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# Dielectric properties, thermal decomposition and related aspects of BiAlO<sub>3</sub>

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## 1. Introduction

The ferroelectric material most widely used in devices is the distorted perovskite, Lead Zirconium Titanate (PZT) [1,2]. However, the toxicity of lead in PZT is a serious environmental concern. Therefore, it is essential to look for non-toxic materials whose properties are comparable or superior to PZT. In the recent vears, a series of materials with the general formula BiMO<sub>3</sub>(M = transition metals) have been reported to exhibit not only ferroelectricity but magnetism as well. Except BiFeO<sub>3</sub>, all other perovskites with Bi<sup>3+</sup> at A site are prepared at high pressure and high temperature conditions [3-6]. In these multiferroic materials, the origin of ferroelectricity is in the A-site Bi<sup>3+</sup> ions with the 6s<sup>2</sup> lone pair whereas magnetism is due to transition metal ions [7,8]. A large ferroelectric polarization ( $\sim$ 90  $\mu$ C/cm<sup>2</sup>) was reported [9] in thin films of BiFeO<sub>3</sub> and substantiated on the basis of first-principles calculations [10]. An ordered perovskite  $BaBi^{3+}_{0.5}Bi^{5+}_{0.2}Nb^{5+}_{0.3}O_3$  with  $Bi^{3+}$  ion at the B-site was reported recently to exhibit ferroelectricity at room temperature [11]. These facts demonstrate that the  $Bi^{3+}$  ion with the  $6s^2$  lone pair would be an alternate candidate to replace the toxic  $Pb^{2+}:6s^2$ ion in ferroelectric materials. Recent theoretical calculations do

## ABSTRACT

BiAlO<sub>3</sub>, prepared under high-pressure and high-temperature conditions has a rhombohedral perovskite structure (*R*3*c* with *a* = 5.3747(4) Å and *c* = 13.391(1) Å) and decomposes around 550 °C to form the intermediate Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> phase along with the Bi<sub>26-x</sub>Al<sub>x</sub>O<sub>40-y</sub> and Al<sub>2</sub>O<sub>3</sub>. Above 580 °C, the intermediate phase changes into the Bi<sub>26-x</sub>Al<sub>x</sub>O<sub>40-y</sub>. Dielectric measurements show an anomaly at the decomposition temperature and hysteresis at room temperature with a maximum polarization of ~16  $\mu$ C/cm<sup>2</sup>. Raman scattering measurements suggest softening of optical phonon modes, and are consistent with the occurrence of thermal decomposition of the rhombohedral phase to form the thermodynamically stable phase.

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predict that BiAlO<sub>3</sub> (BAO) and BiGaO<sub>3</sub> (BGO) perovskites with Bi<sup>3+</sup> ions at the A-site will have large ferroelectric polarization and piezoelectricity [12]. We, therefore, considered important to investigate these materials experimentally. Our attempt to prepare both BAO and BGO at ambient-pressure resulted in  $Bi_{26-x}(Al/Ga)_xO_{40-y}$  with the  $\gamma$ - $Bi_2O_3$  structure (space group I23) rather than the predicted perovskite structure. These materials, however, exhibited ferroelectric hysteresis at room temperature with low polarization values [13]. Belik et al. [14] have reported the structures of BAO and BGO prepared under high pressure. BAO has a perovskite-like non-centrosymmetric trigonal (R3c) structure while BGO crystallizes in a pyroxene-like structure with a centrosymmetric orthorhombic symmetry (Pcca). Recently BAO is reported to be a ferroelectric material by Zylberberg et al. [15]. Here, we report dielectric, thermal properties and the temperature dependence of optical phonon modes of BAO prepared under highpressure and high temperature conditions.

# 2. Experimental

BAO was prepared at high-pressure using a cubic anvil high pressure apparatus. Since the commercially available bismuth oxide was found to include  $Bi_2O_2CO_3$ , it was heated at 700 °C in oxygen atmosphere to make it pure  $Bi_2O_3$  and kept in a dry box. A 1:1 ratio of  $Bi_2O_3$  and  $Al_2O_3$  was mixed in the glove box, pelletized and packed inside a gold capsule. The capsule was placed in the high pressure apparatus and a pressure of



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**Fig. 1.** Observed, calculated and difference X-ray diffraction patterns of BAO. Vertical tick marks are symmetry-allowed reflections and the second row corresponds to the  $Bi_{24}Al_2O_{40}$  secondary phase.

