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Phase transition in $BaBi_2Nb_2O_9$: Implications for layered ferroelectrics

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Synchrotron powder diffraction methods have been used to determine the structure of the layered ferroelectric oxide $BaBi_2Nb_2O_9$ (BBN) above and below its Curie temperature. Although BBN is found to be tetragonal above and below the ferroelectric-paraelectric transition, there is clear evidence for a structural phase transition. The low-temperature ferroelectric structure is found to be well described in space group $I4mm$, while the high-temperature structure is in the more common $I4/mmm$ space group. The identification of the low-temperature tetragonal structure resolves a long-standing question as to the origin of ferroelectric behavior in BBN and related oxides.

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Layered Bi oxides such as $BaBi_2Nb_2O_9$ (BBN) and $SrBi_2Nb_2O_9$ (SBN), together with their Ta analogs $BaBi_2Ta_2O_9$ (BBT) and $SrBi_2Ta_2O_9$ (SBT), have received renewed interest following the observation that their ferroelectric properties are superior, for use in memory devices, to those of the currently employed $PbZrO_3$-$PbTiO_3$ solid solution (PZT) ceramics.[1] The complex electrical properties of these Bi oxides originate from an intimate interplay of structural and electronic effects associated with the Bi 6s lone-pair electrons.

The crystal structures of both BBN and BBT are described as consisting of $[Bi_2O_2]^{2+}$ layers and perovskitelike $[BaM_2O_7]^{2-}$ units that contain two layers of corner sharing MO_6 moieties. It has been suggested using both powder neutron and synchrotron x-ray methods that both BBN and BBT are tetragonal at room temperature, with their structures described in the centrosymetric $I4/mmm$ space group. Despite this, both BBN and BBT are clearly ferroelectric at room temperature.

There have been intense discussions on the cause of the ferroelectric behavior in BBN and BBT.[2,3] In one interpretation tetragonal $BaBi_2Nb_2O_9$ is regarded as containing clusters with orthorhombic symmetry, and the observed ferroelectric properties are a consequence of polarization fluctuations within the (ab) plane induced by these domains.[3] On the other hand, Blake *et al.* concluded that the broad phase transition in BBN can be attributed to the Bi and Ba atoms disordering,[2] as originally postulated in Ref. 4.

Recently the authors of Refs. 5 and 6 reported the presence of two crystallographic phase transitions in both $Sr_{0.85}Bi_{2.1}Ta_2O_9$ and $SrBi_2Ta_2O_9$. In each case the room-temperature orthorhombic (space group $A2_1am$) ferroelectric phase transforms to the high-temperature tetragonal ($I4/mmm$) paraelectric phase via an intermediate orthorhombic ($Amam$) paraelectric phase. Macquart *et al.*[6] noted that both these transitions are allowed to be continuous. Shimakawa *et al.*[3] found no evidence of a low-temperature tetragonal to orthorhombic phase transition in BBT[3] although their study, employing a conventional x-ray source, did not extend to above room temperature, and so did not probe the transition to the paraelectric phase that occurs above 330 K.

In the present work we use high-resolution synchrotron x-ray-diffraction methods to investigate the structure of BBN over a wide temperature range. This study revealed strong evidence for a crystallographic phase transition, near 300 K, that is near the observed ferroelectric to paraelectric transition. We conclude that this involves the transition from a low-temperature noncentrosymmetric structure.

$BaBi_2Nb_2O_9$ was prepared from a stoichiometric mixture of $BaCO_3$, Bi_2O_3, and Nb_2O_5 that was heated at 900 °C for 15 h, 1000 °C for 15 h, and 1200 °C for 24 h, regrinding between steps. The variable temperature structural properties of BBN were studied by monochromatic ($\lambda = 0.748896$ Å) x-ray powder diffraction at the National Synchrotron Light Source (NSLS BNL, Beamline X7A). Diffraction patterns were recorded with increasing temperature from 20 K using a closed-cycle cryofurnace to obtain the desired temperatures. A linear position sensitive detector was employed in these measurements. Typical diffraction patterns of BBN are shown in Fig. 1 for the temperature range 20–500 K. At all temperatures the patterns could be indexed on a tetragonal cell. All diffraction patterns were suitable for Rietveld refinements, yielding lattice parameters and atomic positions. Additional neutron diffraction patterns were recorded on the high resolution powder diffractometer for thermal neutrons (HRPT) at the Swiss Neutron Source (SINQ). Tables I and II show the results of refinements at 500 and 250 K, respectively, while Table III shows the lattice parameters over the entire temperature range.

