Suppression of strain coupling in perovskite La$_{0.6}$Sr$_{0.1}$TiO$_3$ by cation disorder

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(Received 23 March 2007; published 7 August 2007)

An octahedral tilting transition has been investigated in two samples of La$_{0.6}$Sr$_{0.1}$TiO$_3$ by powder neutron diffraction. One (slowly cooled) sample had a degree of cation/vacancy ordering on the A sites and was tetragonal, $P4/mmm$, at high temperatures. The second (quenched) sample had disordered cations and cubic, $Pm$

3$m$, symmetry at high temperatures. On cooling, both underwent the same $P$-point tilting transition at $\sim 560–570$ K, to give symmetry changes $P4/mmm \leftrightarrow Cm

mm$ and $Pm3m \leftrightarrow 14/mcm$, respectively. From the evolution of the tilt angles, the transition appears to be close to tricritical in both cases. As expected from a Landau expansion in the two order parameters, the transition temperature was found to be only weakly dependent on the degree of cation order. In contrast with the expectation of standard patterns of strain to order parameter coupling, however, the tilted (tetragonal) form of the disordered sample remained metrically cubic, implying that coupling of the tetragonal shear strain with the octahedral tilting was suppressed. It is proposed that cation disordering causes the development of local strain heterogeneities in crystals of La$_{0.6}$Sr$_{0.1}$TiO$_3$ which prevent a coherent, long-range shear strain from developing. Manipulation of the degree of cation order in perovskites with carefully selected compositions might therefore provide a means by which the magnitudes of ferroelastic strains could be engineered according to the requirement of particular applications.

DOI: 10.1103/PhysRevB.76.054108 PACS number(s): 64.70.Kb, 61.50.Ks, 61.12.Ld

INTRODUCTION

Multiple phase transitions in a single material can, in principle, give rise to the development or modification of more than one distinct property of technological interest. In this context, the current search for “multiferroic” materials is motivated by a desire to be able to manipulate different combinations of properties simultaneously by the application of external fields. In one class of such materials, the relevant atomic scale mechanisms all occur on a short time scale such that the responses to an applied field occur more or less instantaneously. This includes properties that are associated with changes in electronic structure, small atomic displacements, and realignment of magnetic or electric dipoles. There is a second class of materials, however, in which the local processes operate on quite different time scales. Here a key mechanism is chemical diffusion, and possibilities arise for focusing in particular on how cation ordering impacts on the spontaneous strain behavior of these otherwise identical perovskites at different degrees of cation ordering, examine the spontaneous strain behavior of these otherwise identical perovskites at different degrees of cation ordering, focusing in particular on how cation ordering impacts on the octahedral tilting transition and how it modifies the ferroelastic response.

LANDAU THEORY

The perovskite structures formed by combining layered ordering on the A sites with in-phase (+) and out-of-phase transitions of the BX$_6$ octahedral tilting have been enumerated by Howard and Zhang. The layered ordering of cations (or vacancies) to have been applied to ferroelastic transitions in perovskites, however, and the purpose of the present paper is to describe an octahedral tilting transition for which the ferroelastic response displays a strong and unexpected sensitivity to ordering of cations and vacancies on A sites of the perovskite structure.

The work reported here follows our previous structural studies of A-site deficient perovskites with compositions close to La$_{2/3}$TiO$_3$. These perovskites, when prepared by slow cooling, show an ordering of cations and vacancies onto alternate planes such that the A sites in one plane are essentially fully occupied and those on the next only about one-third occupied. The structures also show a tilting of the TiO$_6$ octahedra at room temperature that is removed via a continuous phase transition as the temperature is raised. It became evident that, by varying the preparation, in particular by rapid cooling, the development of cation ordering could be largely prevented. The objectives of this work were to examine the spontaneous strain behavior of these otherwise identical perovskites at different degrees of cation ordering, focusing in particular on how cation ordering impacts on the octahedral tilting transition and how it modifies the ferroelastic response.
on the perovskite $A$ site was recognized as transforming with the symmetry of the irreducible representation [irrep (Ref. 14)] $X_1^{\pm}$ ($k=0,0,1/2$) of the aristotype $Pm\bar{3}m$ space group. As always, the in-phase and out-of-phase octahedral tilting were taken to be associated with irreps $M'_1^1$ ($k=1/2,1/2,0$) and $R'_1^2$ ($k=1/2,1/2,1/2$), respectively.

