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High temperature lead-free relaxor ferroelectric: Intergrowth Aurivillius phase BaBi_{2}Nb_{2}O_{9}–Bi_{4}Ti_{5}O_{12} ceramics

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Intergrowth BaBi_{2}Nb_{2}O_{9}–Bi_{4}Ti_{5}O_{12} (BaBi_{2}Ti_{4}Nb_{2}O_{21}) Aurivillius phase ceramic has been found to be a relaxor ferroelectric (RFE) with the highest reported temperature of the maximum of the dielectric permittivity (T_m) of all of the known RFE systems. Dielectric characterization revealed that it has two dielectric anomalies. The first one is a frequency independent broad dielectric constant peak at ~280 °C, while the second anomaly shows relaxor behavior at 636 °C (100 kHz). There is obvious frequency dispersion of dielectric response at room temperature, which is in agreement with dielectric properties of a typical relaxor. Ferroelectric hysteresis loops and a measurable value of piezoelectric constant d_{33} confirmed the ferroelectric nature of BaBi_{2}Ti_{4}Nb_{2}O_{21} ceramics. The piezoelectric response remained even after annealing at temperatures above 636 °C.

I. INTRODUCTION

High-temperature sensing technology is important in the chemical and material processing, automotive, aerospace, and power generating industries. Electromechanical transducing materials are required to sense strains, vibrations, and noise under harsh thermal conditions.1 Relaxor ferroelectrics (RFE) have large dielectric permittivity and electromechanical constants,2 which make them very attractive for the above applications.5,6 RFE exhibit a broad frequency dependent dielectric anomaly. With increasing frequency, the temperature (T_m) of the maximum of dielectric permittivity (ε_{r,max}) increases and the magnitude of ε_{r,max} decreases.5 However, their relatively low T_m temperature may limit their application in high temperature fields.5,6 Consequently, a great deal of effort has recently been put into exploring new RFE materials with higher T_m value.5–12

RFE exist in the different crystal structures that host ferroelectricity, including perovskites, tungsten bronzes, rutile structure, and Aurivillius phase.7,8 In perovskites, RFE behavior occurs predominantly in lead-based complex compositions with the general formula Pb(B_{1}B_{2})O_{3}, (B_{1}=Mg^{2+},Zn^{2+},Ni^{2+},Sc^{3+},... B_{2}=Nb^{5+},Ti^{3+},W^{6+},...) or lanthanum-substituted PbZr_{1−x}Ti_{x}O_{3} (PLZT).3 Among lead-based perovskite compounds, Pb(Zn_{1/3}Nb_{2/3})O_{3} has the highest T_m of 140 °C (100 kHz).9,10 To increase the piezoelectric activity and T_m of RFE, lead-based perovskite, ferroelectric solid solutions, especially those containing PbTiO_{3} as one of the end components, have been developed. Their superior piezoelectric properties can be observed in compositions close to the morphotropic phase boundary (MPB).13 A MPB separates strong RFE behavior from normal ferroelectric behavior in the phase diagram of Pb(B_{1}B_{2})O_{3}–PbTiO_{3} solid solutions.14 Compositions of Pb(B_{1}B_{2})O_{3}−PbTiO_{3} that are rich in Pb(B_{1}B_{2})O_{3} and close to the MPB usually display RFE behaviors. Solid solution of (1−x)Pb(Yb_{1/2}Nb_{1/2})O_{3}−xPbTiO_{3} with x=0.2 to 0.49 are RFE and the composition of x=0.49 has a T_m of ~300 °C at 10 kHz, which is the highest T_m among all Pb(B_{1}B_{2})O_{3}–PbTiO_{3} RFE systems studied to date.15,16 Recently, a qualitative relationship between perovskite tolerance factor and the Curie point (T_c) at the MPB in PbTiO_{3} based systems was proposed.11,17–19 In general, the smaller the tolerance factor of the non-PbTiO_{3} end member, the higher T_c at the MPB.14,20 Guided by this relationship, low tolerance factor bismuth perovskite compounds with PbTiO_{3} have been shown to be promising candidates for new, lead-free or lead reduced, high T_m RFEs. The compounds xBi_{2}ScO_{5}−(1−x)PbTiO_{3} in the range of 0.5≤x≤0.6 are RFE with T_m up to ~323 °C (100 kHz) at x=0.5.18 The solid solution of xPbTiO_{3}−(1−x)Bi_{2}Mn_{1/2}Ti_{1/2}O_{3} with x=0.30−0.35 exhibit RFE behavior with T_m = 400 °C at 100 kHz.20 In tungsten bronzes, Pb_{1−x}Ba_{x}Nb_{2}O_{6} with x=0.25 exhibit RFE response with T_m = 389 °C at 100 kHz.21 Rutile-based FeTiTaO_{6} is reported to be RFE with T_m=550 K at 530 Hz.8

