0.5$ composition using electron

diffraction [6, 7], the space-group symmetry of the metrically tetragonal structure was found to be not *Cmcm* but *Pnma*. With this correction we might conclude that the structural sequence is simply *Pnma* ($0 \leqslant x \leqslant 0.6$), *I4/mcm* ($0.65 \leqslant x \leqslant 0.9$), then *Pm$\bar{3}$m* ($x \geqslant 0.95$), just as found in CaTiO$_3$ on heating. This sequence has been found using both powder and single-crystal methods [8, 9], and has been assumed in certain subsequent work [10, 11].

A different sequence of structures has been proposed by Pandey and co-workers [7, 12, 13]. The particular difference of interest in the present letter is the claim that the structure of Ca$_{1-x}$Sr$_x$TiO$_3$ in the composition range $0.6 \leqslant x < 0.88$ is not tetragonal in *I4/mcm* as indicated above, but rather a pseudo-tetragonal structure in orthorhombic space group *Imma*. This is immediately problematic because it would imply a discontinuous (as a function of composition) transition somewhere between the structures in this composition range and the cubic structure of the end member SrTiO$_3$ [4]. No such transition is apparent in the published data [5]. The assignment to *Imma* is based largely on the perception, from the examination of somewhat noisy laboratory x-ray data [12], that there are two phase transitions above room temperature, together with the tenet that the tetragonal *I4/mcm* structure is achieved only above the first of these. Ranjan and Pandey [12] show raw x-ray data at $x = 0.88$, and derived data (for example peak full widths at quarter maximum) at $x = 0.79$, 0.82 and 0.85. The assignment may be supported by the observation of some slight asymmetry (not splitting) of the E_g line in the Raman spectra [14]. Pandey and co-workers refer to this *Imma* structure often in their later work [15–17].

We report here on an examination of the structure of Ca$_{0.3}$Sr$_{0.7}$TiO$_3$, leading to the unequivocal determination of its space-group symmetry. This is not a composition specifically mentioned by Ranjan and Pandey [12] in their initial x-ray study, but at $x = 0.7$ it certainly falls within the range of dispute. It can be inferred from later papers [13, 16] that it was considered to show two transitions above room temperature, at about 580 and 620 K, and that its space-group symmetry at room temperature was thought to be *Imma*, or possibly *Pnma*.

