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Structures and phase transition in the layered perovskite $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$: a new orthorhombic structure solved from high-resolution diffraction in combination with group theoretical analysis

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Abstract

The crystal structure of the layered perovskite $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ at room temperature has been solved by synchrotron x-ray powder diffraction in combination with group theoretical analysis. The structure is orthorhombic in $Cmmm$, on a cell with $a = 7.7556(1)$, $b = 7.7349(1)$ and $c = 7.7910(1)$ Å. It is believed that this is also the structure adopted by $\text{La}_{2/3}\text{TiO}_3$. Pertinent features are the alternation of fully and partly occupied layers of La (Sr) cations, and out-of-phase tilting of the TiO_6 octahedra around an axis perpendicular to the direction of the cation ordering. The compound undergoes a second order transition to a tetragonal structure, the transition temperature being estimated as 360 °C.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Among the many variants of perovskite, ABX_3 , those in which the A site is only partially occupied are attracting considerable interest. Such a situation arises, for example, when a divalent ion in the A site is replaced by a trivalent ion and the additional charge is compensated by the development on the same site of an appropriate number of vacancies. The system $\text{SrTiO}_3 - \text{La}_{2/3}\text{TiO}_3$, which we will write as $(1-3x/2)\text{SrTiO}_3 - (3x/2)\text{La}_{2/3}\text{TiO}_3$ or $\text{La}_x\text{Sr}_{(1-3x/2)}\text{TiO}_3$, represents an example system. This has been reported to show remarkable dielectric relaxation [1–3], this being attributed to increased latitude for the B-site ion when the A site is only partially occupied. At compositions close to the $x = 2/3$ end member, the ionic conductivity at 800 K is comparable with that of calcia-stabilized zirconia (CSZ) [3], and thus the material is considered a candidate for use in solid oxide fuel cells [4]. Additionally, the system has

been studied within the programme on synroc, a titanate based ceramic designed for the immobilization of high-level radioactive waste [5]. In particular, the system shows an interesting but unexplained variation with composition of resistance to amorphization by radiation [6].

The study reported here also forms part of our own systematic programme of research on the structures and phase transitions in perovskites and related materials [7–11].

The $x = 0$ end member, SrTiO_3 , is of course the perovskite aristotype, cubic, lattice parameter $a = 3.905 \text{ \AA}$, space group $Pm\bar{3}m$. This cubic structure is retained up to $x = 0.4$ [1, 12, 13], and to somewhat higher x for air-quenched samples [1, 13]. The interest of this paper, however, is the structure of the $x = 2/3$ end member, $\text{La}_{2/3}\text{TiO}_3$. It is not yet clear whether this end member can be obtained in totally pure, single-phase form. But it does seem that the structure can be stabilized at slight oxygen deficiency [14], or by various low level (5%) substitutions for La and Ti respectively on the perovskite A and B sites [1–3, 13–15]. A number of different structural models have been proposed. Tien and Hummel [1] recorded superlattice reflections indicative of cell doubling in more than one direction, whereas Abe and Uchino [14] and Bouwma *et al* [2] found evidence for cell doubling along one direction only, and attributed this to different ionic populations (layering) on successive layers of the perovskite A site. This implies a tetragonal structure on a cell of dimensions (referred to the edge of the cubic aristotype) $1 \times 1 \times 2$, probable space group $P4/mmm$. Abe and Uchino, however, noted an orthorhombic distortion at room temperature, and found the symmetry reverted to tetragonal somewhere above 300°C . More recently, MacEachern *et al* [16] fitted neutron diffraction patterns from $\text{La}_{0.67}\text{TiO}_3$ and $\text{La}_{0.7}\text{TiO}_3$ assuming an orthorhombic structure, in space group Pbn on a $\sqrt{2} \times \sqrt{2} \times 2$ cell. Their model has been used to fit the x-ray data recorded by Battle *et al* [13] from a slowly cooled specimen at $x = 0.5$. It is interesting to note that Battle *et al* were unable to index the more complex pattern recorded from a slowly cooled specimen at $x = 0.6$. Yoshioka, Yashima and their co-workers [3, 4, 15, 17] confirmed the orthorhombic distortion in the materials they studied ($\text{La}_{0.683}\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_3$ and $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$), and proposed an orthorhombic structure in space group $Pmmm$ on a $1 \times 1 \times 2$ cell. Temperature studies [15, 17] reveal that the structure reverts to the tetragonal $P4/mmm$ at about 360°C . The proposed room temperature structure is however problematic, in that it suggests no mechanism at all for the orthorhombic distortion [18]. The various proposed structures will be revisited briefly in section 2.