$$G = \frac{1}{2}a_1\Theta_{11}\left[\coth\left(\frac{\Theta_{11}}{T}\right) - \coth\left(\frac{\Theta_{11}}{T_{c1}}\right)\right](q_1^2 + q_2^2 + q_3^2) + \frac{1}{2}a_2\Theta_{22}\left[\coth\left(\frac{\Theta_{22}}{T}\right) - \coth\left(\frac{\Theta_{22}}{T_{c2}}\right)\right](q_1^2 + q_2^2 + q_3^2) + \frac{1}{4}b_1(q_1^2 + q_2^2 + q_3^2)^2$$

$$+ \frac{1}{4}b'_1(q_1^4 + q_2^4 + q_3^4) + \frac{1}{4}b_2(q_1^2 + q_2^2 + q_3^2)^2 + \frac{1}{4}b'_2(q_1^4 + q_2^4 + q_3^4) + \frac{1}{6}c_1(q_1^2 + q_2^2 + q_3^2)^3 + \frac{1}{6}c'_1(q_1q_2q_3)^2$$

$$+ \frac{1}{6}c''_1(q_1^2 + q_2^2 + q_3^2)(q_1^2 + q_2^2 + q_3^2) + \frac{1}{6}c_2(q_1^2 + q_2^2 + q_3^2)^3 + \frac{1}{6}c''_2(q_1^2 + q_2^2 + q_3^2)(q_1^2 + q_2^2 + q_3^2)$$

$$+ \lambda_4(q_1^2 + q_2^2 + q_3^2)(q_1^4 + q_2^4 + q_3^4) + \lambda'_4(q_1^2q_2^2 + q_2^2q_3^2 + q_3^2q_1^2) + \lambda_5e_1(q_1^4 + q_2^4 + q_3^4) + \lambda_6e_2(q_1^2 + q_2^2 + q_3^2) + \lambda_7e_3(q_1^2 + q_2^2 + q_3^2)$$

$$+ \lambda_8[\sqrt{3}e_0(q_3^2 - q_1^2) + e_1(2q_2^2 - q_3^2 - q_1^2)] + \lambda_9[\sqrt{3}e_0(q_3^2 - q_2^2) + e_1(2q_2^2 - q_3^2 - q_1^2)] + \lambda_{10}(e_3q_2q_3 + e_3q_2q_3 + e_3q_2q_3)$$

$$+ \lambda_{11}(q_1^2 + q_2^2 + q_3^2)(e_1^2 + e_2^2 + e_3^2) + \lambda_5(q_1^2e_1^2 + q_2^2e_2^2 + q_3^2e_3^2) + \frac{1}{4}(C_{11}^0 - C_{12}^0)(e_1^2 + e_2^2) + \frac{1}{6}(C_{11}^0 + 2C_{12}^0)e_1^2 + \frac{1}{4}C_{44}^0(e_1^2 + e_2^2 + e_3^2).$$

(1)

Here $q_1$, $q_2$, and $q_3$ are components of the order parameter for cation (or vacancy) layered ordering. They correspond to ordering of cations onto planes perpendicular to the crystallographic $y$, $z$, and $x$ axes, respectively, of the parent $Pm\bar{3}m$ perovskite [where these $x$, $y$, and $z$ axes are aligned parallel to the reference axes $X$, $Y$, and $Z$ of Eq. (1)]. The quantities $q_4$, $q_5$, and $q_6$ are components of the order parameter for tilting—they can be considered to correspond to tilts of the TiO$_6$ octahedra around the $Z$, $X$, and $Y$ reference axes, respectively. Note that this free-energy expression is closely similar to that obtained for in-phase ($M'_1$) and out-of-phase ($R'_1^2$) tilts acting together. The only difference is that the components $q_1$, $q_2$, and $q_3$ representing $M'_1$ tilting have been cycled, being replaced here by $q_2$, $q_3$, and $q_1$, respectively. The quantities $a_1$, $a_2$, $b_1$, etc., are normal Landau coefficients, $\Theta_{11}$ and $\Theta_{22}$ are saturation temperatures, $T_{c1}$ and $T_{c2}$ are critical temperatures for the cation ordering and tilting transitions, respectively, $\lambda_1$, $\lambda_3$, etc., are coupling coefficients, $C_{11}^0$, $C_{12}^0$, and $C_{44}^0$ are bare elastic constants (i.e., of the parent cubic structure), and $e_4$, $e_5$, and $e_6$ are shear strain components. The symmetry-adapted strains $e_{1a}$, $e_{0a}$, and $e_1$ are combinations of the linear strain components $e_1$, $e_2$, and $e_3$ as

