Ferroelectricity in Ordered Perovskite $BaBi_{0.5}^{3+}(Bi_{0.2}^{5+}Nb_{0.3}^{5+})O_3$ with Bi^{3+}:$6s^2$ Lone Pair at the B-site

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Development of lead-free ferroelectric materials are important because of the toxicity of lead in the widely used material lead zirconium titanate (PZT) in devices.[1,2] Although PZT is isostructural and isovalent with $BaTiO_3$ (BTO), the ferroelectric properties are superior to BTO because of the contribution from stereochemically active $6s^2$ lone pair of Pb^{2+} ions. A similar role of lone pair electrons has been recognized in other materials with Bi^{3+}: $6s^2$ ions.[3] For example, in the Aurivillius family of layered bismuth oxides, a class of ferroelectrics with general formula $Bi_2O_2^{2+}$-$(M_{n-1}R_nO_{3n+1})^{2-}$, the contribution to ferroelectricity comes mainly from Bi^{3+} ions. The structure of these materials consists of perovskite blocks $(M_{n-1}R_nO_{3n+1})^{2-}$, separated and sheared along 1/2[111] by rock-salt-structured $Bi_2O_2^{2+}$ layers.[4] There exist another class of materials that exhibit ferroelectricity as well as ferromagnetism in the same phase. These materials have the perovskite structure with the formula ABO_3, where A is a cation containing a stereoactive lone pair such as Bi^{3+}: $6s^2$ and B is the transition metal ions with unpaired electrons.[5−7] In these perovskites, the origin of ferroelectricity is associated with the stereochemical activity of the A-site cation and the magnetism is due to transition metal ions at the B-site.[8,9] In all these compounds discussed above, the contribution to the electric polarization comes from the cation with lone pair electrons that occupies rock-salt type layers or the A-site of the perovskite structure.

Ferroelectric study of perovskite materials having B-site cations with lone pair electrons is not known in the literature. Such studies would be interesting because the coordination and bonding with oxygen are different at A and B sites. Furthermore, the BO_6 octahedra are known to undergo cooperative distortion and tilting because of various bond length mismatches. From this point of view, the perovskite $BaBiO_3$ (BBO) would be an ideal compound, which is a well-known charge density wave semiconductor that becomes superconducting upon substitution of Ba^{2+} ions by K^+ ions.[10,11] BBO is a charge-ordered perovskite, where Bi^{3+} ions with $6s^2$ lone pair and Bi^{5+} ions with $6s^0$ are ordered in a 1:1 or rock-salt type at the B-site so that the formula can be written as $Ba^{2+}Bi_{0.5}^{3+}Bi_{0.5}^{5+}O_3$. The crystal structure of BBO has been reported to be monoclinic with a centrosymmetric *I2/m* space group on the basis of the Rietveld refinement of powder X-ray and neutron diffraction data and analysis of electron diffraction patterns.[12] On the other hand, analysis of convergent beam electron diffraction (CBED) revealed broken inversion symmetry with a triclinic ($P1$) space group.[13] Though there is no consensus on the structure of BBO, we thought that there could be a polar distortion due to the lone pair electrons that may not be revealed by the average crystal structure but may manifest on the ferroelectric properties. Because the BBO shows considerable dc conductivity, we decided to replace Bi^{5+} ions by other pentavalent cations such as Sb^{5+}, Nb^{5+}, and Ta^{5+} ions and investigated structural and ferroelectric properties. In this paper, we report the observation of ferroelectricity with high Curie temperature ($T_C \approx 400$ °C) in $BaBi_{0.5}^{3+}(Bi_{0.2}^{5+}Nb_{0.3}^{5+})$-$O_3$ (BBN). Analysis of room-temperature neutron diffraction data of BBN showed that the room-temperature structure is rhombohedral with centrosymmetric space group $R\bar{3}$. High-temperature X-ray diffraction (XRD) patterns revealed that there is a structural transition from the room-temperature rhombohedral phase to high-temperature cubic phase with the space group $Fm\bar{3}m$.

Stoichiometric amounts of $BaCO_3$, Bi_2O_3, and Nb_2O_5 were mixed and heated at 750 and 800 °C for 12 h with several intermittant grindings. The resulting material was pressed into pellets and sintered at 950 °C for 12 h in a flowing O_2 atmosphere. The phase purity was checked by Bruker D8 Discover X-ray diffractometer. Powder neutron diffraction data were collected using a D2B instrument ($\lambda = 1.5938$ Å) at Institut Laue Langevin (ILL), Grenoble, France. Rietveld refinement was carried out on the neutron data using the program General Structure Analysis System (GSAS).[14] A capacitor for ferroelectric measurement was made by sputtering gold on both sides of the pellet by DC sputtering. The ferroelectric hysteresis was measured with a RT Precision Workstation tester (Radiant Technologies Inc.). Capacitance and dissipation of the sample were measured using Agilent impedance analyzer between room temperature and 550 °C in a frequency range 100 Hz to 1 MHz.