In this paper, we report a new orthorhombic structure for the composition $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ ($x = 0.6$). The structure has been deduced through a combination of synchrotron x-ray powder diffraction and group theoretical analysis. The structure is in space group $Cmmm$ on a $2 \times 2 \times 2$ cell, and incorporates a mechanism (octahedral tilting about an axis perpendicular to the direction of A-site layering) to produce the orthorhombic distortion. Temperature studies of the transition to the tetragonal structure are also reported.

2. Symmetry considerations

A reflection corresponding to a d -spacing of about 7.8 \AA , ($\times 2$ referred to the edge of the cubic aristotype) was reported in early work [1, 2, 14] and is quite evident (at 11.4°) in the diffraction from air-quenched $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ as displayed by Battle *et al* [13]. It is also seen as the lowest angle reflection in the pattern that we obtained (see figure 2, section 3). This 001 reflection provides a clear indication of cell doubling in at least one direction, and its strength in the x-ray pattern suggest this doubling is associated with the cation distribution. We concur with the suggestion by Abe and Uchino [14], now universally accepted, that the doubling arises from a layered ordering of La/Sr such that one layer is rich in the cations, and the next is poorer in cations since it contains a greater number of vacancies.

We are in agreement not only with the idea that the cations on the A sites show ordering into layers successively richer and poorer in cations, but also with the specific model in $P4/mmm$ on a $1 \times 1 \times 2$ cell proposed for the high temperature tetragonal structures of $\text{La}_{0.683}\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_3$ and $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ [3, 15, 18]. Based on this model, and the x-ray pattern recorded from $\text{La}_{0.683}\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_3$ at 500 °C, the occupancies of A-site layers by La^{3+} ions have been determined to alternate between 98 and 39% [18]. There is some movement of O^{2-} ions toward the (nearly) fully occupied layers, and a movement of Ti^{4+} atoms away from them, as might be expected given the additional positive charge on these layers. The tetragonal c/a ratio changes little up until 1000 °C, but decreases above this temperature [4]. The decrease in c/a is most likely due to the onset, above 1000 °C, of cation diffusion, leading towards a randomization of the cation (or vacancy) distribution.

The orthorhombic distortion at room temperature first seen by Abe and Uchino [14], and confirmed by Yoshioka and co-workers, is intriguing. Synchrotron x-ray studies on $\text{La}_{0.683}\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_3$ [17] and $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ [15] show that the orthorhombic structure develops by a continuous transition from the tetragonal $P4/mmm$ on cooling through 350 and 370 °C respectively. The driving mechanism for this distortion has not been identified [18]. One possibility is cation (or vacancy) ordering within the cation poor layers, but, since we have concluded that cation diffusion occurs only above 1000 °C, this could not provide the mechanism for distortion occurring around 360 °C. Based on our previous experience, we believe that octahedral tilting, that is, the tilting of corner-linked BX_6 octahedral units relative to one another, is a more likely cause. For this reason, we consider the structures that might arise from octahedral tilting in combination with a layered ordering of cations on the A sites. These possible structures were obtained from a group theoretical analysis, completed with the aid of the computer program ISOTROPY¹.