Aurivillius phase materials have generated increasing attention due to their potential use in nonvolatile ferroelectric random-access memory22 and high-temperature piezoelectric applications.23,24 Moreover, they are environment friendly lead-free piezoelectric materials. Their general formula is (B_{1}O_{2})_{2}^{2+}(A_{n−1}B_{n}O_{3})^{2−}, where A is a 12-coordination site and B is an octahedral coordination site with m indicating the number of octahedra stacked along the c-axis between two neighboring (B_{1}O_{2})^{2+} layers.25 The ferroelectric properties for even-(m=2n) and odd-layer (m=2n+1) Aurivillius phase compounds are different.26 The spontaneous polarization P_s of even-layer compounds is only along the...
a-axis. Based on their orthorhombic space group $A_2am$, the polarization along the c-axis is cancelled because of mirror symmetry. However, in odd-layer compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$, monoclinic, space group $P_m$) a small degree of spontaneous polarization along the c-axis can be observed besides the major polarization along the a-axis. Some Aurivillius phase compounds show interesting relaxor and multiferroic properties when Ba/lanthanides and Fe (Ref. 33) are on the A- and B-site in the general formula, respectively. $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ is reported to show RFE behavior with $T_m=400^\circ \text{C}$ at 1 MHz. Mixed-layer Aurivillius phase compounds were first discovered by Kikuchi et al. They consist of a regular intergrowth of one half the unit cell of a m member structure and one half the unit cell of a $m+1$ member structure. Recently, they have generated a renewed interest because of their superior and interesting ferroelectric properties. For example, in intergrowth $\text{Bi}_4\text{Ti}_3\text{O}_{12–}\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ single crystals, remanent polarization ($P_r$) was observed for intergrowth oxides not only along the a-axis but also along the c-axis, and the c-axis component is suggested to originate from the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ layers in the intergrowth structure. An enhanced $P_r$ was found in intergrowth $\text{Bi}_4\text{Ti}_3\text{O}_{12–}\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ceramics and $\text{Bi}_4\text{Ti}_3\text{O}_{12–}\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics, where $P_r$ was larger than that of either $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ or $\text{SrBi}_4\text{Ti}_4\text{O}_{15}/\text{BaBi}_4\text{Ti}_4\text{O}_{15}$.

In this paper, a new Aurivillius phase RFE, $\text{BaBi}_4\text{Ti}_3\text{Nb}_2\text{O}_{21}$ (BBTN), with the highest value of $T_m$ (636 °C at 100 kHz) of all the known RFEs is reported. It is an intergrowth of $\text{BaBi}_4\text{Nb}_2\text{O}_{9}$ (BBN, $m=2$)–$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT, $m=3$). Although this compound was reported by Kikuchi et al., they only provided the dielectric spectrum of BBTN ceramics at 1 MHz, so the RFE behavior of BBTN was not reported. What makes this system of additional interest is that one of constituent compound is ferroelectric (BIT) (Ref. 40) and the other is relaxor (BBN). The aim of this paper is to present the results of an investigation of the electrical properties of BBTN ceramics and to discuss them with respect to those of two constituent oxides, BBN and BIT.