$$e_{1a} = (e_1 + e_2 + e_3),$$

$$e_{0a} = (e_1 - e_2),$$

$$e_1 = \frac{1}{\sqrt{3}}(2e_5 - e_1 - e_2).$$

To this point, only the lowest-order strain-order parameter coupling terms have been included. Direct biquadratic coupling, $\lambda_4q_4q_4^2$, etc., is included for completeness although the coupling mechanism might be indirect via the common strain, in which case the direct coupling terms would not be required. Table I lists space groups for product structures described by this free-energy expansion for the $La_{0.6}Sr_{0.1}TiO_3$ system. Figure 1 shows the unit cells of these structures in relation to the cell of the parent $Pm\bar{3}m$ perovskite and the reference system of Eq. (1).

**TABLE I.** Properties of parent group $Pm\bar{3}m$ and selected subgroups derived by coupling between separate order parameter components associated with irreps $X'_3^1$ and $R'_1^2$. The orientations are those indicated by computer program ISOTROPY.

<table>
<thead>
<tr>
<th>Subgroup</th>
<th>Order parameter components</th>
<th>$X'_3^1$</th>
<th>$R'_1^2$</th>
<th>Lattice vectors</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pm\bar{3}m$</td>
<td>0 0 0 0 0 0 0</td>
<td>(100),(010),(001)</td>
<td>(000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P4_{1}mmm$</td>
<td>0 q_3 0 0 0 0</td>
<td>(100),(010),(002)</td>
<td>(00 1/2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I4/mcm$</td>
<td>0 0 0 0 q_5 0</td>
<td>(011),(0T1),(002)</td>
<td>(000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Cmmm$</td>
<td>0 q_3 0 0 q_5 0</td>
<td>(200),(020),(002)</td>
<td>(111/2 - 1/2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Applying the equilibrium conditions $\partial G/\partial e=0$ leads to the following relationships between strains and order parameters:

\begin{align}
\frac{\partial G}{\partial e_1} &= \frac{1}{3}(C_{11}^0 + 2C_{12}^0) - \frac{1}{2}(C_{11}^0 - C_{12}^0)
\end{align}

(6)

\begin{align}
\frac{\partial G}{\partial e_2} &= \frac{1}{2}(C_{11}^0 - C_{12}^0)
\end{align}

(7)

\begin{align}
\frac{\partial G}{\partial e_3} &= -\frac{1}{2}(C_{11}^0 - C_{12}^0)
\end{align}

(8)

\begin{align}
\frac{\partial G}{\partial e_4} &= \frac{1}{2}(C_{11}^0 + 2C_{12}^0)
\end{align}

(9)

\begin{align}
\frac{\partial G}{\partial q_1} &= \frac{1}{3}(C_{11}^0 + 2C_{12}^0) - \frac{1}{2}(C_{11}^0 - C_{12}^0)
\end{align}

(10)

Substituting these into (5) gives

\begin{align}
G &= \left[ a_1 \Theta_{s1} \left( \frac{\coth(\Theta_{s1}/T)}{\coth(\Theta_{c1}/T)} \right) \right] q_2^2 \\
&+ \left[ a_2 \Theta_{s2} \left( \frac{\coth(\Theta_{s2}/T)}{\coth(\Theta_{c2}/T)} \right) \right] q_3^2 \\
&+ \left[ b_1 \Theta_{s1} \left( \frac{\coth(\Theta_{s1}/T)}{\coth(\Theta_{c1}/T)} \right) \right] q_4^2 \\
&+ \left[ b_2 \Theta_{s2} \left( \frac{\coth(\Theta_{s2}/T)}{\coth(\Theta_{c2}/T)} \right) \right] q_3^2 \\
&+ \left[ \lambda_1 e_1 q_2^2 + \lambda_2 e_2 q_3^2 + \lambda_3 e_3 q_4^2 + \lambda_4 e_4 q_5^2 + \lambda_5 e_5 q_6^2 + \lambda_6 e_6 q_7^2 \right] \\
&+ \left[ \lambda_7 e_7 q_8^2 + \lambda_8 e_8 q_9^2 + \lambda_9 e_9 q_{10}^2 + \lambda_{10} e_{10} q_{11}^2 \right] \\
&+ \left[ \lambda_{11} e_{11} q_{12}^2 + \lambda_{12} e_{12} q_{13}^2 + \lambda_{13} e_{13} q_{14}^2 + \lambda_{14} e_{14} q_{15}^2 \right] \\
&+ \left[ \lambda_{15} e_{15} q_{16}^2 + \lambda_{16} e_{16} q_{17}^2 + \lambda_{17} e_{17} q_{18}^2 + \lambda_{18} e_{18} q_{19}^2 \right]
\end{align}

