

Order-disorder octahedral tilting transitions in SrSnO₃ perovskite

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High-temperature powder neutron diffraction has been used to characterize two structural phase transitions in the perovskite SrSnO₃. A continuous orthorhombic *Pnma* to *Imma* symmetry transition occurs at 636 °C, and a first-order transition to a tetragonal *I4/mcm* phase occurs at 800 °C. Such octahedral tilting transitions are very common in perovskite oxides and are generally assumed to be displacive. However, a displacive description of the transitions in SrSnO₃ gives physically unrealistic results, and a considerable dynamic order-disorder component is found. A more realistic order-disorder modeling shows that the population difference between majority and minority tilt states is an appropriate order parameter, and the onset of tilting fluctuations ~ 300 °C below the *Pnma* to *Imma* transition leads to an unusual divergence of the lattice parameters on warming towards the transition.

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Structural phase transitions in *ABO*₃ oxide perovskites are of intrinsic interest as well as being tied to more complex phenomena such as electron-lattice couplings in manganites. There has been a long-running debate about the nature of ferroelectric transitions in perovskites. The ferroelectric phase transitions in BaTiO₃ were originally considered a typical example of a displacive transition. An alternative order-disorder description was suggested by Comes *et al.*¹ based on the observation of diffuse x-ray scattering, although it was subsequently suggested that this scattering could result from the strong anisotropy of the soft mode.² More recent studies of these transitions using Raman spectroscopy³ and nuclear magnetic resonance⁴ reinforce the argument that the transition has a significant order-disorder component. In contrast, phase transitions resulting from the most common type of distortion in perovskites, octahedral tilting, are invariably assumed to be displacive in character.^{5,6} In this paper we demonstrate that a typical octahedral tilting transition, in the simple perovskite SrSnO₃, is principally of order-disorder character.

Sn⁴⁺ is similar in size to Ti⁴⁺ and other transition-metal ions but has no off-center, Jahn-Teller, or other single-ion electronic distortions. SrSnO₃ therefore gives useful insights into the evolution of a representative perovskite structure via octahedral tilting. SrSnO₃ is also a good analog to the MgSiO₃ perovskite, believed to be the main constituent of the earth's lower mantle. Detailed investigations on MgSiO₃ are difficult due to the instability of this phase at ambient temperatures and pressures, so SrSnO₃ may provide useful information about structural transformations in MgSiO₃.

A 10-g polycrystalline SrSnO₃ sample was prepared by sintering a mixture of SrCO₃ and SnO₂ at 1380 °C. High-resolution powder neutron diffraction patterns were collected in the range $2\theta = 4^\circ - 160^\circ$ at a wavelength of $\lambda = 1.593$ Å using the D2B diffractometer at the Institute Laue Langevin (ILL), Grenoble. Diffraction patterns were obtained while heating, every 10 °C between 50 and 800 °C, and every 25 °C up to 875 °C. Rietveld fitting of the data was per-

formed using the GENERAL STRUCTURE ANALYSIS SYSTEM (GSAS) software package,⁷ using a linear background function and a pseudo-Voigt diffraction peak shape.

Structural transitions from *Pnma* to *Imma* to *I4/mcm* phases with increasing temperature are found in SrSnO₃ (Fig. 1). The same sequence of transitions has been observed in SrZrO₃ (Ref. 8) and SrRuO₃ (Ref. 9) with temperature, and with increasing *x* at 300 K in the solid solution Sr_xBa_{1-x}SnO₃ (Ref. 10). The *Imma* to *I4/mcm* transition is first order as it involves a discontinuous change from a structure with tilts around a diad axis of the oxygen octahedron to one with the tilts around a tetrad axis.⁶ This is consistent with the discontinuity observed in the lattice parameters at the transition temperature of 800 °C (Fig. 1).¹¹ There is no symmetry discontinuity to the *Pnma* to *Imma* transition since it involves loss of the in-phase tilting, so it may be continuous in Landau theory. The lattice parameters vary continuously through the transition, but their divergence on heating towards the transition is very unusual.