As a first step, we undertook x-ray diffraction measurements above room temperature, thus revisiting the question as to whether there were two transitions or just one above room temperature. The sample for this work was prepared by the alkoxide/nitrate route [20] in which aqueous solutions of Sr and Ca nitrates were first mixed with stoichiometric amounts of Ti isopropoxide, stir-dried, calcined for 1 h at 750 °C, and wet-milled. The powders were then pelletized and sintered for 96 h at 1550 °C in air. The sample composition was verified by SEM using a JEOL 6400 instrument operated at 15 keV and fitted with a Tracor Northern Voyager IV x-ray microanalysis system (EDS). The x-ray measurements were made using the high-resolution powder diffractometer installed on beam line BL02B2, at the SPring-8 synchrotron, Hyogo, Japan [21]. The wavelength was 0.7765 Å as determined by calibration with a CeO$_2$ standard specimen. The sample was housed in a 0.2 mm quartz-glass capillary, and all the diffraction patterns recorded on a single image plate. High temperatures were achieved using a heated nitrogen gas flow, and measured using a type K (chromel–alumel) thermocouple located at the head of the nozzle. Patterns were recorded at (sample) temperatures 300, 400, 450, 500 and 550 K, in 10 K steps to 650 K, at 700, 750, and finally at 800 K. The finer steps between 550 and 650 K were intended to cover the range in which the transition (or transitions) might be observed. All the patterns were recorded to 75°(2θ), but we do not show the full patterns here. Instead we focus (figure 1) on the doublet indexing as $\{400\}_p$ on the pseudo-cubic (parent) subcell, and on the weak $\frac{1}{2}\{311\}_p$ superlattice reflection associated with TiO$_6$ octahedral tilting. The $\{400\}_p$ is the same doublet as that shown by Ranjan and Pandey [12] in their figure 5. The splitting of the doublet here decreases steadily with increasing temperature, until the doublet collapses to a singlet above about 650 K. Certainly, the collapse of the doublet to a singlet can be taken to correspond to a phase transition, but we discern no evidence in our
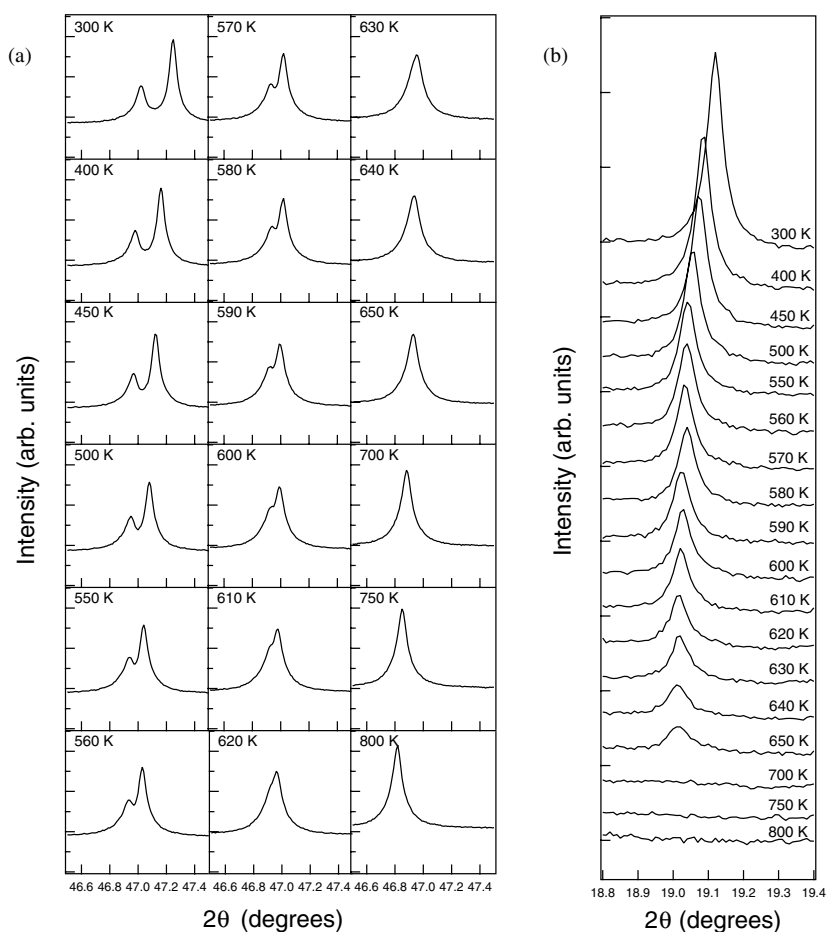
Figure 1. Extracts from the x-ray diffraction patterns from $Ca_{0.3}Sr_{0.7}TiO_3$. (a) The $\{400\}_p$ doublet as a function of temperature. The profiles here are to be compared with those shown for the same doublet by Ranjan and Pandey [12] in their figure 5. (b) Temperature dependence of the $\frac{1}{2}\{311\}_p$ superlattice reflection associated with TiO_6 octahedral tilting. This reflection vanishes between 650 and 700 K, indicative of the transition to the cubic phase.

