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Ferroelectric phase transitions in $SrBi_2Nb_2O_9$ and $Bi_5Ti_3FeO_{15}$: A powder neutron diffraction study

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Structural phase transitions in the Aurivillius phase ferroelectrics $SrBi_2Nb_2O_9$ and $Bi_5Ti_3FeO_{15}$, containing two and four perovskite layers, respectively, have been studied using powder neutron diffraction. At temperatures below the ferroelectric Curie temperature both materials crystallize in the polar orthorhombic space group $A2_1am$. On passing through T_C, both phases appear to transform *directly* to a tetragonal paraelectric phase, space group $I4/mmm$. This behavior contrasts with that of the analogs $Sr_{0.85}Bi_{2.1}Ta_2O_9$ and $SrBi_4Ti_4O_{15}$, both of which have been shown unambiguously to transform via an intermediate paraelectric orthorhombic phase, space group *Amam*.

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Ferroelectric materials of the Aurivillius family are currently being widely studied for potential uses in nonvolatile memory (FeRAM) applications.[1] The Aurivillius phases (Fig. 1) are a series of layered bismuth-containing oxides of general formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$, consisting of a regular intergrowth of fluorite-like $[Bi_2O_2]$ blocks and perovskitelike $[A_{n-1}B_nO_{3n+1}]$ blocks.[2,3] For $n=2$ or 4 (''even-layer'') materials, it has now been well established that the ferroelectric phase adopts the orthorhombic space group $A2_1am$, which may be considered as derived from an archetypal parent phase, space group $I4/mmm$, by polar displacements of the A cation and co-operative tilting of the BO_6 octahedral units.[4–6] The nature of the ferroelectric-paraelectric phase transition in these materials has been uncertain until quite recently. In early studies using birefringence measurements, it was suggested that some phases of this type underwent a two-step transition from $A2_1am$, via an intermediate phase, to $I4/mmm$.[4] Observations made using electron diffraction at elevated temperature supported this hypothesis,[7] but the exact nature of the transition remained unclear. Using powder neutron diffraction (PND) data, we have recently shown unambiguously that both $Sr_{0.85}Bi_{2.1}Ta_2O_9$ $(n=2)$ (Ref. 8) and $SrBi_4Ti_4O_{15}$ $(n=4)$ (Ref. 6) do indeed undergo a two-step transition, proceeding from $A2_1am$ to $I4/mmm$ via an intermediate paraelectric but orthorhombic phase in space group *Amam*. This phase corresponds to a ''freezing out'' of both a displacive mode and a tilt mode relative to the ferroelectric phase, but the remaining tilt mode is maintained. In the light of our recent confirmation[9,10] of the single first-order transition in the $n=3$ phase $Bi_4Ti_3O_{12}$, the cumulative evidence so far suggests a distinction between ''even-layer'' (two-step, continuous transition) and ''odd-layer'' materials (single-step, discontinuous transition). In order to explore this hypothesis further, we have now carried out detailed PND studies on two further even-layer systems, $SrBi_2Nb_2O_9$ $(n=2)$ and $Bi_5Ti_3FeO_{15}$ $(n=4)$. To our surprise, the results presented here suggest that both these materials adopt a *single-step* crystallographic transition $(A2_1am \rightarrow I4/mmm)$ coincident with the ferroelectric-paraelectric transition.

Samples of $SrBi_2Nb_2O_9$ and $Bi_5Ti_3FeO_{15}$ were prepared as described previously.[6,11] Phase purity was confirmed by powder x-ray diffraction using a Stoe STADI/P transmission diffractometer. PND data were collected on the high-resolution powder diffractometer HRPD (for $Bi_5Ti_3FeO_{15}$) or the high-flux powder diffractometer Polaris (for $SrBi_2Nb_2O_9$) at the ISIS spallation source, Rutherford-Appleton Laboratory, Chilton, UK. Rietveld analysis was