II. EXPERIMENTAL

BBTN, BBN, and BIT were prepared by the conventional solid-state reaction sintering. The starting materials were $\text{BaCO}_3$ of 99.0% purity, $\text{Bi}_2\text{O}_3$ of 99.975% purity, $\text{TiO}_2$ of 99.6% purity, and $\text{Nb}_2\text{O}_5$ of 99.5% purity. The stoichiometric mixtures of oxides were thoroughly milled. The calcination conditions were 950 °C 4 h for BBN and BIT, and 1050 °C 4 h for BBTN. After calcination, the powders were pressed into disks and sintered for 1 h at 1100 °C for BBN, 1150 °C for BIT, and 1080 °C for BBTN. The samples obtained were >95% of their theoretical density. X-ray diffraction (XRD) patterns for the calcined powders were obtained using Cu $K_{\alpha}$ radiation in a Siemens D5000. The microstructures of the BBTN ceramics were analyzed with a scanning electron microscope (SEM; JEOL JSM 6300). The samples for the SEM study were polished and then thermally etched at 1010 °C for 20 min. Electrical property measurements were performed on Pt-electroded samples (Gwent Electronic Materials Ltd., C2011004DS). The temperature dependence of the dielectric constants $\varepsilon$, and losses $D$ were measured at different frequencies using an LCR meter (Agilent 4284A). The frequency dependence of the dielectric constants and losses were measured at room temperature using an impedance analyzer (Agilent 4294A). The ferroelectric $I–E$ (current-electric field) and $P–E$ (polarization—electric field) loops were measured by a ferroelectric hysteresis measurement tester at 25 and 200 °C at 100 Hz. The measurement procedure involved the application of triangular voltage waveform for two complete cycles. BBTN ceramics for piezoelectric measurements were poled in silicone oil at 200 °C under a dc electric field of 9 MV/m. BIT ceramics could only be poled at room temperature due to its high electrical conductivity. The piezoelectric constant, $d_{33}$, was measured using a piezo $d_{33}$ meter (ZI-3B, Institute of Acoustics, Chinese Academic of Science, Beijing). Thermal depoling experiments were conducted by holding the poled samples with platinum electrodes for 2 h at high temperatures, cooling to room temperature, measuring $d_{33}$, and repeating the procedure at increasing temperature.

III. RESULTS AND DISCUSSION

A. Crystal structure

Figure 1 shows the XRD patterns of the calcined BIT, BBTN, and BBN powders. The materials are all single-phase. The XRD pattern of BBTN is not a simple mixture of BIT and BBN, which clearly indicates the formation of an intergrowth Aurivillius phase. The strongest diffraction peak is (115) for BBN ($m=2$), (116) for BBTN ($m=2.5$), and (117) for BIT ($m=3$), which is consistent with the (1 1 2$m+1$) highest diffraction peak in Aurivillius phase. Figure 2 shows the microstructure of BBTN ceramic; it is composed of platelike grains, ~2 µm long, and 0.5 µm thick.

B. Dielectric properties

Figure 3 illustrates the temperature dependence of dielectric constants and losses of BBTN ceramic at different frequencies up to 750 °C. A double dielectric anomaly is clearly observed at $T_{m1}$ (≈280 ± 5 °C at 100 kHz) and $T_{m2}$...
In addition, both dielectric peaks are broad. Kikuchi et al.\textsuperscript{35} also reported a double dielectric anomaly at about 280 and 650 °C at 1 MHz, which is consistent with the present work (652 ± 5 °C at 1 MHz). The temperature ($T_m$) of the first anomaly of $\varepsilon_r$ is frequency independent, while $T_m2$ of the second anomaly of $\varepsilon_r$ is frequency dependent. The $T_m2$ shifts from 632.9 ± 5 °C at 10 kHz to 652.3 ± 5 °C at 1 MHz. The losses increase with increasing temperature. Unlike Pb(B$_2$O$_3$)$_3$, where frequency dispersion of the loss peaks can be observed, the frequency dispersion of loss peaks of BBTN are lost in the background produced by the high electrical conductivity of BBTN above 500 °C.\textsuperscript{45} Two mechanisms are proposed to explain the two dielectric anomalies for intergrowth Aurivillius phase materials. Based on the dielectric properties of intergrowth Bi$_3$Ti$_{1.5}$W$_{0.5}$O$_9$–Bi$_4$Ti$_3$O$_{12}$ ($m$=2 and 3) ceramics, Luo et al.\textsuperscript{46} suggested that there are two ferroelectric phase transitions above room temperature, which correspond to the $T_c$ of the members of the intergrowth compound transforming from their ferroelectric to paraelectric state. Maalal et al.\textsuperscript{47} suggested from their study of intergrowth Bi$_3$TiNbO$_9$–Bi$_4$Ti$_3$O$_{12}$ ($m$=2 and 3) ceramics that the higher transition temperature corresponds to the Curie point, whereas the lower one can be assigned to a phase transition within the orthorhombic symmetry produced by a change in the space group.

In order to compare the dielectric properties of BBTN ceramics with those of the two constituent oxides: (a) BBN and (b) BIT.