data for a second transition in the temperature range under study. The $\frac{1}{2}\{311\}_p$ superlattice peak becomes progressively weaker with increasing temperature, and vanishes at a temperature somewhere between 650 and 700 K. This can be taken as further clear evidence for one phase transition, but there is no indication at all of two successive phase transitions. The analysis has been quantified by performing both Le Bail [22] and Rietveld method [23] fits. Computer program LHPM [24] with the Rietica interface [25] was used for both. Space-group symmetry $I4/mcm$ was assumed for temperatures to 650 K, and $Pm\bar{3}m$ for 700 K and above. All the fits obtained were good, and close inspection of the fits at the $\{400\}_p$ and $\frac{1}{2}\{311\}_p$ peaks—those peaks shown in figure 1—revealed no anomalies that might suggest two phase transitions in the range. Lattice parameters from the Rietveld refinements are shown in figure 2(a), and the octahedral tilt angle ϕ as derived from the one variable oxygen position parameter (in the $I4/mcm$ structure) is shown in figure 2(b). Both lattice parameters and tilt angle show a smooth variation with temperature as the transition is approached. The temperature dependence of the
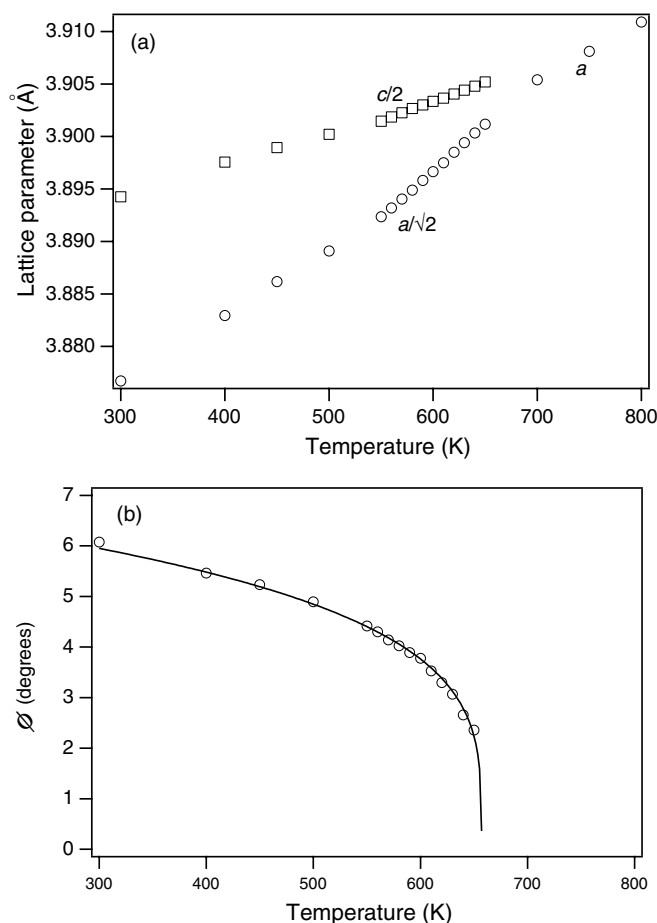
Figure 2. (a) Reduced lattice parameters for $Ca_{0.3}Sr_{0.7}TiO_3$ as a function of temperature. The plot shows $a/\sqrt{2}$ and $c/2$ in the tetragonal $I4/mcm$ and a for the cubic phase. (b) The temperature dependence of the octahedral tilt angle, as derived from the oxygen position in the tetragonal $I4/mcm$ structure. This has been fitted with the function $\phi = A(T_c - T)^{1/4}$ with $A = 1.37°$ and $T_c = 657.1$ K.

tilt angle is in fact very well described by $\phi \propto (T_c - T)^{1/4}$ (figure 2(b)), indicative of a *single* transition, tricritical in nature, occurring at 657 K. The lattice parameter variation is consistent with this interpretation.