(5)

The situation considered in this paper is that in which the parameter $q_2$, corresponding to the state of cation order, is fixed at different values according to the sample preparation procedure and remains fixed over the temperature range in which the octahedral tilting order parameter $q_5$ is studied. Equation (10) then reads as a 2-4-6 expansion for the tilting order parameter $q_5$, and the equilibrium condition giving the value of this order parameter will be

\begin{align}
\frac{\partial G}{\partial q_5} &= \frac{1}{3}(C_{11}^0 + 2C_{12}^0) - \frac{1}{2}(C_{11}^0 - C_{12}^0)
\end{align}

(11)

\begin{align}
\frac{\partial G}{\partial q_2} &= \frac{1}{3}(C_{11}^0 + 2C_{12}^0) - \frac{1}{2}(C_{11}^0 - C_{12}^0)
\end{align}

(12)

\begin{align}
\lambda_4^* &= \frac{\lambda_1 \lambda_2}{\lambda_3} + \frac{\lambda_1 \lambda_2}{\lambda_3} \\
&+ \frac{\lambda_1 \lambda_2}{\lambda_3}
\end{align}

(13)

For $T$, $T_{c2} \gg \Theta_{s2}$, $a_2 \Theta_{s2} \left( \coth(\Theta_{s2}/T) - \coth(\Theta_{c2}/T) \right)$ be-
comes $a_2(T - T_c)$ and the renormalized transition temperature is given by

$$T'_c = T_c - 2\lambda_4 q_4^2 a_2.$$  \hspace{1cm} (15)

If the transition is close to tricritical in character ($b_2^* = 0$), the result from Eq. (14) will be, again for $T, T_c \ll \Theta_{c2}$,

$$q_4^2 = \frac{a_2(T_c^* - T)}{c_2 + e_2^\alpha}.$$  \hspace{1cm} (16)

For $La_{0.6}Sr_{0.1}TiO_3$, the relationships among $T_{c1}, T_{c2}, \Theta_{c1}$, and $\Theta_{c2}$ are $T_{c1} > T_{c2} > \Theta_{c1}, \Theta_{c2}$. The Landau description therefore leads to simple predictions of how the tilting transition should develop in crystals with different but fixed degrees of cation order. First, the effect of direct coupling through the biquadratic term, $\lambda_4 q_2^2 q_4^2$, and indirect coupling through the common strains [Eq. (13)] should be for the tilting transition to occur at a different transition temperature according to the degree of cation order present [Eq. (15)]. Second, the tilting transition is expected to give rise to an orthorhombic strain $\varepsilon_0$ [Eq. (8)] and a change in the tetragonal strain $\varepsilon_1$ [Eq. (7)]. The excess tetragonal strain due to $q_2^2$ will be a factor of $\sqrt{3}$ smaller than $\varepsilon_0$ and have opposite sign. Finally, the evolution of the order parameter (effectively the octahedral tilt angle) below $T'_c$ should be independent of $q_2$, since the fourth order coefficient $b_2^*$ remains a constant [Eq. (12)]. What we observe experimentally, below, is that reducing $q_2$ leads to a substantial reduction in the magnitude of the tetragonal strain as well as causing a more subtle change in the evolution of the tilt angle. This can be understood if the coupling coefficient $\lambda_4$ is itself sensitive to $q_2$ in a manner not anticipated in Eq. (1).

**EXPERIMENT**

**Sample preparation**

The $La_{0.6}Sr_{0.1}TiO_3$ samples were produced by a standard alkoxide-nitrate route, wherein stoichiometric quantities of ethanolic titanium isopropoxide were hydrolyzed by mixed lanthanum and strontium nitrate aqueous solutions. After thorough mixing and stir drying, the materials were calcined in air for 1 h to remove nitrates and alcohol, then subjected to 16 h of wet milling using zirconia balls. The slurry was thoroughly mixed and stir dried, the materials were calcined in air at 1400 °C for 96 h and furnace cooled to room temperature, followed by a subsequent quenching process from 1350 °C (comprising 2 h at 1350 °C before being quenched to room temperature). The quenching here was intended to preserve the disorder as presumed to exist at 1350 °C.