A layered ordering of cations and vacancies on the perovskite A site, as occurs in this structure in its tetragonal form, can be recognized as transforming according to the irreducible representation X_3^- ($k = 0, 0, 1/2$) of the parent space group $Pm\bar{3}m$. We take the z -axis to be normal to these layers. A full analysis of corner-linked tilting of the BX_6 octahedra, without the cation ordering, has been given previously [7]. The relevant irreducible representations (irreps) of the parent space group are (in the notation of Miller and Love [19]) R_4^+ ($k = 1/2, 1/2, 1/2$), corresponding to modes with out-of-phase tilting of octahedra in successive layers, and M_3^+ ($k = 1/2, 1/2, 0$), associated with in-phase octahedral tilting. The different possible structures produced by X_3^- cation displacements, followed by M_3^+ and/or R_4^+ octahedral tilting, have been enumerated using the computer program ISOTROPY. The methodology is described at greater length in earlier publications [7, 9–11], and at the ISOTROPY web site (see footnote 1). The results from the analysis are summarized in figure 1. This figure includes a description of the tilt system in each structure using Glazer's notation [20, 21]—briefly, the symbol $a^\#b^\#c^\#$ is used to indicate no tilt, in-phase octahedral tilting or out-of-phase octahedral tilting around the $\langle 001 \rangle$ axes of the parent $Pm\bar{3}m$ perovskite by showing the superscript # as 0, + or – respectively. The figure also includes an indication of group–subgroup relationships, and we have found using ISOTROPY that in all cases where a group–subgroup relationship is indicated the corresponding phase transition is allowed to be continuous.

It is interesting to re-examine the literature in the light of this analysis. Evidently, layered ordering of cations (relative to vacancies) on the perovskite A site, in the absence of octahedral tilting, gives a tetragonal structure in $P4/mmm$ on a $1 \times 1 \times 2$ cell. This is just the structure reported for $\text{La}_{0.683}\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_3$ and $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ at elevated

¹ ISOTROPY is a software package developed by Stokes and Hatch at Brigham Young University. ISOTROPY is available at www.physics.byu.edu/~stokesh/isotropy.html

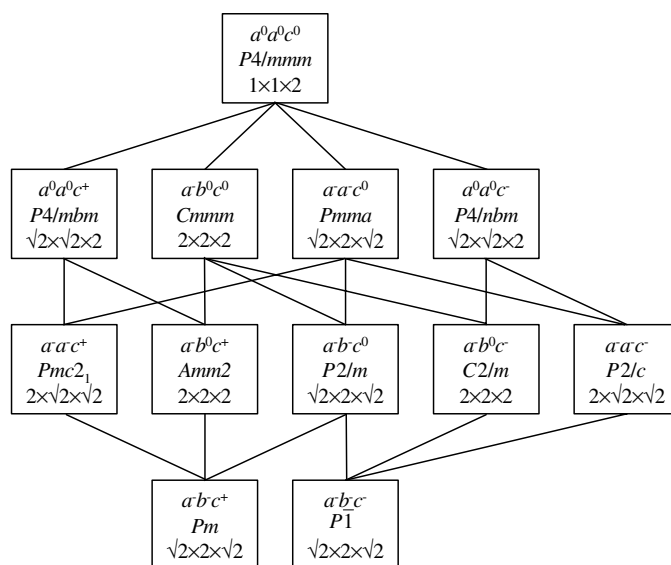


Figure 1. A schematic diagram showing the different possible structures generated by layered ordering of cations on the perovskite A site, followed by corner-linked tilting of the BX_6 octahedra. The tilting pattern is indicated using Glazer's notation, explained in the text. The space group is shown, along with the approximate cell dimensions in terms of the cell edge of the $Pm\bar{3}m$ parent—angles not required to be 90° are approximately 90° . The lines on the schematic diagram indicate group–subgroup relationships among the 12 space groups shown—the corresponding phase transitions are all allowed to be continuous.

temperatures [3, 15, 17, 18]. The indication from the literature [14, 15, 17] is that the room temperature structure is an orthorhombic structure derived from the tetragonal via a continuous phase transition. In this case, it can be seen from figure 1 that the only candidates are those in $Cmmm(a^-b^0c^0)$ and $Pmma(a^-a^-c^0)$. The symmetry at room temperature is clearly not tetragonal, and proposed orthorhombic structures in $Pmmm$ on a $1 \times 1 \times 2$ cell [3, 4, 15, 18], and in $Pban$ on a $\sqrt{2} \times \sqrt{2} \times 2$ cell [13, 16], do not appear as possibilities. As regards the former, we have observed (see figure 2(b)) weak reflections that cannot be indexed on a $1 \times 1 \times 2$ cell, and we find that an orthorhombic $\sqrt{2} \times \sqrt{2} \times 2$ cell does not account for the peak splitting observed in the synchrotron x-ray studies. We note that this rules out not only $Pban$, but also the structure in $Pmma(a^-a^-c^0)$ appearing in figure 1. These arguments leave the $Cmmm$ structure as the only real possibility.