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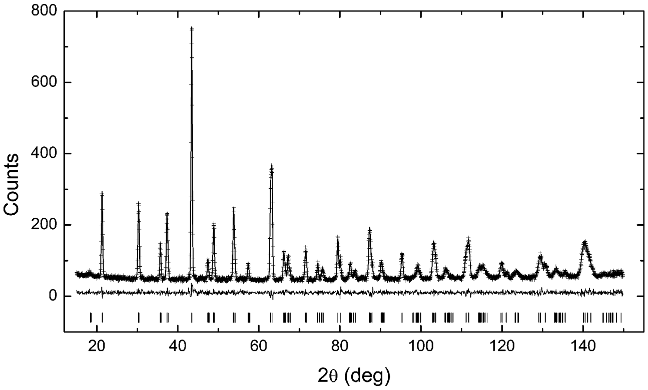

Figure 1. Observed, calculated, and difference neutron difraction pattern of $BaBi_{0.5}{}^{3+}$ $(Bi_{0.2}{}^{5+}Nb_{0.3}{}^{5+})O_3$ at room temperature, fitted in the $R\bar{3}$ space group. Tick marks are the symmetry allowed reflections. Neutron diffraction data were collected using the instrument D2B at ILL, Grenoble, France.

Although our intent was to replace Bi^{5+} ions in $BaBi_{0.5}{}^{3+}Bi_{0.5}{}^{5+}O_3$ by Nb^{5+} ions, we could succeed in getting a single-phase material only up to 60% substitution. Beyond this limit, $Ba_5Nb_4O_{15}$ appeared as secondary phase. Therefore, we have investigated the material with the composition $BaBi_{0.5}{}^{3+}(Bi_{0.2}{}^{5+}Nb_{0.3}{}^{5+})O_3$. X-ray and neutron diffraction patterns of BBN could not be indexed in the monoclinic structure ($I2/m$) of the parent compound BBO, but they were found to be similar to those of $BaBi_{0.5}Sb_{0.5}O_3$, which has a rhombohedral structure ($R\bar{3}$) at room temperature.[15] It should be mentioned here that the $R\bar{3}$ phase also exists in the parent compound BBO as one of the high-temperature phases.[15,16] Subsequently, all diffraction lines in both X-ray and neutron diffraction patterns of BBN could be indexed with the rhombohedral symmetry. Further, structural refinement was carried out on the neutron data using the structural model of $BaBi_{0.5}Sb_{0.5}O_3$.[15] The fitted neutron diffraction pattern obtained at the convergence is shown in Figure 1. A good fit with reliable agreement factors (see the Supporting Information) confirmed that the BBN has rhombohedral structure with $R\bar{3}$ space group. There are two crystallographic sites for B cations, {0,0,0} and {0.5, 0.5, 0.5}. The first one is completely occupied by Bi(I) ions and other one is occupied by Bi(II) and Nb ions. The average bond lengths of Bi(I)−O and Bi(II)/Nb−O are 2.300(3) and 2.052(3) Å, respectively. The different bond lengths can be understood from the difference in ionic radii of Bi^{3+}, Bi^{5+}, and Nb^{5+} ions in octahedral coordination.[16] From the inspection of the bond lengths and a comparison with their corresponding bond lengths for BBO and $BaBi_{0.5}Sb_{0.5}O_3$ (2.29 and 2.11 Å and 2.31 and 2.199 Å, respectively), we suggest that Bi ions occupying the {0,0,0} site are in the trivalent state and those occupying the {0.5, 0.5, 0.5} site are in a pentavalent state. The Bi^{5+} and Nb^{5+} ions are distributed randomly in the {0.5, 0.5, 0.5} site. Although this structural model, $R\bar{3}$, resulted in reliable agreement factors and structural parameters, we made an attempt to verify the noncentrosymmetric space group $R3$, a subgroup of $R\bar{3}$, because of the present observation that BBN shows ferroelectricity at room temperature. The refinement gave a fairly good fit ($\chi^2 = 1.25$), but the errors on oxygen positions were at the third decimal with $R_{wp} = 5.58\%$ which is slightly higher than that (5.44%) for $R\bar{3}$. Therefore, we conclude that the space group $R\bar{3}$ better describes the structure of BBN.