Both types of samples were characterized by scanning electron microscopy, using a JEOL 6400 instrument fitted with a Tracor Northern energy dispersive spectrometer operated at 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 samples to be homogeneous, with very small amounts of rutile (<1%, just detectable in the diffraction patterns) in the slowly cooled sample and of La$_4$Ti$_6$O$_{24}$ (<1%, not detectable by diffraction) in the quenched one. Finally, both samples were crushed to fine powder using a mortar and pestle for neutron powder diffraction.

**Neutron diffraction**

Time-of-flight powder neutron diffraction data were recorded using the high-resolution powder diffractometer (HRPD) at the ISIS neutron facility, Rutherford Appleton Laboratories, UK. The two powdered samples—slow cooled and quenched—were loaded into thin-walled 11-mm-diameter vanadium sample cans. For room temperature measurement, the sample can was suspended in the vacuum tank from the standard ISIS candlestick. For the higher-temperature measurements an ISIS-designed furnace was used. This furnace employs a cylindrical vanadium element and operates under high vacuum (pressure < 10^-6 mbar). The thermometry is based on type $K$ (Chromel-Alumel) thermocouples positioned in contact with the sample about 20 mm above the beam center. The diffraction patterns were recorded in both back-scattering and 90° detector banks, over the time-of-flight range 30–130 ms, corresponding to $d$ spacings from 0.6 to 2.6 Å (at a resolution $\Delta d/d \sim 4 \times 10^{-4}$) and from 0.9 to 3.7 Å ($\Delta d/d \sim 2 \times 10^{-3}$), respectively. The patterns were normalized to the incident beam spectrum as recorded in the upstream monitor, and corrected for detector efficiency according to prior calibration with a vanadium scan. Room temperature patterns were recorded to a total incident proton beam in the range 35–40 $\mu$A h corresponding to a minimum 1 h of data collection, and the high-temperature patterns to a total incident proton beam of about 8 $\mu$A h, corresponding to roughly 15 min of data collection. The temperature intervals ranged from 25 down to 5 K in the vicinity of the octahedral tilting phase transition. Thermal equilibration was achieved by delaying data collection for a period of at least 5 min (depending on the size of the temperature step) after stability at the set temperature had been achieved.

**Diffraction patterns and phase identification**

Four different structures have been encountered in this work, the details of which have been recorded in Table I. We remark that $q_2 \neq 0$ will lead to the appearance of what we term X-point reflections, indexing with two even and one odd index when referred to a doubled perovskite cell, and that $q_3 \neq 0$ leads to R-point reflections with indices all odd.

The slowly cooled sample shows, as before, both cation ordering ($q_2 \neq 0$) and octahedral tilting ($q_3 \neq 0$) at room temperature, hence its space group is $Cmmm$. The X-point re-
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FIG. 2. (Color online) Extracts (1.85 < d < 2.4 Å) from the neutron diffraction patterns recorded in the back-scattering detector banks from (a) slowly cooled and (b) quenched La$_{0.6}$Sr$_{0.1}$TiO$_3$. The plots are the usual Rietveld method graphics, wherein crosses represent the observed data, continuous lines through these are the fitted patterns, vertical markers show the expected peak positions, and the line beneath the pattern records the difference between the observed pattern and that calculated in the Rietveld analysis. The peaks are indexed on cells of dimensions $2 \times 2 \times 2$ or $\sqrt{2} \times \sqrt{2} \times 2$ (referred to the edge of the cubic aristotype) as appropriate for the space group and structure assumed. In the pattern from the quenched sample, (b), the almost total absence of intensity around the X points confirms that in this sample the cation/vacancy ordering has been largely suppressed. For further discussion, see text.

flections, indicative of cation and vacancy ordering, as well as R-point reflections arising from the octahedral tilting, are both readily seen [Fig. 2(a)]. The combination of these two effects induces an orthorhombic distortion, evident through the resolved triplet at (004).

The room temperature diffraction pattern from the quenched sample shows only trace diffuse intensity at the X points [Fig. 2(b)], confirming that cation ordering is largely suppressed ($q_5$ = 0). However, there remain significant, if broadened, peaks at the $R$ points, attributed as usual to octahedral tilting ($q_5$ ≠ 0). Accordingly, the space group is taken to be $I4/mcm$. The coincidence of the 220 and 004 peaks in this tetragonal structure indicates that this structure is metrically very nearly cubic.