Figure 2 illustrates the temperature dependence of the lattice parameters. There is a clear change in the rate of expansion of the cell parameters near 300 K. Since the measurements were conducted in a cryofurnace, this change is not a consequence of changing from a cryostat to furnace. We propose that this anomaly is a result of a structural phase transition. We note that the lattice parameters refined in either $I4mm$ or $I4/mmm$ are essentially identical. As indicated above, the patterns remain consistent with a tetragonal structure to 20 K. An additional very-high resolution pattern was collected at 20 K using a secondary monochromator crystal in front of the detector. This improves the resolution of the instrument to $\Delta d/d = 2\times10^{-5}$. Even at this very high reso-

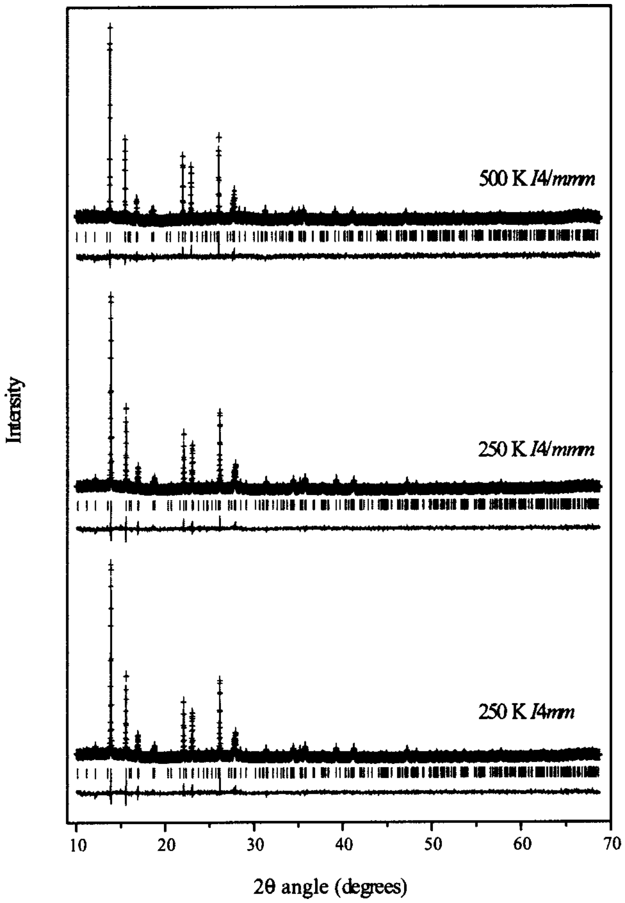

FIG. 1. Diffraction patterns for $BaBi_2Nb_2O_9$ at 500 and 250 K fitted with the $I4/mmm$ structure; the pattern at 250 K is also fitted with the $I4mm$ structure.

lution there was no evidence to suggest the structure at 20 K was orthorhombic, although there was some anisotropic peak broadening consistent with an incommensurate structure. Therefore, we concluded that the structure is tetragonal from 20 to 500 K, and that there is a tetragonal-tetragonal phase transition near 300 K. Neutron-diffraction measurements at room temperature and 20 K failed to reveal any evidence of superlattice reflections indicative of orthorhombic symmetry. Likewise, attempts to observe orthorhombic domains using TEM have been unsuccessful.

TABLE I. Atomic coordinates for $BaBi_2Nb_2O_9$ at 500 K ($I4/mmm$).

Atom	x	y	z	B_{iso} (Å)^2
Ba	0	0	0.5	1.4(1)
Bi	0	0	0.7027(2)	3.4(1)
Nb	0	0	0.0888(2)	0.3(1)
O1	0	0	0	0.7(3)
O2	0	0.5	0.25	0.7(3)
O3	0	0	0.158(1)	0.7(3)
O4	0	0.5	0.0772(7)	0.7(3)

TABLE II. Atomic coordinates for $BaBi_2Nb_2O_9$ at 250 K ($I4mm$). Neutron-diffraction data were used in the refinement.