4.5 GPa was applied and heated to  $\sim$ 800 °C and kept at this temperature for 2 h. After 2 h, the heater was switched off and the sample was allowed to cool to room temperature and the pressure was reduced slowly. The solid sample was removed from the Au capsule. This preparation procedure is slightly different from the one adopted in our previous work [13] and the present method was necessary to obtain the perovskite BiAlO<sub>3</sub> phase. Phase purity was checked with a Rigaku X-ray Diffractometer and high temperature XRD data were collected using Bruker D8 Discover using Cu K $\alpha$  radiation. Rietveld refinement was carried out on the X-ray data using the program Fullprof [16]. Capacitors were prepared by depositing gold on both sides of the pellets using DC sputtering. Ferroelectric measurements were carried out using Radiant Technologies Precision workstation. Capacitance and dielectric measurements were carried out using Agilent Impedance analyzer from 100 Hz to 1 MHz in the temperature range of 30-500 °C. Temperature-dependent Raman spectra of the BAO were recorded using LabRAM HR800 Raman spectrometer with an Ar laser (514.5 nm) as the excitation source. Thermogravimetric and differential thermal analysis (TG-DTA) was carried out (Mettler Toledo, TG-850) on BAO in the range between room temperature and 700 °C (heating rate =  $10 \circ C \min^{-1}$ ) in oxygen atmosphere.

## 3. Results and discussion

Rietveld refinement of the XRD data of BAO gave a structure with the rhombohedral symmetry (space group R3c) with the lattice parameters a = 5.3747(4) Å and c = 13.391(1) Å, in agreement with the literature report [14]. The XRD pattern obtained from the final Rietveld refinement is shown in Fig. 1. A small amount (5%) of the ambient-pressure phase  $(Bi_{26-x}Al_xO_{40})$  is present as a secondary phase. Differential thermal analysis (DTA) carried out while heating in the temperature range 30-700 °C is shown in Fig. 2(a). It can be seen from this figure that there are two peaks, an endothermic one at 550 °C and an exothermic one at 580 °C. The cooling curve did not show any anomaly, suggesting that the process associated with the exothermic peak is irreversible. One can easily miss the endothermic peak unless the DTA curve is recorded carefully (slowly). In the earlier study [14] only an irreversible exothermic peak was found around 580 °C and was attributed to the decomposition of BAO into  $Bi_2Al_4O_9$ ,  $Bi_{26-x}Al_xO_{40-y}$  and  $Al_2O_3$  phases based on the XRD patterns obtained after heating the sample above 580 °C. Thermal decomposition is an endothermic process while a phase formation can be exothermic. In order to confirm that the endothermic peak was irreversible, a sample was heated up to 570 °C and then cooled to room temperature. The XRD patterns of BAO heated



**Fig. 2.** (a) DTA curve of BiAlO<sub>3</sub> showing endothermic and exothermic peaks at 550 and 580 °C, respectively. The endothermic peak corresponds to the decomposition of the high-pressure rhombohedral structure while the exothermic peak indicates the formation of  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> structure. (b) Temperature-dependent of the real part of the dielectric constant exhibiting a maximum at the decomposition temperature.

at 570 and 600 °C were characteristic of a mixture of Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>,  $Bi_{26-x}Al_xO_{40-y}$  and  $Al_2O_3$  confirming that both the DTA peaks are irreversible. The material heated to 750 °C, however, showed only the latter phases, suggesting that the thermodynamically stable phase is the  $Bi_{26-x}Al_xO_{40-y}$ , while  $Bi_2Al_4O_9$  may be an intermediate one. From these results, we suggest the origin of the endothermic peak to be the decomposition of the metastable high pressure rhombohedral phase and the subsequent formation of the intermediate Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>. The exothermic peak is associated with the formation of  $Bi_{26-x}Al_xO_{40-y}$  which has a large number of atoms per unit cell than the orthorhombic Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>. It is noteworthy that we do not observe a structural transformation of rhombohedral BAO till it decomposes at 570 °C, all our measurements having been carried out in air or in an oxygen atmosphere. High temperature XRD data recorded in vacuum (10<sup>-5</sup> bar) indeed showed that there was no structural transformation or decomposition up to 700 °C.