Ranjan *et al* [13] present a phase diagram implying that, with decreasing temperature, $Ca_{0.3}Sr_{0.7}TiO_3$ first undergoes a transition from cubic $Pm\bar{3}m$ to tetragonal $I4/mcm$ (the transition we observe at 657 K), then a second transition to orthorhombic $Imma$ at a temperature perhaps 40 K lower than this. This $I4/mcm$ to $Imma$ transition would be discontinuous [4]. There is no evidence for any second transition 40 K below that to cubic, let alone a discontinuous one. Further on this point, we recall that Glazer [26] has recorded the expected relationships among the pseudo-cubic cell parameters in the different perovskite structures under the approximation that these are determined by the tilting of nearly rigid octahedra. Glazer finds $a_p = b_p < c_p$ and $a_p < b_p = c_p$ for the tetragonal $I4/mcm$ and orthorhombic $Imma$ structures, respectively. Thus, an $Imma$ to $I4/mcm$ transition should be accompanied by a reversal of the (pseudo-) tetragonal doublet. Such a reversal has been observed in other
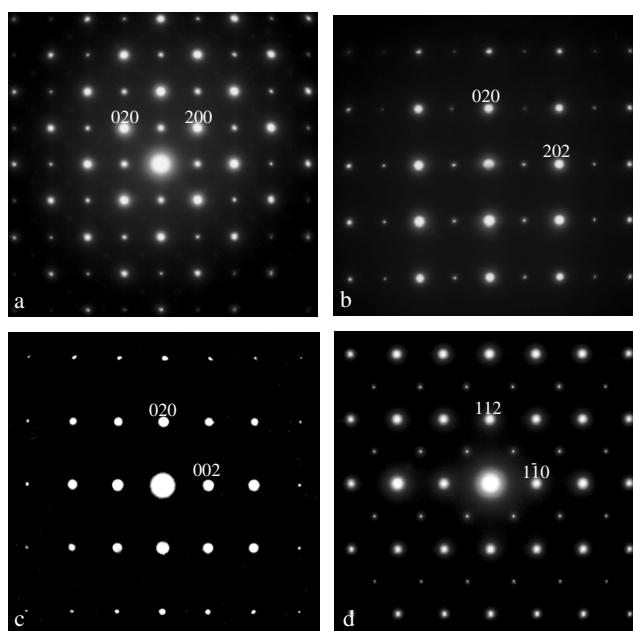
Figure 3. Electron diffraction patterns from single domain $Ca_{0.3}Sr_{0.7}TiO_3$ along the (a) [001], (b) [10$\bar{1}$], (c) [100] and (d) [11$\bar{1}$] zone axes of the tetragonal $I4/mcm$, or orthorhombic $Icmm$, cell. Patterns (b) and (d) show {101} reflections that are allowed in $Icmm$ but forbidden in $I4/mcm$. The presence of these reflections here is, however, due to multiple scattering (see figure 4).

instances of transitions from $Imma$ to $I4/mcm$ [27, 28] but, as evident from figure 1(a), is not observed here.