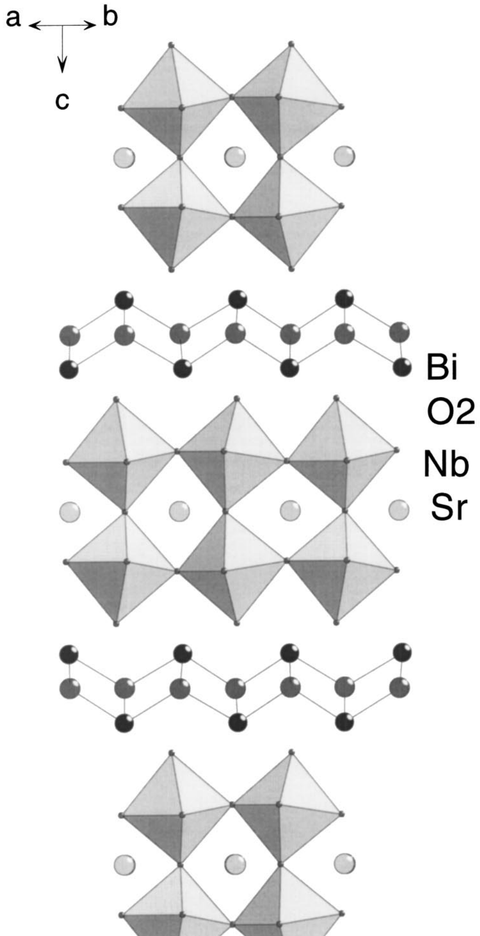

FIG. 1. Crystal structure of the $n=2$ Aurivillius phase $SrBi_2Nb_2O_9$, space group $A2_1am$.

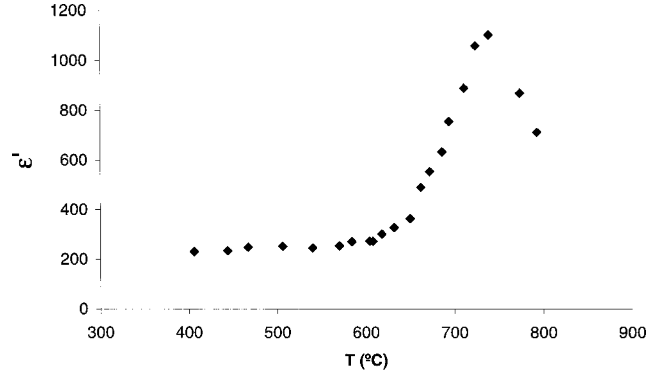

FIG. 2. Dielectric constant vs temperature for $Bi_5Ti_3FeO_{15}$.

carried out using the GSAS program suite.[12] ac impedance data for $Bi_5Ti_3FeO_{15}$ were collected using a Solartron 1255 FRA with a 1287 electrochemical interface. Measurements were performed using an ac amplitude of 20 mV in the range 100–1 MHz.

We previously published the room-temperature structures of both $SrBi_2Nb_2O_9$ (Ref. 11) and $Bi_5Ti_3FeO_{15}$.[6] These were used as starting models for Rietveld refinements, with the modification of the model for $SrBi_2Nb_2O_9$ by an origin shift, to define the A site as $x=0$, for compatibility with the work of other authors.[13] Both structures were refined in the polar space group $A2_1am$ up to temperatures near T_C—for $SrBi_2Nb_2O_9$ this was recently confirmed as 440 °C;[14] for $Bi_5Ti_3FeO_{15}$ we have determined this as ~730 °C from a.c. impedance data (Fig. 2), in agreement with an earlier study,[15] and corresponding to the higher temperature transition of Kubel and Schmid[16] (we note that neither the dielectric data nor the crystallographic refinements give any evidence of a lower temperature phase transition reported by these authors). Above T_C refinements for both structures were carried out in the highest symmetry, $I4/mmm$ model. Note that this phase has a unit cell of half the volume of the ferroelectric phase—i.e., $a_{\mathrm{orth}} \sim b_{\mathrm{orth}} = \sqrt{2} a_{\mathrm{tet}}$.