Heating either sample leads to the removal, at around 280 °C, of octahedral tilting, evidenced by the disappearance of the R-point reflections. For the slowly cooled sample, this corresponds to a transition from the orthorhombic structure in $Cmmm$ ($q_5$ ≠ 0, $q_z$ = 0) to the tetragonal in $P4/mmm$ ($q_5$ ≠ 0, $q_z$ = 0). The disappearance of the R-point reflections, and the increase in symmetry from orthorhombic to tetragonal, are both seen through the diffraction data presented in Fig. 3. For the quenched sample, the transition is one from a metrically cubic $I4/mcm$ ($q_2$ = 0, $q_5$ ≠ 0) to the cubic structure in $Pm\bar{3}m$ ($q_2$ = $q_5$ = 0).

Structure refinement

Phase identification was followed by structure refinement. In this, the neutron diffraction patterns were fitted, and both lattice parameters and atomic positions determined, using the Rietveld method$^{20}$ as implemented in the GSAS computer program.$^{21,22}$ Patterns from both the back-scattering and 90° detector banks were fitted simultaneously, the diffractometer constant for the 90° bank being refined once for each independent experimental setup and then fixed at the value so obtained. The peak shapes were modeled as convolutions of back-to-back exponentials with a pseudo-Voigt function and, for the back-scattering and 90° data, respectively, two and three peak width parameters were varied. The background was modeled as a sum of Chebyshev polynomials. The starting models for the structures in the slowly cooled sample, in space groups $Cmmm$ and $P4/mmm$, were taken from our earlier publication.$^{11}$ The starting models for the structures in the quenched sample were in space groups $I4/mcm$ and $Pm\bar{3}m$, as for standard $ABX_3$ perovskites in the same space groups, apart from reduced A-site occupancy. Internal coordinates were refined along with displacement parameters, the latter being taken to be isotropic except for the oxygen displacement parameter in the $Pm\bar{3}m$ structure which was taken to be anisotropic. Cation occupancies were set, not refined, in this work. In the slowly cooled sample the A sites in one layer were assumed to be fully occupied by La$^{3+}$ ions, and
the A sites in the next occupied 20% by La$^{3+}$ and 20% by Sr$^{2+}$. (There are, along with limited experimental evidence, theoretical grounds$^{23}$ for believing that the cation arrangement will be such as to maximize charge on the occupied layer.) In the quenched samples all A sites were considered to be 60% occupied by La$^{3+}$ and 10% by Sr$^{2+}$.

The lattice parameters obtained from these refinements, suitably scaled for comparison with the cubic reference structure, are shown in Fig. 4. The orthorhombic to tetragonal transition in the slowly cooled sample is evident. The transition tetragonal to cubic in the quenched sample can be seen quite readily in the diffraction patterns. The orthorhombic to tetragonal transition in the slowly cooled sample is evident. The structure, which it has cubic symmetry.

The evolution of the octahedral tilt angle $\phi$ for both quenched and slowly cooled samples is shown in Fig. 5(a). The tilting transition appears to be close to tricritical in character, since $\phi^2$ varies approximately linearly with temperature for both samples $[q_5 \times (T^*_c - T)$; Fig. 5(b)]. The linear fits shown in Fig. 5(b) give $T_c = 561$ and 571 K, respectively, for the slowly cooled and quenched samples. Slight differences in the slopes of these fits suggest that the evolution of tilt angle with temperature may be not quite the same in both samples.

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The linear strain components $e_1$, $e_2$, and $e_3$ have been calculated for the unit cell orientations shown in Fig. 1 as, for the P4/mmm structure,

$$e_1 = e_2 = \frac{a - a_0}{a_0}, \quad e_3 = \frac{c/2 - a_0}{a_0},$$

for the Cmmm structure,

$$e_1 = \frac{a/2 - a_0}{a_0}, \quad e_2 = \frac{b/2 - a_0}{a_0}, \quad e_3 = \frac{c/2 - a_0}{a_0},$$

and, for the I4/mcm structure,

$$e_1 = \frac{a/2 - a_0}{a_0}, \quad e_2 = \frac{b/2 - a_0}{a_0}, \quad e_3 = \frac{c/2 - a_0}{a_0}.$$
Here $a_0$ is the reference parameter for the $Pm\bar{3}m$ structure and $a$, $b$, and $c$ are observed lattice parameters. The orientation of the relevant $I4/mcm$ cell has its unique axis aligned parallel to the reference $X$ axis, and the tetragonal strain shown in Fig. 6 has been calculated as

$$e_1 = \frac{c/2 - a_0}{a_0}, \quad e_2 = e_3 = \frac{a/\sqrt{2} - a_0}{a_0}. \quad (19)$$