3. Experimental and data analysis

$La_{0.6}Sr_{0.1}TiO_3$ samples were produced by our standard alkoxide/nitrate route [22] in which stoichiometric quantities of ethanolic titanium isopropoxide were hydrolysed by mixed lanthanum/strontium nitrate aqueous solutions. After thorough mixing and stir drying, the materials were calcined in air at 750°C for 1 h to remove nitrates and alcohol, followed by wet milling for 16 h using zirconia balls. The slurry was then dried at 110°C overnight, and the dried clumps were crushed in a mortar and pestle into fine powder. The powder was pelletized and sintered in air at 1550°C for at least 20 h, then furnace cooled. A polished surface was carbon coated and characterized by scanning electron microscopy (SEM), using a JEOL 6400 instrument fitted with a Tracor Northern energy dispersive spectrometer (EDS) operated at

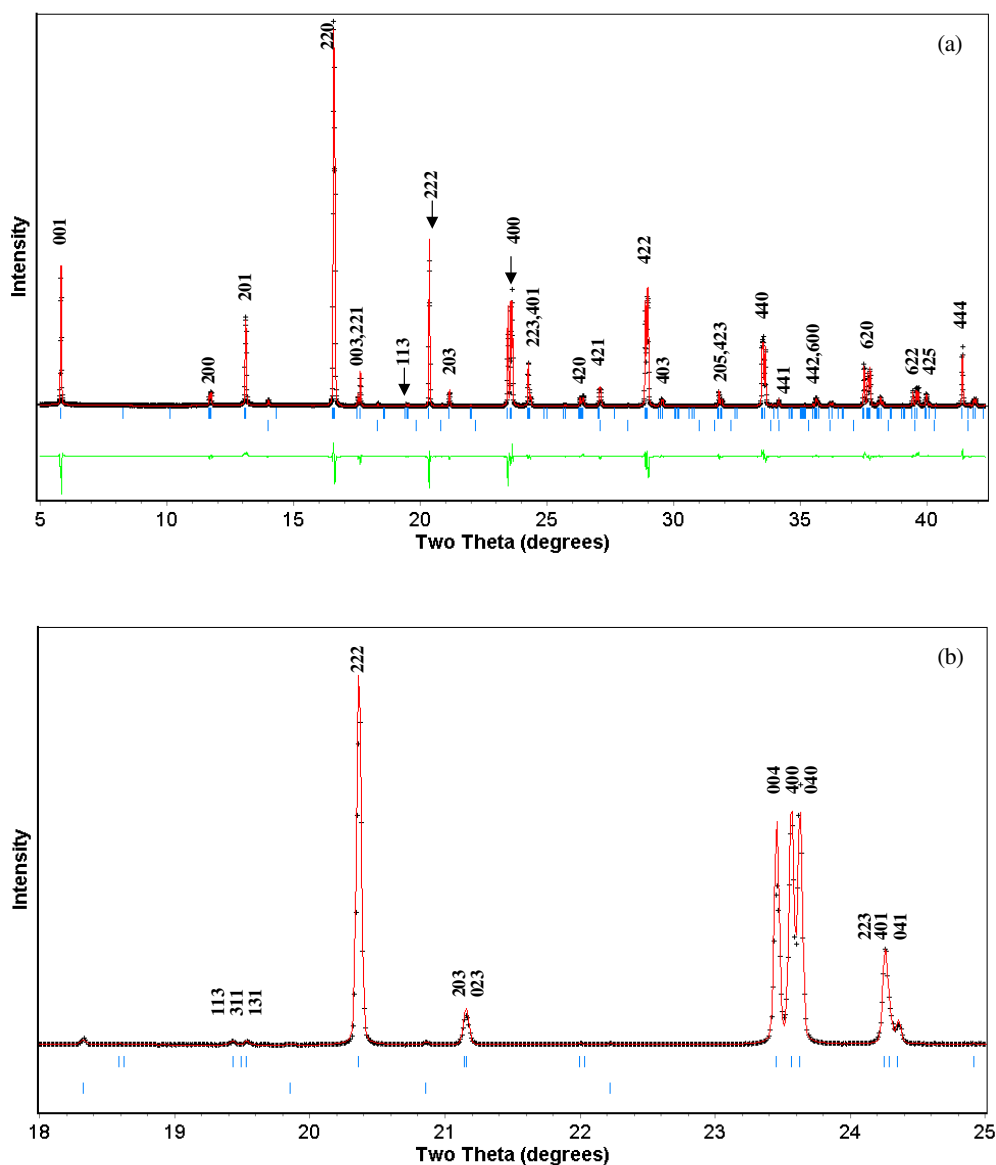


Figure 2. (a) The diffraction pattern (crosses), from $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ at room temperature, as recorded on the first image plate. The peaks are indexed on a cell of dimensions (referred to the edge of the cubic aristotype) $2 \times 2 \times 2$, and the three arrowed peaks will be discussed in the text. In fact, the plot is Rietica output, and includes the calculated pattern for the proposed structure in $Cmmm$ (continuous curve through the crosses), vertical markers showing the peak positions expected in this structure, a second set of markers for the peaks of the impurity rutile and a line beneath the pattern recording the difference between the observed pattern and that calculated in the Rietveld analysis. (b) Detail of the observed and calculated patterns in the 2θ range from 18° to 25° .

15 kV. A comprehensive set of standards was used for quantitative work, giving a high degree of accuracy. This verified the sample composition and showed the sample to be homogeneous