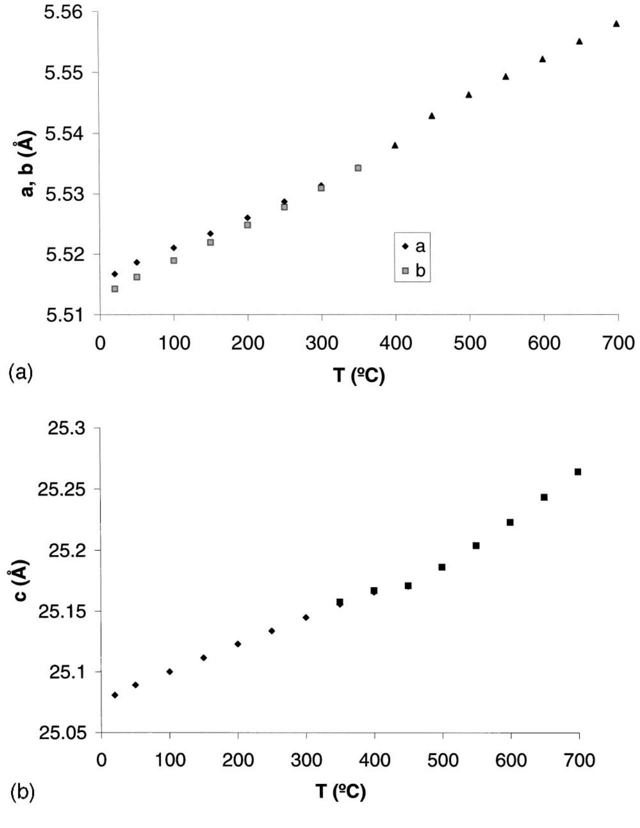

FIG. 3. Thermal evolution of lattice parameters for $SrBi_2Nb_2O_9$ (a) a/b parameters and (b) the c parameter. Above T_C the data represent values of $\sqrt{2}a_{\mathrm{tet}}$ (see the text).

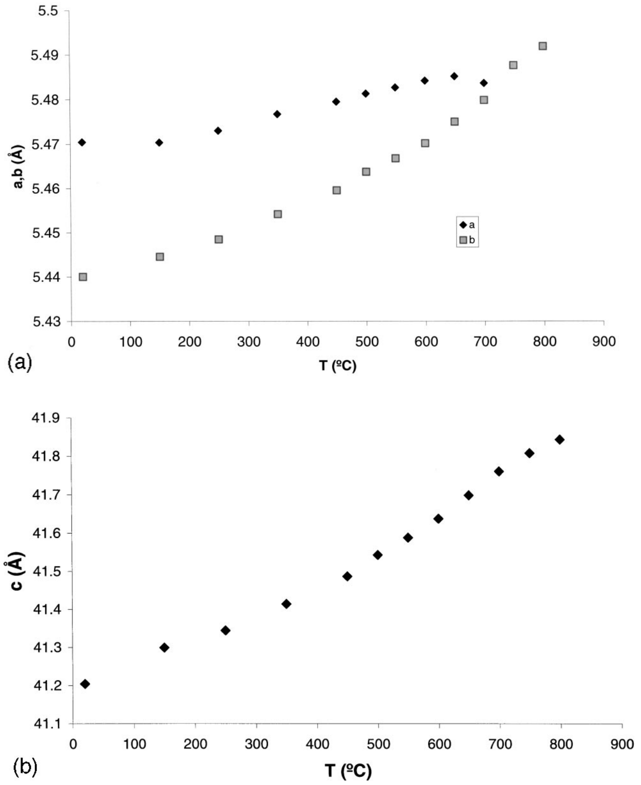

FIG. 4. Thermal evolution of lattice parameters for $Bi_5Ti_3FeO_{15}$ (a) a/b parameters and (b) the c parameter. Above T_C the data represent values of $\sqrt{2}a_{\mathrm{tet}}$ (see the text).