The temperature dependence of $a_0$ must be such that it has zero slope as $T \to 0$. This can be effectively described by a function of the form

$$a_0 = a_1 + a_2 \Theta_{s0} \coth \left( \frac{\Theta_{s0}}{T} \right), \quad (21)$$

where $\Theta_{s0}$ is the saturation temperature for the lattice parameter of the cubic structure. The experimental data for cubic La$_{0.6}$Sr$_{0.1}$TiO$_3$ are those of the quenched sample collected at temperatures above $\sim 570$ K. They are not of sufficient quality to allow a fit of Eq. (21) with $\Theta_{s0}$ as a free parameter. However, for SrTiO$_3$ it has been found$^{17}$ that $\Theta_{s0}$ is $\sim 130$ K, while for LaAlO$_3$ and (La,Pr)AlO$_3$, $\Theta_{s0}$ values are $\sim 250$ and $\sim 300$ K, respectively.$^{27,29}$ For present purposes $\Theta_{s0}$ =250 K has been fixed arbitrarily in order to obtain some estimates of the volume strain $e_s$. The fit for $a_0$ in Fig. 4 was obtained for data from the quenched sample collected in the range 573–773 K and has $a_1$=3.8679 Å and $a_2$ =0.000 039 76 Å K$^{-1}$ ($\Theta_{s0}$=250 K). This was then used in calculations of $e_1$, $e_2$, and $e_3$ and, hence, of the symmetry-adapted strains shown in Fig. 6. Shear strains ($e_1$, $e_3$) are relatively insensitive to the choice of $a_0$ values.

The slowly cooled sample has effectively constant values of $e_1$ and $e_3$ in the temperature range 573–773 K. This is consistent with the expectation that the degree of cation order ($q_2$) remains constant in this temperature interval over the time scale of data collection. The onset of octahedral tilting is clearly indicated by the development of an orthorhombic strain and a change in the trend of the tetragonal strain near 570 K. Also as expected, $e_2$ scales linearly with $\phi^2$ [Fig. 7(a)], consistent with Eq. (8), and $e_3^2$ scales linearly with temperature [Fig. 7(b)], consistent with the tricritical character suggested by Fig. 5(b). The straight line fit in Fig. 7(b) gives a $P4/mmm \leftrightarrow Cmmm$ transition temperature ($T^*_c$) of 560 K. Changes in $e_2$ and $e_3$ due to this transition are given by the difference between observed values for the $Cmmm$ structure and constant values for the $P4/mmm$ structure. The latter have been obtained by averaging data collected in the temperature range 673–773 K (Fig. 6) and lead to the variations of $e_2$ and $e_3$ associated only with the tilting transition shown in Fig. 7(c). When analyzed in this way, there is a small tail in $e_2$ above $T^*_c$ that implies the existence of precursor effects ahead of the transition point. While $e_1$ behaves in a regular and predictable manner in relation to coupling with the order parameter, $e_3$ apparently does not. The volume strain perhaps only starts to develop $\sim 50$ K below $T^*_c$ and then deviates substantially from the expected trend below $\sim 450$ K. The precise values of $e_s$ are highly sensitive to the choice of $a_0$ but a similar reversal in the trend of $e_s$ with falling temperature has also been observed in (Ca,Sr)TiO$_3$ (Refs. 28 and 30) and NaMgF$_3$ (Refs. 31 and 32) perovskites. Equations (7) and (8) require that $e_1/\sqrt{3} = -e_3$, where $e_1$ is now the tetragonal strain due to $P4/mmm \leftrightarrow Cmmm$ alone, and this is indeed obtained [Fig. 7(d)].

Lattice parameters for the sample quenched from high temperature show quite different patterns of evolution from...
those of the slowly cooled sample (Fig. 4). The $Pm\bar{3}m \rightarrow I4/mcm$ transition occurs near 570 K, as shown by the evolution of the tilt angle (Fig. 5), but the tetragonal distortion is barely detected. At $e_1$, $e_5 < 0.001$, the strains calculated from these data are close to the instrumental limit of resolution, and details of their evolution probably do not merit close analysis. It is notable, however, that both the magnitude and pattern of evolution of $e_5$ (Fig. 6) are very similar to those shown by the $P4/mmm \rightarrow Cmmm$ transition [Fig. 7(c)]. Octahedral tilting is not substantially modified by disordering of the cations in La$_{0.6}$Sr$_{0.1}$TiO$_3$, but coupling of the order parameter to the shear strain $e_1$ appears to be almost entirely suppressed.