Thermal variations of the octahedral tilt angle, the mean Sn-O distance, and the oxygen temperature factors were de-

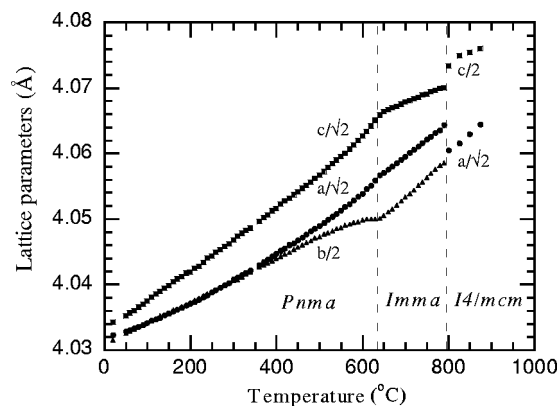


FIG. 1. Thermal variation of the lattice parameters of SrSnO₃.

TABLE I. Atomic positions (x, y, z) for the conventional $Imma$ and $Pnma$ superstructure models, and the disordered model used to fit both phases. \pm displacements are for the majority (upper) and minority (lower) tilt states.

	$Imma$	$Pnma$	Disordered
Sr	$(0, 0.25, z)$	$(\delta_{xSr}, 0.25, z)$	$(\pm\delta_{xSr}, 0.25, z)$
Sn	$(0, 0, 0.5)$	$(0, 0, 0.5)$	$(0, 0, 0.5)$
O1	$(0.5, 0.25, z)$	$(0.5 - \delta_{xO1}, 0.25, z)$	$(0.5 \mp \delta_{xO1}, 0.25, z)$
O2	$(0.25, y, 0.75)$	$(0.25 + \delta_{xO2}, y, 0.75 - \delta_{zO2})$	$(0.25 \pm \delta_{xO2}, y, 0.75 \mp \delta_{zO2})$

rived by refinement of the atomic parameters in the conventional models (see Tables I and II) for the three phases. The tilt angle is a measure of the order parameter for a displacive transition involving loss of an octahedral tilt. The tilt angles were calculated from the oxygen atomic positions by the method of Kennedy *et al.*,¹² as implemented in a previous study,¹⁰ and the results are shown in Fig. 2. The variation of the in-phase tilt angle with temperature is described well by a critical equation: $\phi_+ = \phi_+(0)(1 - T/T_c)^\beta$ and the fitted parameters are $\phi_+(0) = 7.43(2)^\circ$, $T_c = 908.6(6)$ K ($= 636^\circ$ C), $\beta = 0.187(2)$ for data fitted between 50 and 630 $^\circ$ C. The value of β is lower than expected for a second-order ($\beta = 0.50$) or a tricritical ($\beta = 0.25$) displacive phase transition, indicating a first-order or a dynamic order-disorder transition. The latter is particularly likely since similar low values for the critical exponent are found for well-characterized dynamic order-disorder transitions, e.g., that in KH_2PO_4 (KDP) for which $\beta = 0.168$ (Refs. 13 and 14) and $CaTiSiO_3$ (titanite) where $\beta = 0.15$ (Ref. 15).

Figure 3 shows the thermal variation of the average Sn-O bond distance given by the standard (displacive) refinement model. The average distance remains approximately constant within the range of each superstructure but shows an unphysical contraction at the transitions to higher-temperature phases. This apparent shortening of the Sn-O distance is an artefact of averaging over disordered tilts (and hence, disordered oxygen positions) in the mean crystallographic structure. Uncorrelated static disorder is not possible in the perovskite framework, as it leads to structural singularities across domain walls. However, short-range correlation can be accommodated in dynamically disordered perovskites through disordered local rigid unit modes, and so our obser-

variations of $\langle Si-O \rangle$ behavior point towards the transitions being order-disorder type (similar in character to disordered ferroelectrics, or as is observed in the high-temperature phase of SiO_2 cristobalite^{16,17}). The apparent shortening arises when there is significant disordered bending of the Sn-O-Sn bridges around a crystallographic mean in which the Sn-O-Sn angle is near or equal to 180° .