with minor amounts of rutile (~ 1 wt%, see below). The sample for the synchrotron x-ray work was subject to further heat treatment, comprising 2 h at 1100 °C, slow cooling at 0.05 °C min⁻¹ to 500 °C, then furnace cooling to room temperature. The intention was to produce a sample something akin to the Battle *et al* [13] slowly cooled samples. Finally, a small piece was broken off and crushed to fine powder using a mortar and pestle.

X-ray diffraction patterns were recorded using the Australian National Beamline Facility's powder diffractometer on beamline 20B [23], located at the Photon Factory, KEK, Japan. The instrument is a 573 mm (radius) Debye–Scherrer camera, the data being recorded on image plates. Measurements above room temperature were made using a custom-built furnace; temperatures were measured using a K-type thermocouple positioned adjacent to the sample, and controlled to within $\pm 1^\circ$ of the set point during measurement. Two image plates covering the 2θ ranges 5° – 45° and 45° – 85° , at a step size of 0.01° , were used, although in the high temperature work the furnace obscured the data above 75° . All exposures were for 15 min. The x-ray wavelength, determined by calibration using NIST silicon standard reference material 640b, was $\lambda = 0.79120$ Å. The sample was held in 0.3 mm capillaries, glass for the room temperature measurements and quartz glass for the measurements in the furnace. Samples were rotated during the measurements to reduce the effects of preferred orientation and improve powder averaging.

Patterns were inspected closely for peak splitting and for the presence of any weak superlattice peaks that might help to identify the structure. Lattice parameters were determined by Le Bail fitting [24] as implemented in the Rietveld program, Rietica [25]. The same program was used in its Rietveld mode for refinement of the structural models.