<FIG. 3. Temperature dependence of dielectric constant $\varepsilon_r$ and loss factor $D$ for BBTN ceramics.>

<FIG. 4. (Color online) Comparison of dielectric properties of BBTN ceramics with those of two constituent oxides: (a) BBN and (b) BIT.>
The dielectric loss of BIT slightly drops from 10^2 to 10^3 Hz growth. Tc/H_11006/BBTN was 3.2/Tc/H_11006/BBTN decrease dramatically as the frequency increases. On the contrary, the dielectric constant of BIT just shows a slight decrease. Among all three compositions, BBN shows the highest loss throughout the frequency range. The broad maximum in the dielectric loss of BBN occurs at f=1.68 \times 10^4 Hz. The loss of BBTN continuously increases with increasing frequency and no maximum was observed in the measured frequency ranges. Presumably, the loss peaks of BBTN are shifted to the high frequency range (>10^7 Hz). The dielectric loss of BIT slightly drops from 10^2 to 10^3 Hz and then remains almost constant above 10^3 Hz.

C. Ferroelectric and piezoelectric properties

Although BBTN shows relaxor behavior, its ferroelectric nature is still unclear. So P-E loop measurements of the three different ceramics were performed first at room temperature and 100 Hz. Only BIT exhibited ferroelectric switching, as evidenced by obvious current peaks in the I-E loop (Fig. 6). However, both BBTN and BBN (Ref. 31) did not show any ferroelectric switching at room temperature. This suggested that either BBTN is not ferroelectric or its coercive field is too high at room temperature. Then P-E loop measurements were performed at 200 °C and 100 Hz. The leakage current of BIT was too large to obtain a P-E loop. Although saturated loops were not obtained for BBTN due to its very high coercive field, the onset of ferroelectric switching, as indicated by current peaks (arrowed in Fig. 6), was observed. In addition, BBN still did not show ferroelectric switching at 200 °C, as shown in Fig. 6. The piezoelectric constant d_33 of BBTN was 3.2 ± 0.2 pC/N after poling at 200 °C and BIT was 4.5 ± 0.2 pC/N after poling at room temperature. The results of ferroelectric and piezoelectric property measurements show that BBTN is a RFE.

Figure 7 shows the d_33 of a BBTN ceramic as a function of the annealing temperature. The d_33 of BBTN ceramics continuously dropped with increasing annealing temperature and larger decreases occurred at about T_m1 and T_m2. The BBTN ceramics still showed weak piezoelectric response after annealing at temperatures above T_m2. Finally, after annealing at 775 °C, the BBTN ceramics exhibited no piezoelectric response. The existence of weak piezoelectric response above T_c has been reported in mixed-layer Bi_3TiNbO_9 –Bi_4Ti_3O_12 (T_c=935 °C) clusters in Bi_3TiNbO_9 –Bi_4Ti_3O_12 ceramics.\textsuperscript{55} This was ascribed to the existence of poled Bi_3TiNbO_9 clusters. However, the thermal depoling behavior of BBTN in the present work cannot be explained by the existence of poled BIT clusters present in BBTN ceramics because BIT will totally lose piezoelectric activity after annealing above 700 °C.\textsuperscript{44} The weak piezoelectric activity of BIT ceramic above T_m2 suggests that spontaneous polarization of BBTN ceramics is not suddenly lost at T_m2 but decays more gradually to zero, which is consistent with it being a RFE.\textsuperscript{52}
IV. CONCLUSION

In summary, intergrowth BaBi$_2$Nb$_2$O$_9$–Bi$_4$Ti$_3$O$_{12}$ (BaBi$_3$Ti$_3$Nb$_2$O$_{21}$) ceramic was found to be a RFE with the highest $T_m$ value (636 °C at 100 kHz) of all of the known RFE systems. The electrical properties of BaBi$_3$Ti$_3$Nb$_2$O$_{21}$ are greatly different from its two constituent oxides, BaBi$_2$Nb$_2$O$_9$ and Bi$_4$Ti$_3$O$_{12}$. The dielectric spectrum of BaBi$_3$Ti$_3$Nb$_2$O$_{21}$ was characterized by two dielectric anomalies. Relaxor behavior was confirmed by the dielectric anomaly at about 636 °C (100 kHz). An obvious frequency dependence of dielectric response was observed at room temperature, as is the case for a typical relaxor. The detectable ferroelectric domain switch and measurable value of piezoelectric constant $d_{33}$ clearly indicated the ferroelectric nature of BaBi$_3$Ti$_3$Nb$_2$O$_{21}$ ceramics. The weak piezoelectric response above 636 °C indicates the existence of spontaneous polarization of BBTN ceramics above $T_m$, which is consistent with it being a RFE.

42. XRD PDF Number 80–2143.
43. XRD PDF Number 86–1191.