Finally, we sought to examine the space-group symmetry of the room-temperature structure directly using electron diffraction. The sample for this study was prepared at the same composition by methods similar to those employed by Ball *et al* [5]. The idea was to distinguish the space groups by inspection of the $\frac{1}{2}\{111\}_p$ (more generally $\frac{1}{2}\{hhh\}_p$, h odd) satellite reflections. These index as {101} on the $I4/mcm$ cell ($\mathbf{a} = \mathbf{a}_p + \mathbf{b}_p$, $\mathbf{b} = -\mathbf{a}_p + \mathbf{b}_p$, $\mathbf{c} = 2\mathbf{c}_p$; $\mathbf{a}^* = \frac{1}{2}[110]_p^*$, $\mathbf{b}^* = \frac{1}{2}[\bar{1}, 1, 0]_p^*$, $\mathbf{c}^* = \frac{1}{2}[001]_p^*$), and as such would be space-group forbidden by the c glide plane symmetry [29] (see e.g. figure 3(c)). In $Imma$ ($\mathbf{a} = \mathbf{b}_p + \mathbf{c}_p$, $\mathbf{b} = 2\mathbf{a}_p$, $\mathbf{c} = \mathbf{b}_p - \mathbf{c}_p$; $\mathbf{a}^* = \frac{1}{2}[011]_p^*$, $\mathbf{b}^* = \frac{1}{2}[100]_p^*$, $\mathbf{c}^* = \frac{1}{2}[0, 1, \bar{1}]_p^*$), they index variously as {110} and {011}, and though the first is forbidden by the glide plane symmetry, the second is not [29]. For the purposes of direct comparison, we have re-set this $Imma$ cell to the same cell as used for $I4/mcm$. In this setting, the space group becomes $Icmm$. The difference between the two space groups then, in terms of systematic extinction conditions, is that {101} reflections are allowed but {011} reflections are forbidden for $Icmm$, whereas both are forbidden for $I4/mcm$. In summary, all four $\frac{1}{2}\{111\}_p$ type reflections are forbidden in $I4/mcm$ but two of the four are allowed in $Icmm$. It has been argued [26] that under the assumption of rigid octahedral tilting the intensity in these reflections would be zero, so in reality they would be expected to be weak. Therefore, the failure to find these reflections in x-ray or neutron patterns cannot necessarily be taken as proof of the structure in $I4/mcm$. In electron diffraction, however, we would expect to observe any reflection that is not space-group forbidden, so we have a basis on which the two proposed structures can be distinguished.

The observed electron diffraction patterns at major zone axis orientations (figure 3) are compatible with both space-group symmetries when the effects of multiple scattering are taken
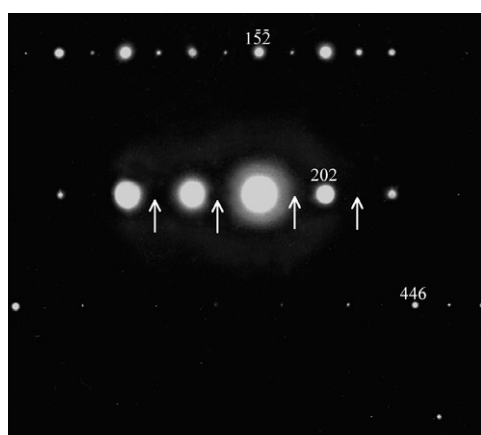
Figure 4. This pattern shows the same 202* row as figure 3(b) after tilting to dramatically reduce, if not eliminate, the effect of multiple scattering. The zone axis orientation is now close to $[\bar{5}\bar{3}5]$. Reflections 101, 303, etc (arrowed), are now totally absent, consistent with space group $I4/mcm$ but not with $Icmm$.

into account. However, eliminating or dramatically reducing the effects of multiple scattering by tilting away from such major zone axis orientations around the $\{101\}$ axis in reciprocal space led to the disappearance of the $\{101\}$ reflections in every case. Figure 4 shows a typical result. We conclude that the $\{101\}$ (thus all $\frac{1}{2}\{111\}_p$) reflections are space-group forbidden, consistent with the assumption of space group $I4/mcm$ but not with $Icmm$. This provides further strong if not irrefutable evidence that $I4/mcm$ rather than $Imma$ is the correct space-group symmetry of $Ca_{0.3}Sr_{0.7}TiO_3$.

In summary, a synchrotron x-ray powder diffraction study of $Ca_{0.3}Sr_{0.7}TiO_3$ shows one phase transition above room temperature, but no evidence at all for the two previously reported [12]. Arguments based on the effects of octahedral tilting on peak splitting suggest that the space-group symmetry of $Ca_{0.3}Sr_{0.7}TiO_3$ at room temperature is $I4/mcm$, a result that has been confirmed rather directly using electron diffraction. The weight of evidence presented here is such that the claim of space-group symmetry $Imma$ for $Ca_{0.3}Sr_{0.7}TiO_3$ at room temperature [12] can no longer be sustained.

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