If we do not incorporate such disorder of oxygen into our refinements, the oxygen atomic temperature factors increase steadily across the temperature range of the $Pnma$ phase but show a sudden increase at the transition to $Imma$ (Fig. 4). This suggests that the distribution of oxygen positions broadens rapidly on heating through T_c . A similar thermal variation is observed for linewidths in the Raman spectrum of $BaTiO_3$ (Ref. 3) and is indicative of order-disorder character for the phase transition. Furthermore, this suggests that the spatial distribution of oxygen about the midpoint of Sn-Sn vectors (and associated apparent $\langle Si-O \rangle$ bond shortening) is not simply due to an increase in the librational amplitude of oxygen perpendicular to the Sn-O bond, as this would increase close to T_c both on cooling and heating, with critical softening approaching T_c from above or below. Such a displacive transition with a large anion libration has been reported for the perovskite $NaMgF_3$ (Ref. 18).

To model the structures more realistically, and thereby the dynamic order-disorder characteristics of the transitions in $SrSnO_3$, the structure refinements were repeated with site disorder specifically included. To model the $Pnma$ to $Imma$ transition, the two superstructures were described by a single model (Table I) containing two sets of atomic positions that

TABLE II. Atomic positions for the $I4/mcm$ phase in a conventional (displacive) description and the two-tilt state disordered model.

	$I4/mcm$	Disordered
Sr	$(0, 0.5, 0.25)$	$(0.75, 0.25, 0.75)$ $(0.75, 0.25, 0.25)$ $(0.25, 0.25, 0.25 \pm \delta_{xSr})$
Sn	$(0, 0, 0)$	$(0, 0, 0)$
O1	$(0, 0, 0.25)$	$(0.5 + \delta_{xO1}, 0.5 + \delta_{xO1}, 0.25)$
O2	$(0.25 + x, 0.75 + x, 0.75)$	$(0.25, y, \pm \delta_{zO2})$ $(0.25, 0.5 + y, 0.5 \pm \delta_{zO3})$

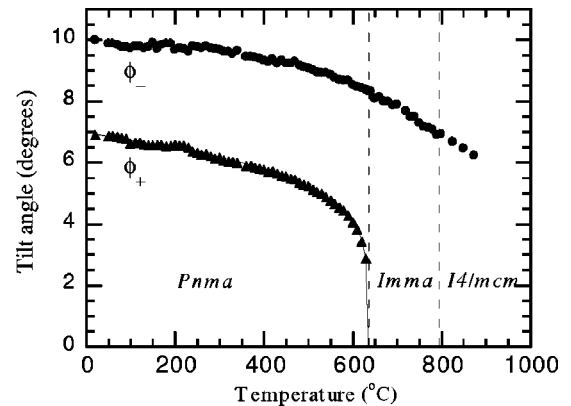


FIG. 2. Thermal variation of in-phase tilt angles ϕ_+ and out-of-phase tilt angles ϕ_- in a displacive description. The fitted line is given by the critical equation $\phi_+ = \phi_+(0)(1 - T/T_c)^\beta$.

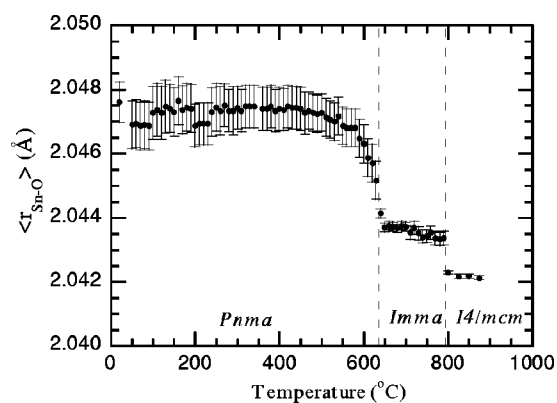


FIG. 3. Variation of the average Sn-O bond length with temperature in the displacive description of SrSnO_3 .

correspond to the two possible directions of the in-phase tilting distortion. In the *Imma* regime, the populations of the two sets of atomic positions were constrained to be equal ($1-p=p=0.5$) and the displacement coordinates δ_x, δ_z , were refined in addition to the other variable positions. In the *Pnma* region, the same coordinates were refined, but the populations of two sets were varied in the ratio $1-p:p$.

The high-temperature *I4/mcm* phase also shows evidence of oxygen disorder; for example, the low average Sn-O bond distance seen in Fig. 3. *Imma* is not a subgroup of *I4/mcm* so the disorder present in *I4/mcm* is not obtained by averaging over that in *Imma*. The approach we have taken is to model the dynamic disorder of the in-phase tilting in *I4/mcm* on that of $P4_2/nmc$, a subgroup of *I4/mcm* (see Table II).