In Fig. 2(b), we show the temperature-dependent real part ( $\varepsilon$ ') of the dielectric response of BAO at various frequencies in the temperature range 27–600 °C. The dielectric constant at low frequencies has a well-defined maximum around 550 °C and increases further with increase of temperature above 580 °C. Fig. 2(a) and (b) suggest that the dielectric maximum corresponds to the decomposition temperature of the high-pressure rhombohedral phase and not to a high-symmetry phase. Furthermore, the dielectric constant exhibits frequency dispersion over the entire range of temperature employed without any appreciable shift in the dielectric maximum. It is known that Bi<sub>26-x</sub>Al<sub>x</sub>O<sub>40-y</sub> is ferroelectric constant increases with temperature due to dc conduction. The increase in the dielectric constant of BAO observed above 570 °C in the present study may have such an origin.

In Fig. 3, we show a polarization-electric field curve of BAO recorded at room temperature on a 200  $\mu$ m thin sample using Ag electrode. The shape of the curve is typical of ferroelectric material with a maximum polarization value of 16  $\mu$ C/cm<sup>2</sup> and remanent polarization of 11.5  $\mu$ C/cm<sup>2</sup>. A coercive field of 69 kV/cm was



Fig. 3. Ferroelectric hysteresis of BiAlO<sub>3</sub> at room temperature.

obtained for an applied voltage of 2.25 kV with a frequency of 10 Hz. However, the observed polarization value for BAO at room temperature is lower than that predicted (75.6  $\mu$ C/cm<sup>2</sup>) [12] and also calculated using structural data (32  $\mu$ C/cm<sup>2</sup>) [14]. The literature value of polarization reported for bulk BaTiO<sub>3</sub> is 26  $\mu$ C/cm<sup>2</sup> at room temperature which is considerably higher than that observed in the BAO system [17]. The remanent polarization of commercial PZT samples reported by PI Ceramics (PIC 151) is 0.36 C/m<sup>2</sup> with a coercive field of 0.9 kV/mm [18]. However, the polarization value obtained for BAO is in agreement with value reported by Zylberberg et al. [15].

In order to obtain an insight into the behavior of soft-mode phonons and thermal behavior of the high-pressure rhombohedral phase and the subsequent appearance of the ambient pressure phase, we have recorded Raman spectra of BAO at various temperatures. Due to limitations in our instrument, we could record the spectra only up to 520 °C. Group theoretical analysis of the perovskite with R3c symmetry predicts 13 Raman active modes  $(\Gamma = 4A_1 + 9E)$ . We observe all the 13 modes at room temperature in agreement with spectrum reported in the literature [14]. With increase in temperature, frequencies of all the A1 modes decrease and the peaks become broader. The temperature dependence of frequency and intensity of some of the Raman modes are shown in Fig. 4. The figure reveals that both the frequency and the intensity of the Raman bands decrease with increasing temperature up to 520 °C. The room temperature Raman spectrum of a sample heated to 600 °C showed a completely different Raman spectrum with 22 modes. This finding supports the suggestion that the rhombohedral structure decomposes above 550 °C.

#### 4. Conclusions

We have demonstrated that BiAlO<sub>3</sub> undergoes an endothermic transition at 550 °C due to the decomposition of the metastable high pressure rhombohedral phase, and an exothermic transition at 580 °C due to the formation of Bi<sub>26-x</sub>Al<sub>x</sub>O<sub>40-y</sub> and Al<sub>2</sub>O<sub>3</sub>. The exothermic peak is accompanied by a dielectric constant maximum. The material is ferroelectric at room-temperature with a maximum polarization of ~16  $\mu$ C/cm<sup>2</sup> and the Raman bands show decrease in frequency and intensity up to 520 °C.



**Fig. 4.** Temperature dependence of the frequency and the intensity of various Raman bands in BiAlO<sub>3</sub>.

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