4. Results and discussion

The x-ray diffraction pattern recorded from $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ at room temperature is shown in figure 2. The figure shows only that part of the pattern recorded on the first (5° – 45°) image plate. The peaks in the figure are identified by indices based on the $2 \times 2 \times 2$ cell. Peaks with all even indices correspond to peaks from the ideal cubic aristotype. From an inspection of these peaks (see the detail in figure 2(b)) we note, in agreement with previous authors [4, 14, 15, 17], that the 222 is a single peak whereas the 400 peak (aristotype 200) is a triplet. At this juncture, we comment that structures on an orthorhombic $\sqrt{2} \times \sqrt{2} \times 2$ cell, such as that in *Pmma* (figure 1), give only a doublet at aristotype $h00$ reflections and so cannot account for the splitting observed. Peaks with just one index odd are superlattice peaks that imply doubling along one axis and are associated with the layered ordering of the A site cations. As foreshadowed earlier, these peaks (001, 201 etc) are quite strong. It is on this basis that previous authors have indexed the pattern on a $1 \times 1 \times 2$ cell. But, from figure 1, there is no orthorhombic structure on such a cell. Furthermore, when we look closely at the pattern (figure 2(b)), we see weak superlattice reflections indexing as 113 type, and these cannot be indexed on the $1 \times 1 \times 2$ cell. But they are just the reflections to be expected from out-of-phase (R-point) octahedral tilting [9]. The resolution afforded by the synchrotron-based diffractometer allows us to separate the 113/311/131, and to see (figure 2(b)) that there is intensity in the 113 and 131 reflections but apparently little in the 311. According to Glazer [21], the appearance of intensity in the R-point reflections with $k \neq l$ together with the absence of intensity at the corresponding $k = l$ reflection implies that only around the *a*-axis does tilting occur. This corresponds well with the model in *Cmmm*, tilt system $a^-b^0c^0$, which we propose here. Though the 113 type reflections are weak, they are well accounted for by our model—in addition, they are more easily seen (as is to be expected) in the neutron diffraction pattern, for example in that shown by MacEachern *et al* [16].

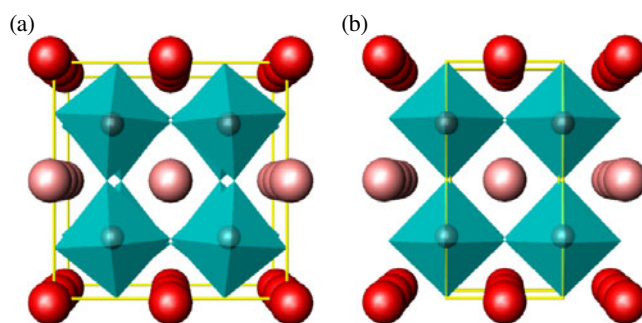


Figure 3. Representations of (a) room temperature orthorhombic and (b) high temperature tetragonal structures of $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$. The TiO_6 are shown as octahedra, the Ti atom being visible within them; the darker and lighter spheres outside these octahedra represent La/Sr in the fully and partly occupied layers respectively. The unit cell is outlined in each case. The figures shown are perspective views along the x -axis. The movements of O^{2-} and Ti^{4+} ions respectively towards and away from the fully occupied La/Sr layers result in an offset of the Ti atom discernible in both figures. The octahedral tilting in the room temperature structures is also clearly visible. These figures were prepared using ATOMS version 5.0.7, ©Eric Dowty, 1999.

The diffraction pattern has been fitted, and the structural model refined, by the Rietveld method. The fitting extended to that part of the pattern (45° – 85°) recorded on the second image plate. First, a Le Bail fit was carried out to determine lattice parameters and suitable peak width and shape parameters. The starting atomic positions in $Cmmm$ were obtained with the aid of ISOTROPY. The refinement proceeded in a straightforward manner, except for some difficulty in determining the distribution of La^{3+} ions, Sr^{2+} ions, and vacancies, over the two crystallographically distinct A sites in the $Cmmm$ structure. This problem is to be expected, since the information on occupancies comes from the superlattice reflections associated with the layered ordering of the La^{3+} and Sr^{2+} cations on the A sites, and is in effect limited to a measure of the difference in scattering power between the successive layers. This difference coupled with a knowledge of total content of La and Sr (amounting to three relations) is insufficient to provide a good determination of the occupancies (four in all) of La and Sr on each of the distinct sites involved. We were able to conclude, however, that one site is essentially fully occupied (97.4% if we assume there is no Sr on this site, or fully occupied with this site partly occupied, 7%, by Sr), so the occupancy on the other site must be close to 40%. The details of the structure, as refined by the Rietveld method, are included in table 1. This orthorhombic structure, along with the structure of the high temperature tetragonal phase, is depicted in figure 3. The impurity rutile has been quantified in the course of the Rietveld analysis [26], at about 1% by weight.