The variation in average Sn-O bond length determined from the refinements of the above disordered models is shown in Fig. 5. The continuous thermal expansion through the *Pnma* to *Imma* transition demonstrates that this approach is physically realistic; a small (but expansive) discontinuity is observed at the first-order *Imma* to *I4/mcm* transition. Figure 6 shows the thermal variation of the tilt angles through the *Pnma* to *Imma* transition, from refinement of the single disordered model for the two space groups. Both the in-phase and out-of-phase tilting angles change by only $\sim 3^\circ$ over the entire temperature interval. The in-phase tilting shows a small critical variation below the *Imma* to *Pnma*

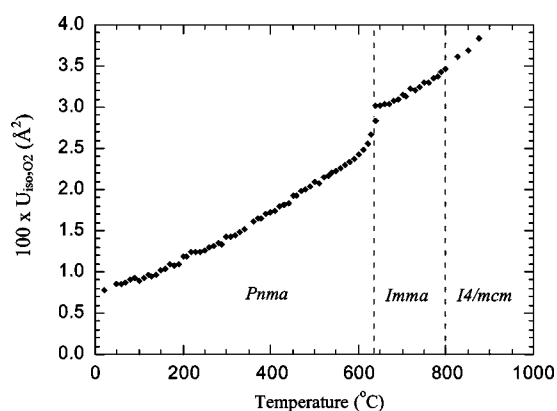


FIG. 4. Thermal variation of the isotropic temperature factor of O_2 .

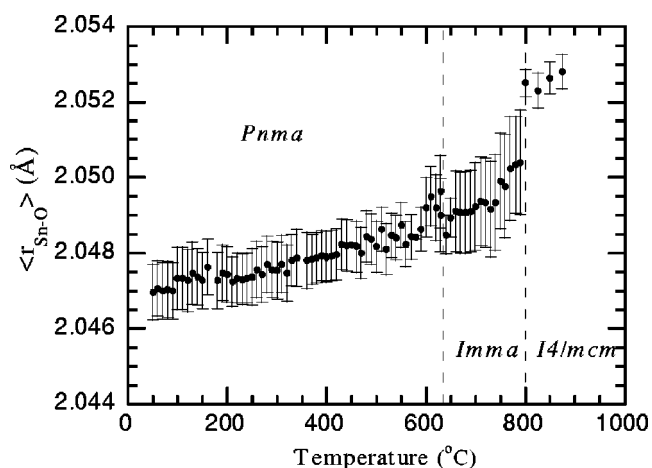


FIG. 5. Variation of the average Sn-O bond length when modeled with an order-disorder model.

transition, but the magnitude of the increase in ϕ_+ is only 1.7° compared to 6.9° in the displacive description (Fig. 2). The ratio of these values, 25%, can be used as a measure of the displacive character of the transition, hence the *Pnma* to *Imma* transition in SrSnO_3 is predominantly (75%) order-disorder.

The order parameter for the transition in this order-disorder description is the population difference between the two tilted states, $\eta_+ = 1 - 2p$. Fitting to a generic critical equation of the type $\eta_+ \propto (1 - T/T_c)^\beta$ gives $T_c = 903.9(5)$ K. and $\beta = 0.160(5)$ for data fitted between 50 and 630 °C (Fig. 7). The fitted parameters are similar to those derived from fitting the tilt angles in Fig. 2, indicating that tilt angle in a displacive model and occupancy in the order-disorder approach are both measures of the order parameter, and $\beta = 0.16$ is again consistent with an order-disorder transition.^{13,14} However, the quality of this fit is less good since the ordering saturates to unity relatively quickly on cooling from T_c . We have, therefore, also applied a modified Bragg-Williams model to the η_+ data using the method of Hayward *et al.*¹⁹ Fitting the equation $T = a\eta + b\eta^3 / R(\ln(1+\eta) - \ln(1-\eta))$ to the data we obtain $a = 15.0(6)$ kJ mol⁻¹ and $b = 4.8(9)$ kJ mol⁻¹, with $T_c = 903.9$ K. This modified Bragg-Williams fit, shown by