**DISCUSSION**

In La$_{0.6}$Sr$_{0.1}$TiO$_3$, one of the order parameters operates on a time scale that is determined by the rate of diffusion of cations between A sites of the perovskite structure, while the second responds rapidly to changes in temperature. The coupling is biquadratic and is thus analogous to the combination of Al/Si ordering and a displacive transition in the mineral anorthite, CaAl$_2$Si$_2$O$_8$, as described in several publications elsewhere.\textsuperscript{5,6,33-35} A standard Landau description [Eq. (1)], combined with an understanding of these different time scales, leads to predicted behavior which appears to be broadly correct. The transition temperature of the tilting transition, $T'_{c2}$, is only weakly dependent on the degree of cation ordering in that a difference of $\sim 10$ K was found between the quenched and slowly cooled samples [Fig. 5(b)]. However, the strength of coupling between octahedral tilting and the shear strain appears to be highly sensitive to the degree of cation order, and there is perhaps also a small difference in the evolution of $q_5$ below $T'_{c2}$ such that the slopes of $\phi^4$ against $T$ are slightly different for the two samples [Fig. 5(b)]. This is contrary to the expectation from Eq. (5) that the coefficients $b_1^z$ and $c_2^z$ remain the same for both cases [Eqs. (10)–(12)]. The implication is that the coupling coefficient $\lambda_4$ might itself be explicitly dependent on $q_5$. In the lowest order permitted by symmetry, $\lambda_4$ could be replaced by $\lambda_4' q_5^2$ such that $\lambda_4 = 0$ when $q_5 = 0$. A term of the form $\lambda_4' q_5^2$ then appears in Eq. (5), with interesting consequences for unusual variations of $e_1$ in crystals investigated under time-temperature conditions which allow simultaneous equilibration of both cation ordering and octahedral tilting. It follows from replacing $\lambda_4$ by $\lambda_4' q_5^2$ that $b_2^z$ is also sensitive to cation disordering [Eq. (12)], and the precise evolution of the octahedral tilt angle will then also be different in crystals with different degrees of order.

It has previously been found that strain–order-parameter coupling can be suppressed in (Ca,Sr)TiO$_3$ perovskites while octahedral tilting is hardly affected.\textsuperscript{28} This effect was explained as being due to the development of local (unit cell scale) strain heterogeneities caused by lattice relaxations around Ca substituted for Sr and around Sr substituted for...
Ca. The local strain fields were construed to act in such a way that the development of a coherent, long-ranging relaxation due to the tilting transition becomes frustrated. More direct evidence for the existence of local strain heterogeneities in perovskites is provided by line broadening in infrared absorption spectra,\(^{36}\) while in silicates the heterogeneities appear to be eliminated by cation ordering.\(^{37-43}\) It is therefore proposed that similar local strain fields are induced by cation disordering in La\(_{0.6}\)Sr\(_{0.1}\)TiO\(_3\), and that it is these local heterogeneities which are responsible for the suppression of strain–order-parameter coupling. A slight increase in the widths of superlattice reflections from the disordered sample, relative to those from the ordered sample, suggests smaller antiphase domain sizes and may imply that domain growth is also hindered by the disordering.

The influence of cation disordering appears to be quite different between ferroelastic and ferroelectric materials. Rather than retaining a discrete transition as in the ferroelastic case considered here, cation disorder can cause smearing of a ferroelectric transition.\(^8-10\) It is likely that there are equivalent local strain relaxations in the ferroelectric material but these appear to give rise to regions of crystal with different transition temperatures. Potential applications of the strain–order-parameter suppression mechanism in ferroelastic materials might involve predetermination of the properties of twin walls. For example, ferroelastic switching involves transformation of one twin orientation to another. If the spontaneous strain associated with each twin can be reduced to a negligible value by the choice of chemical composition and state of cation disorder, the stresses accompanying switching might be substantially lowered. Alternatively, if the requirement is to have a high resistance to switching in some multiferroic material, the choice of an ordered material with large strains might be more appropriate.

**ACKNOWLEDGMENTS**

The authors thank Mugdha Bhati for assistance in the preparation of the samples. The neutron facilities at ISIS are operated by the Science and Technology Facilities Council (STFC), with a contribution from the Australian Research Council. Travel by C.J.H. and Z.Z. to ISIS was funded by the Commonwealth of Australia under the Major National Research Facilities Program. The current studies of perovskites are supported in part by the Australian Research Council, Grant No. DP055722.

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