Atom	x	y	z	B_{iso} (Å)^2
Ba	0	0	0.4983(9)	1.2(1)
Bi1	0	0	0.6945(7)	5.5(3)
Bi2	0	0	0.2926(6)	0.7(1)
Nb1	0	0	0.0857(7)	1.0(1)
Nb2	0	0	0.9093(7)	0.3(1)
O1	0	0	0	2.9(1)
O2	0	0.5	0.2493(7)	1.0(1)
O3*a*	0	0	0.1584(8)	1.9(2)
O3*b*	0	0	0.8392(7)	1.6(2)
O4*a*	0	0.5	0.0787(7)	1.6(1)
O4*b*	0	0.5	0.9221(7)	1.4(1)

Since the pioneering work of Smolenskii numerous workers have examined the electronic properties of BBN. BBN clearly undergoes a ferroelectric-paraelectric transition just above room temperature, i.e., where the crystallographic phase transition occurs. It is most likely that upon cooling the transition is from the paraelectric $I4/mmm$ state to a ferroelectric state. With the aid of the computer program ISOTROPY,[8] we identified those space groups that can be obtained from the parent $I4/mmm$ structure by a recognizable pattern of ferroelectric cation displacements (that is, where the cations were displaced along the 100, 110, or 001 directions). The four possible space groups are shown in Fig. 3. This figure also includes the centrosymmetric space group, *Amam*, that is obtained from $I4/mmm$ by tilting of the MO_6 octahedra around 110-type axes. This space group has been observed, at high temperatures, in $SrBi_2Ta_2O_9$ and $Sr_{0.85}Bi_{2.1}Ta_2O_9$.[5,6] Of these five space groups only $I4mm$ is tetragonal, the remaining space groups are orthorhombic or in the case of *Cm*, monoclinic. A feature in Fig. 3 is that there is no mode involving simple rotation of the octahedra that will allow a continuous transition from $I4mm$ to $A2_1am$. If the MO_6 octahedra in the $I4mm$ structure were to be tilted, the most attractive rotation would be about the *z*-axis to give space group $P4_2nm$. The structures of the

TABLE III. Refined lattice parameters for $BaBi_2Nb_2O_9$ as a function of temperature in space groups $I4mm$ and $I4/mmm$.

Temp. (K)[a]	a (Å)	c (Å)	R_p (%)	R_{wp} (%)	χ^2
20	3.92492(8)	25.5418(7)	6.39	8.02	8.470
50	3.92462(9)	25.5426(8)	6.52	8.21	8.026
100	3.92518(8)	25.5487(8)	6.32	7.99	7.408
150	3.92581(8)	25.5581(8)	6.44	7.97	8.414
200	3.92619(8)	25.5687(7)	6.24	7.91	8.574
250	3.92702(8)	25.5832(8)	6.29	8.03	8.274
300	3.92759(8)	25.5976(8)	6.27	8.00	7.554
350	3.92650(8)	25.5973(7)	5.76	7.17	6.327
400	3.9264(1)	25.6088(9)	5.98	7.65	6.085
450	3.92681(9)	25.6228(7)	5.68	7.29	4.617
500	3.92691(8)	25.6344(7)	6.19	7.87	3.983

[a] The lattice parameters quoted are from the refinements in $I4mm$ for 20–250 K and $I4/mmm$ for 300–500 K.

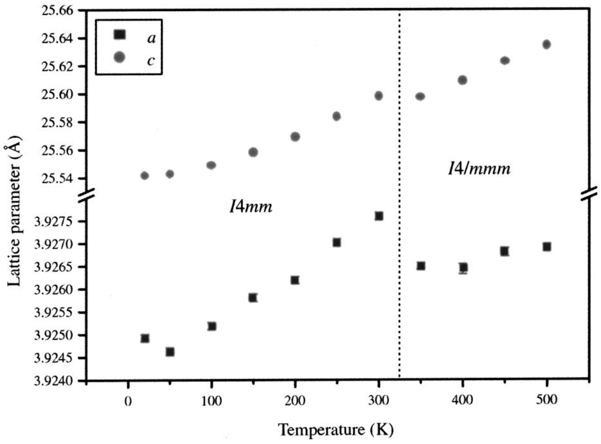

FIG. 2. Lattice parameters for $BaBi_2Nb_2O_9$ as a function of temperature.

paraelectric and the ferroelectric phases are compared in Fig. 4. The two structures are very similar and differ mainly by the displacement of the Nb atoms away from the O4*A* plane in the ferroelectric phase.

We believe three pieces of evidence favor our explanation for the origin of the ferroelectricity in BBN. First, the transition from the paraelectric $I4/mmm$ phase to the ferroelectric $A2_1am$ phase has been observed in both SBT and the Bi-rich oxide $Sr_{0.85}Bi_{2.1}Ta_2O_9$ analog.[5,6] Group theory shows this transition can occur continuously, albeit via the *Amam* intermediate phase.[6] There is no suggestion from our previous study of SBT (Ref. 6) or from the work of Ref. 5 on $Sr_{0.85}Bi_{2.1}Ta_2O_9$ for a two-phase region. This is consistent with a continuous phase transition. All the available experimental evidence suggests the tetragonal to orthorhombic transition will be continuous, and it is reasonable to expect that once domains with orthorhombic character form they will rapidly propagate. Consequently, at 20 K the diffraction pattern should show clear evidence of an orthorhombic phase. The observation that the structure at 20 K is metrically tetragonal and the diffraction patterns do not show any reflections indicative of the orthorhombic ($A2_1am$) phase at 20 K is a strong argument against the microdomain theory.