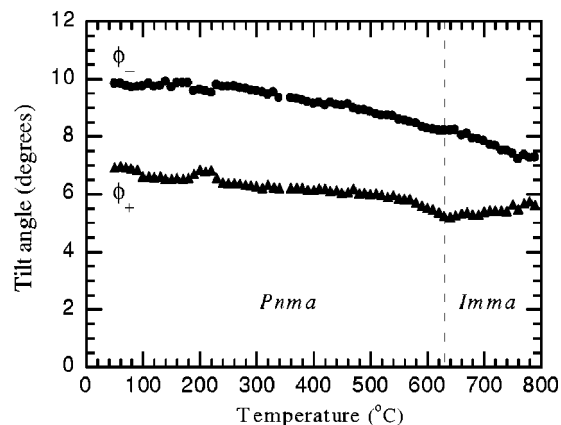


FIG. 6. Variation of the in-phase tilt angles ϕ_+ and out-of-phase tilt angles ϕ_- in the order-disorder description of the *Pnma* to *Imma* transition.

the dashed line in Fig. 7, provides a better description than the generic critical equation, as it takes account of the configurational entropy expected for order-disorder behavior.

The order-disorder description of the *Pnma* to *Imma* transition gives insight into the unusual lattice parameter variation (Fig. 1). The region of divergence of the *Pnma* phase lattice parameters on warming above ~ 350 °C corresponds to the onset of disorder in the *Pnma* phase (Fig. 7). This results in an *increase* in the apparent orthorhombic spontaneous strain on heating towards the transition to *Imma*, in contrast to the reduction in strain expected on approaching a displacive transition. Similar divergence was observed in a study of SrZrO₃ (Ref. 6) although the origins were not explored. This divergence of lattice parameters approaching a phase transition has implications for the interpretation of cell parameter data as indicators of proximity to a phase transition. For example, the divergence of lattice parameters in *Pnma* MgSiO₃ with increasing pressure has been cited as evidence that there is no structural transformation of this phase in the mantle.²⁰ However, we find that diverging cell parameters in the analog *Pnma* SrSnO₃ phase *signify* the approaching transition.

These results also have implications for the interpretation of electronic properties of perovskites. Differences in property (e.g., metal-insulator transitions) resulting from small changes in temperature, pressure, or chemical composition are often rationalized from changes in bandwidth, proportional to $\cos \phi$, where ϕ is an averaged tilt angle. In SrSnO₃, the tilt angles change little over a wide temperature range (Fig. 6), and the large change in apparent tilt angle at the phase transition from a displacive description (Fig. 2) is an artefact of averaging over the changing population difference between majority and minority tilt states.

In conclusion, we have shown that a displacive description of the octahedral tilting transitions in the simple, representative, perovskite SrSnO₃ is misleading, as it neglects a major dynamic order-disorder contribution (76% for the

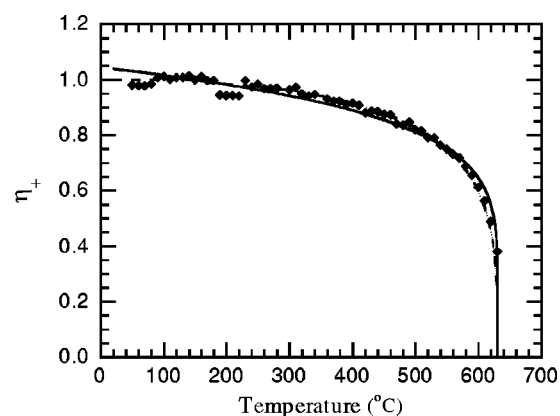


FIG. 7. Thermal variation of the population difference order parameter, η_+ in the order-disorder modeling of the *Pnma* to *Imma* transition. The solid line is a fit of the type $\eta_+ \propto (1 - T/T_c)^\beta$ and the dashed line is the modified Bragg-Williams fit.

Pnma to *Imma* transition). Modeling the continuous *Pnma* to *Imma* transition with an order-disorder model leads to a physically realistic thermal variation of the mean Sn-O distance, and demonstrates that an unusual divergence of cell parameters on heating towards the transition is linked to the onset of tilting fluctuations in the low-temperature phase. While order-disorder descriptions have been applied extensively to ferroelectric perovskites, this study demonstrates that such phenomena can also be significant at the more general, tilting distortions of perovskites. Structure refinements and derived results such as electronic-band structures for other perovskites may require consideration of disordered tilting to provide more realistic descriptions of their properties.

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