Lattice parameters derived from these refinements are shown in Figs. 3 and 4. A smooth transition is seen in the case of $Bi_5Ti_3FeO_{15}$, but for $SrBi_2Nb_2O_9$ slight discontinuities are discernible in the plots of both a/b and c parameters vs. T. This is suggestive of a first-order transition, although we were unable to detect a differential thermal analysis (DTA) or differential scanning calorimetry (DSC) signal. More significantly, however, a careful inspection of the Rietveld plots immediately above and below T_C suggested that the transition for both compounds was indeed a *direct* one from polar orthorhombic to centrosymmetric tetragonal, with no evidence of an intermediate *Amam* phase. This is clearly seen in the case of $SrBi_2Nb_2O_9$ in Fig. 5. Note that this conclusion is deduced on the basis of the complete disappearance of all superlattice reflections associated with the $A2_1am \rightarrow I4/mmm$ transition, rather than merely by the merging of the a/b lattice parameters—for $SrBi_2Nb_2O_9$ the refinement shows that the phase is *metrically* (but not crys-

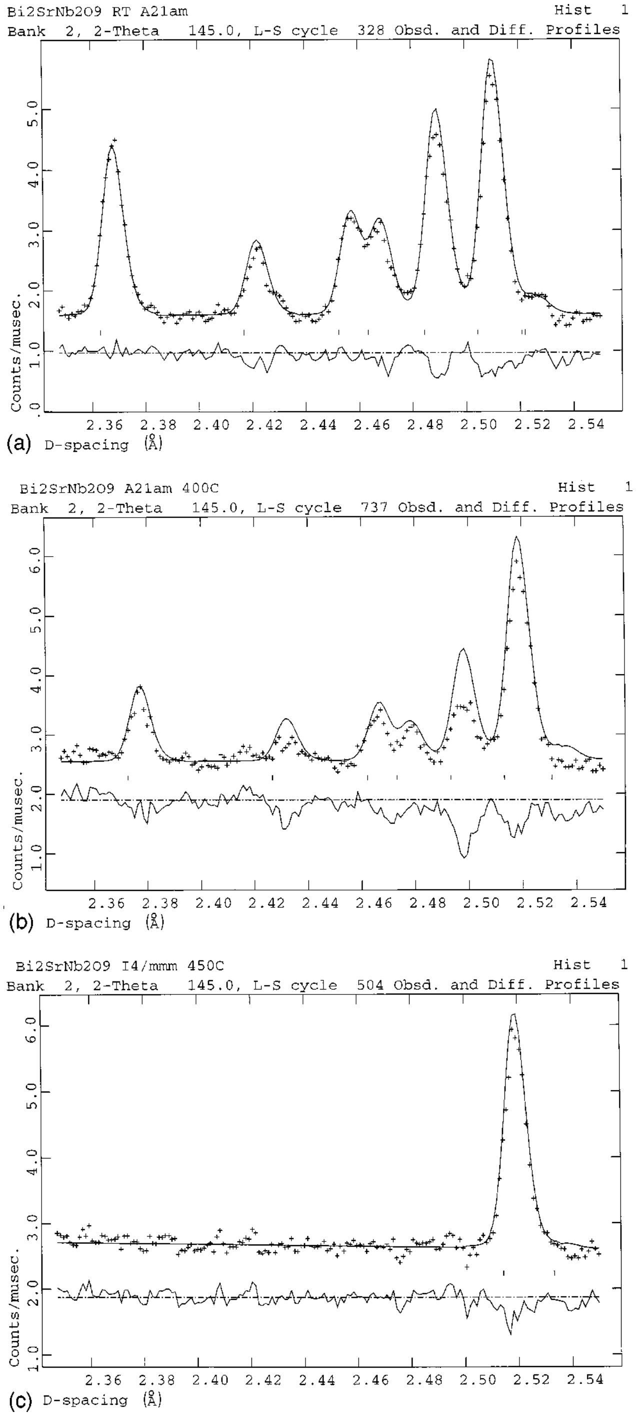

FIG. 5. Details of the final Rietveld plots for $SrBi_2Nb_2O_9$, showing the complete disappearance of superlattice reflections due to A centering above $T_C = 440$ °C. (a) 25 °C. (b) 400 °C. (c) 450 °C.