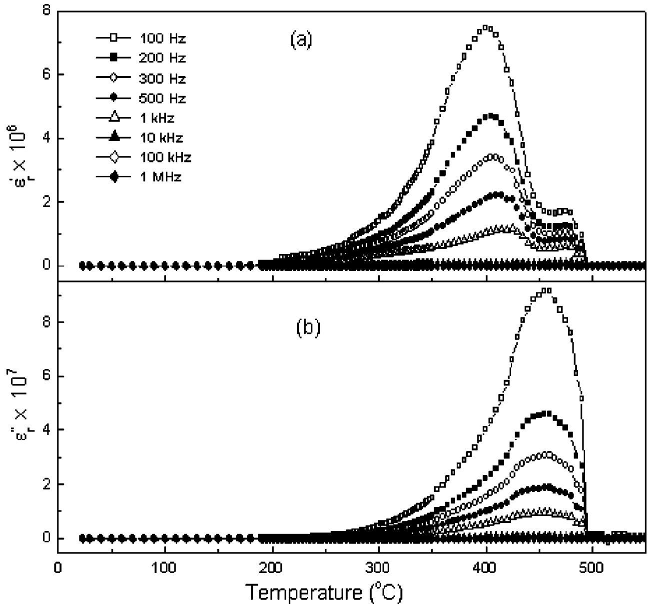

Figure 2. Temperature dependence of (a) real and (b) imaginary part of the dielectric constant.

A brief discussion on various structural transitions occuring in the parent compound (BBO) is essential to understand the structure of BBN. BBO undergoes several structural phase transition in the temperature range 4.2−975 K, the low-temperature monoclinic ($P2_1/n$) to the room-temperature monoclinic ($I2/m$) at 132 K, $I2/m$ to the rhombohedral ($R\bar{3}$) at 430 K, and finally, to the high-temperature cubic ($Fm\bar{3}m$) phase at 820 K. A similar structural behavior is reported for another derivative of BBO, namely, $BaBi_{0.5}Sb_{0.5}O_3$, except that the transition temperatures are lower: 250 K for $I2/m$ to $R\bar{3}$ and 515 K for $R\bar{3}$ to $Fm\bar{3}m$, and the low-temperature structure ($P2_1/n$) is not formed at all. It is interesting and important to note a pressure dependent study on $BaBi_{0.5}Sb_{0.5}O_3$, which revealed that the ambient pressure and temperature rhombohedral phase undergoes a phase transition to the monoclinic $I2/m$ structure. These studies confirm that both pressure and temperature can induce these structural changes. The fact that the transition temperatures are lower in $BaBi_{0.5}Sb_{0.5}O_3$ is due to the substitution of smaller Sb^{5+} ions ($r = 0.60$ Å) for larger Bi^{5+} ions ($r = 0.76$ Å) or a chemical pressure.[16] This is in agreement with the present observation that substitution of smaller Nb^{5+} ions (0.64 Å) at the Bi^{5+} site in BBO results in the rhombohedral structure at room temperature. It must be emphasized that all these structures are characterized by centrosymmetric space groups.

Figure 2a shows the real part of dielectric response of BBN at various frequencies (100 Hz to 1 MHz) as a function of temperature. It can be seen that the dielectric constant has a broad maximum around 400 °C, where the value of the dielectric constant is very high, ~7.5 × 10^6 for 100 Hz. However, the dielectric constant at room temperature is very

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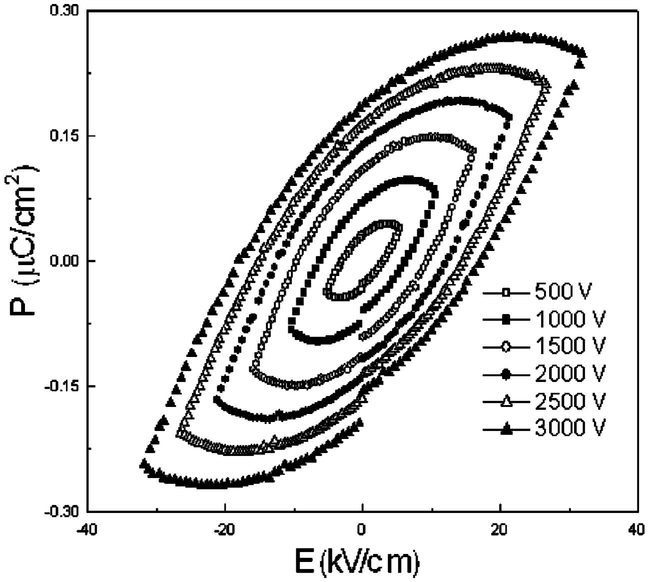