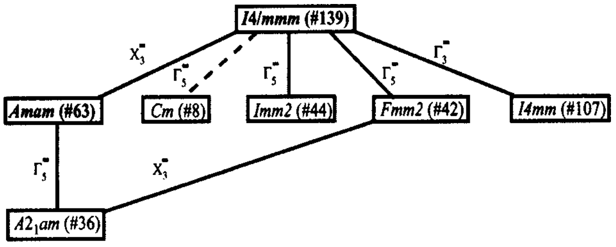

FIG. 3. Relationship between the space groups observed in $ABi_2M_2O_9$, $A=$Ba, Sr and $M=$Nb, Ta. The solid lines show transitions allowed to be continuous by group theory and the dashed line indicates that the transition from $I4/mmm$ to *Cm* must be discontinuous. $I4/mmm$ and $I4mm$ are tetragonal while *Amam*, $Imm2$, $Fmm2$ and $A2_1am$ are orthorhombic, *Cm* is monoclinic. Only $I4/mmm$ and *Amam* are centrosymmetric. The modes associated with the change in symmetry are indicated (Ref. 7).

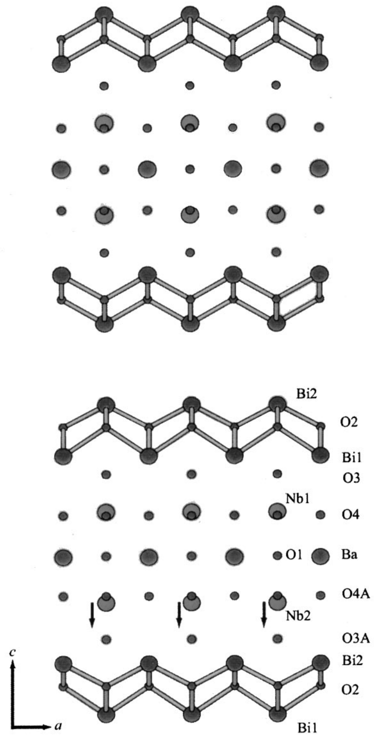

FIG. 4. Comparison of the structure of $BaBi_2Nb_2O_9$ fitted with the $I4/mmm$ model (top) and the $I4mm$ model (bottom).

Finally, Table III shows that while the patterns recorded above 300 K can be adequately fitted in the centrosymmetric $I4/mmm$ structure, the $I4mm$ model provides a comparable quality fit to the low temperature data and accounts for the observed ferroelectric behavior.

The broadness of the ferroelectric-paraelectric transition suggests that local bonding effects are important and cation disorder can alter the transition temperature. To date, how cation disorder alters the transition temperature (does it increase or decrease it) has not been established. It is, however, unlikely that the large change in lattice parameters is due to a change in cation disorder. The structural refinements show there is apparently no change in the extent of the Ba/Bi cation disorder upon heating from 300 to 500 K, with the disorder remaining constant at around 5.8(5)% Ba occupancy in the Bi_2O_2 layers. This is consistent with the previous study of Ismunandar and Kennedy,[9] who reported that heating samples to 1000 °C causes only very minor changes in the extent of cation disorder.

The orthorhombic $A2_1am$ phase can be distinguished from the tetragonal $I4/mmm$ by, among other features, the tilting of the MO_6 octahedra. This tilting is similar to that seen in simple perovskites such as $CaTiO_3$,[10] and is related to the relative size of the perovskite *A*-type cation (Ba^{2+}) and the *M*-type cation (Nb^{5+}). Reducing the effective size of the *A* cation (e.g., by partially replacing Ba^{2+} with Bi^{3+}) will increase the tendency for, and magnitude of, the tilting of the NbO_6 octahedra. Such tilting alone is not sufficient to induce ferroelectricity, as seen in the paraelectric *Amam* phase. We accept that cation disorder is important in these materials (and is most probably responsible for the broadness of the ferroelectric-paraelectric transition); however we contend that this is not the origin of the ferroelectricity.

In conclusion, we have shown the presence of a crystallographic phase transition near room temperature in $BaBi_2Nb_2O_9$. We believe this is from the paraelectric $I4/mmm$ structure to the ferroelectric $I4mm$ structure. The existence of such a transition resolves the long-debated question as to the origin of ferroelectricity in the tetragonal Aurivillius oxides.

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