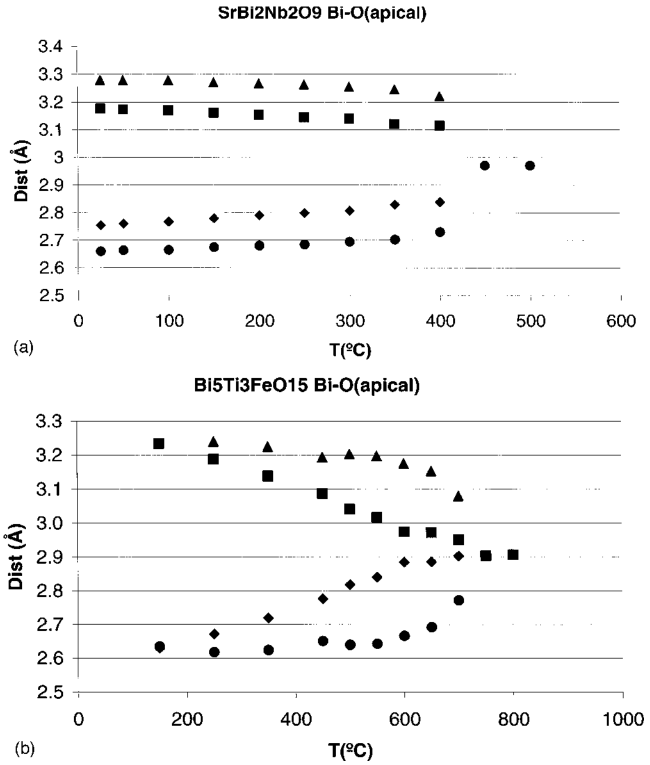

FIG. 6. Differing thermal evolution of the key Bi-O bond lengths (see the text) for (a) $SrBi_2Nb_2O_9$ and (b) $Bi_5Ti_3FeO_{15}$.

tallographically) "tetragonal" (i.e., $a=b$ within measurable limits) even at 400 °C. At 400 °C the superlattice reflections associated with the $A2_1am$ phase are clearly visible, whereas at 450 °C they are absent. Given that the T_C for $SrBi_2Nb_2O_9$ is known to be 440 °C, this sets an upper limit of $\Delta T = 10$ °C only for the range of existence of any intermediate phase. Although both compounds clearly show no evidence of an intermediate phase, there may be a subtle difference in the nature of these two transitions. In addition to the somewhat different behavior of the lattice parameter evolution, the thermal evolution of various structural parameters, in particular the bond distances between the Bi atom within the $[Bi_2O_2]$ layer and the apical O atom of the perovskite block [i.e., O(2) in Fig. 1] may be contrasted. In the $A2_1am$ phase, there are four symmetry-inequivalent Bi-O bond lengths of this type, whereas in the $I4/mmm$ phase there is only one. This thermal evolution of this key structural feature is shown for both materials in Fig. 6. The abrupt merging of the four different bond lengths for $SrBi_2Nb_2O_9$ is in stark contrast to the more gradual merging for $Bi_5Ti_3FeO_{15}$, suggestive of first- and second-order transitions, respectively.

In conclusion, we have shown that the nature of the ferroelectric phase transitions in the Aurivillius phases $SrBi_2Nb_2O_9$ and $Bi_5Ti_3FeO_{15}$ is anomalous when compared to their analogs $Sr_{0.85}Bi_{2.1}Ta_2O_9$ and $SrBi_4Ti_4O_{15}$. The present phases show a single crystallographic transition from $A2_1am$ to $I4/mmm$ at T_C, rather than the proceeding via the intermediate $Amam$ phase.

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