Figure 3. Room-temperature ferroelectric hysteresis measured at various driving voltages at 1 kHz after electric poling at 520 °C.

low (∼100). The broad maximum in dielectric constant indicates a diffuse phase transition from paraelectric to ferroelectric. Also, there is a shoulder at around 480 °C that may result from the disorder at the B-site because of a decrease in the degree of long-range ordering of Bi^{3+} and Bi^{5+} ions at high temperatures. The dielectric maximum decreases drastically with an increase in frequency. Further, the maximum at 400 °C shifts toward higher temperature with increase of frequency, whereas the maximum at 480 °C does not change significantly. The frequency dependence of the dielectric maximum is an indication for relaxor ferroelectric. The imaginary part of dielectric constant also shows a similar broad maximum centered at around 460 °C as seen in Figure 2b. Though the Nb^{5+} ion is ferroelectrically active, the appearance of ferroelectricity in the present system is mainly due to Bi^{3+} ion with a $6s^2$ lone pair. This is supported by the observation of ferroelectricity in $BaBi_{0.5}Sb_{0.5}O_3$, which does not contain niobium.[17]

Temperature dependence of powder X-ray diffraction showed that there is a structural transition between 450 and 700 °C (see the Supporting Information). From the inspection of the peak at $2\theta = 52°$, it appears that the transition occurs continuously, which is consistent with the observed broad dielectric transition. This peak is composed of three reflections (233, 013, and 11$\bar{2}$) in the rhombohedral phase, which becomes a single broad peak at 700 °C. Considering that the broadening of this peak is caused by the high temperature, it can be indexed as a 422 reflection in the $Fm\bar{3}m$ cubic phase, as already reported in BBO and $BaBi_{0.5}Sb_{0.5}O_3$, where the rhombohedral ($R\bar{3}$) phase transforms to high-temperature cubic ($Fm\bar{3}m$) structure.[15] To confirm that the high-temperature phase is cubic, we performed Rietveld refinement using the program Fullprof.[18] This gave a good fit to the data ($\chi^2 = 3.76$) with $R_{\mathrm{Bragg}} = 5.0\%$. Because the temperature dependence of the dielectric constant exhibits a very broad transition with a shoulder at ∼480 °C and because of the absence of XRD data between 450 and 700 °C, it would be difficult to infer the exact temperature at which the structural transition occurs.

The polarization with respect to electric field curve of the sample after an electric poling is shown in Figure 3. The sample shows a hysteresis loop with a remanent polarization of 0.187 $\mu C/cm^2$ and a coercive field of 16.93 kV/cm for a driving voltage of 3 kV at the frequency of 100 Hz. The nonlinear bulky hysteresis loop is indicative of a lossy ferroelectric system. However, the observation of ferroelectricity is in contradiction with the centrosymmetric structure. There are various possible explanations for the observed ferroelectricity. It is probable that the distortion is small, which cannot be identified by X-ray or neutron diffraction, and CBED studies may be required for examining the presence or absence of inversion symmetry as reported for BBO and $BiMnO_3$.[13,19] The other possibility is that there may be a local distortion in the structure due to lone pair electrons of Bi^{3+} ion, which gives rise to the polarization. Such a local distortion has been suggested for the observation of a weak ferroelectricity in a centrosymmetric $YCrO_3$ based on pair distribution function (PDF) analysis.[20]

In summary, the structure of $BaBi_{0.7}Nb_{0.3}O_3$ perovskite has been determined by neutron diffraction. It is an ordered perovskite with a rhombohedral ($R\bar{3}$) structure whose chemical formula can be written as $BaBi_{0.5}{}^{3+}(Bi_{0.2}{}^{5+}Nb_{0.3}{}^{5+})O_3$.

Although the average structure is described by a centrosymmetric space group, it exhibits ferroelectricity at room temperature. The observation of ferroelectricity is consistent with a phase transition at around 420 °C that is revealed by both the temperature dependent on dielectric constant and powder X-ray diffraction measurements. The room-temperature rhombohedral structure transforms to cubic structure at high temperature.

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Supporting Information Available: Powder X-ray diffraction pattern at higher temperatures and table for structural parameters from Rietveld refinement of room tempearature neutron diffraction data for $BaBi_{0.7}Nb_{0.3}O_3$ (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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