In spite of the difficulty mentioned above, the refinements confirm the cation ordering to the extent that the A sites at $z = 0$ are essentially fully occupied by La^{3+} (Sr^{2+}) ions, while the A sites at $z = 1/2$ contain all the vacancies. There is little or no Sr on the $z = 0$ sites. It can be seen, from the values of z tabulated for the room temperature structure, that the Ti^{4+} ions move away from the fully occupied layer, and the O^{2-} ions move (on average) towards it. Similar conclusions have been reached before, even on the basis of incorrect structural models. The distinctive feature of the present model is the movement of O atoms associated with octahedral tilting around the x -axis. The angle of tilt can be estimated from the oxygen coordinates as the angle made by the line joining O3 with O4 to the y -axis. This angle is given by $\tan^{-1} \{ (z(\text{O4}) - z(\text{O3})) / (1/2) \}$ and is $\sim 4.7^\circ$. Another estimate can be obtained from the lattice parameters, since tilting around a is expected to shorten b without affecting a , under the

Table 1. Details of the room temperature orthorhombic and high temperature tetragonal structures of $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$. The Wyckoff symbol for each site is shown. The number in parentheses beside each entry indicates the estimated standard deviation referred to the last digit shown. The La, Sr site at $z = 0$ is essentially fully occupied, and contains little or no Sr; the occupancy of the site at $z = 1/2$ is close to 40%.

Atom	Site	x	y	z
Room temperature, space group $Cmmm$, $a = 7.7556(1)$, $b = 7.7349(1)$, $c = 7.7910(1)$ Å				
(La, Sr)1	4g	0.2528(1)	0	0
(La, Sr)2	4h	0.2554(4)	0	1/2
Ti	8n	0	0.2496(3)	0.2604(1)
O1	4i	0	0.269(1)	0
O2	4j	0	0.226(1)	1/2
O3	4k	0	0	0.214(1)
O4	4l	0	1/2	0.255(1)
O5	8m	1/4	1/4	0.233(1)
Measure of fit: $R_{wp} = 5.7\%$				
<hr/>				
$T = 450$ °C, space group $P4/mmm$, $a = 3.8865(1)$, $c = 7.8299(1)$ Å				
(La, Sr)1	1c	1/2	1/2	0
(La, Sr)2	1d	1/2	1/2	1/2
Ti	2g	0	0	0.2610(2)
O1	1a	0	0	0
O2	1b	0	0	1/2
O3	4i	0	1/2	0.2405(7)
Measure of fit: $R_{wp} = 5.6\%$				

(often dubious) assumption that the octahedra tilt as rigid units. The corresponding estimate is $\cos^{-1}(b/a)$, in this case $\sim 4.2^\circ$. These angles are in the mid-range of typical angles for octahedral tilting in perovskites, and are in reasonable agreement with each other. Certainly, there seems no reason to doubt the model we have proposed.

The phase transition to tetragonal was examined, and the tetragonal structure refined, as part of this work. X-ray diffraction patterns were recorded in furnace runs in 10°C temperature steps from 60 to 300°C , and in steps of 25 up to 600°C . Lattice parameters obtained from Le Bail fitting of these patterns are recorded in figure 4. It was important to include data from the second image plate in the Le Bail analysis, since the $008/800/080$ reflections appearing on the second plate at around 48° were better resolved than the $004/400/040$ reflections shown in figure 2(b). Accordingly, it was possible to resolve the $800/080$ doublet at temperatures where the $400/040$ doublet could no longer be resolved. The $800/080$ doublet could be resolved up to about 250°C , and showed as a broadened peak up to $\sim 290^\circ\text{C}$. The variation of the lattice parameters a and b with temperature is evidently linear, consistent with a classical second order transition and strain proportional to the square of the order parameter [27, 28]. Assuming we have such a classical transition, and extrapolating from temperatures up to 290°C , where the resolution or broadening of the $800/080$ doublet should ensure reliability of these parameters, leads to an estimate of 360°C for the temperature of the transition to the tetragonal phase. It is inevitable that, when studying phase transitions in which the distortions tend continuously to zero, whatever the instrumental resolution there comes a point where this resolution is insufficient to resolve the distortions involved. Despite the higher resolution associated with their use of a crystal analyser, Ali *et al* [15] encountered this ubiquitous problem, and may have underestimated their transition temperature as a result. There is no problem with Le Bail fitting at 360°C and above, since the symmetry there is truly tetragonal, in $P4/mmm$ on a

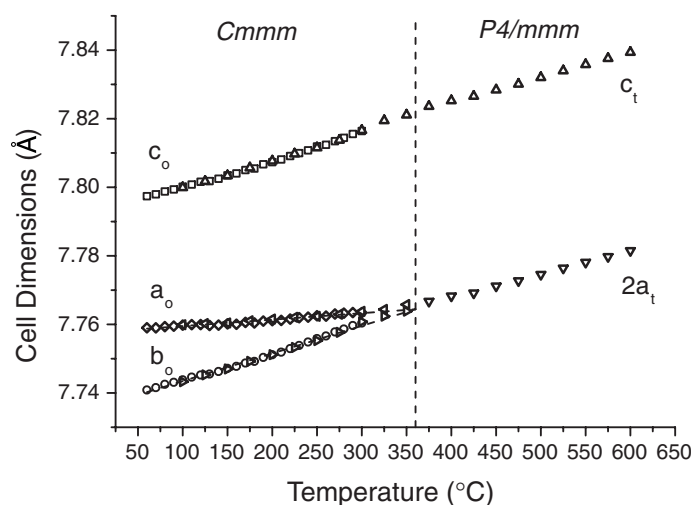


Figure 4. Lattice parameters for $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ as a function of temperature. The transition to tetragonal has been estimated at 360°C , based on a linear extrapolation of the parameters a and b from their values at lower temperatures.

$1 \times 1 \times 2$ cell. We note that the tetragonal distortion is substantial and, if anything, increases at higher temperatures.

To summarize, we find that the transition between the orthorhombic and tetragonal structures is a classical second order transition, with strain proportional to the square of the order parameter, and a transition temperature 360°C . There is no suggestion to 600°C of a tendency towards any higher symmetry structure.

Finally, we carried out a structure refinement from the pattern at 450°C , a temperature at which the tetragonal structure is well established. The results from this refinement are recorded in table 1. The two variable parameters in this structure correspond to movement of the O3 ions towards and the Ti^{4+} ions away from the fully occupied La/Sr layer, as was also noted in the orthorhombic structure at room temperature. The results are in reasonable agreement with those obtained previously [18] in the high temperature x-ray study of $\text{La}_{0.683}\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_3$.

5. Summary and conclusions

The room temperature structure of $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$, which we take to represent the structure of $\text{La}_{2/3}\text{TiO}_3$, has at last been successfully determined, nearly 50 years after the first report [29] of this (latter) compound appeared. Symmetry arguments were used to limit the possibilities, then the structure solution completed from an x-ray synchrotron powder diffraction study revealing both small splittings of the main perovskite peaks and weak superlattice reflections. The structure, orthorhombic in $Cmmm$, has been successfully refined by the Rietveld method.

The phase transition to tetragonal has been examined as part of this work. From the temperature dependence of the lattice parameters we have concluded that the transition is very likely a classical second order transition in which the strain is proportional to the square of the order parameter. Extrapolation on this basis leads to an estimated 360°C for the temperature of the orthorhombic-to-tetragonal transition in $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$.

Both tetragonal and orthorhombic structures show alternately occupied and partly occupied layers of La (Sr) cations. The new feature of the orthorhombic structure is the

out-of-phase tilting of TiO_6 octahedra (through about 4°) around an axis perpendicular to the direction of the cation ordering. This provides, for the first time, a simple plausible explanation for the orthorhombic distortion below the phase transition, as is observed at room temperature.

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Note added in proof. The structure has also been solved in a concurrent but independent study by Yashima and co-workers [30]. The compound examined was $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$, and both electron and neutron diffraction techniques were employed. The structure was refined from the neutron powder diffraction data, the results obtained being identical (generally within the quoted errors) with those presented here.

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