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High temperature lead-free relaxor ferroelectric: Intergrowth Aurivillius phase BaBi$_2$Nb$_2$O$_9$–Bi$_4$Ti$_3$O$_{12}$ ceramics

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Intergrowth BaBi$_2$Nb$_2$O$_9$–Bi$_4$Ti$_3$O$_{12}$ (BaBi$_2$Ti$_3$Nb$_2$O$_{12}$) 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 $\sim 280$ °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$_3$Nb$_2$O$_{12}$ 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.$^{1,2}$ Relaxor ferroelectrics (RFE) have large dielectric permittivity and electromechanical constants,$^{3-14}$ 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 ($\varepsilon_{\text{r, max}}$) increases and the magnitude of $\varepsilon_{\text{r, max}}$ decreases.$^{2}$ 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$_x$Bi$_{2-x}$Bi$_2$O$_3$O$_2$, (Bi$_x$=Mg$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Sc$^{3+}$, ...). Ba$_2$Nb$_{2-x}$Ti$_{2x}$O$_{12}$ or lanthanum-substituted PbZr$_{1-x}$Ti$_x$O$_3$ (PLZT)$^{3}$ Among lead-based perovskite compounds, Pb(Zn$_{1/3}$Nb$_{2/3}$)$_2$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 morphotrophic phase boundary (MPB)$^{15}$ A MPB separates strong RFE behavior from normal ferroelectric behavior in the phase diagram of Pb(Bi$_{1/2}$Bi$_1$)$_2$O$_3$–PbTiO$_3$ solid solutions.$^{14}$ Compositions of Pb(Bi$_{1/2}$Bi$_1$)$_2$O$_3$–PbTiO$_3$ that are rich in Pb(Bi$_{1/2}$Bi$_1$)$_2$O$_3$ and close to the MPB usually display RFE behaviors. Solid solution of (1–$x$)Pb(Yb$_{1/2}$Nb$_{1/2}$)$_3$O$_3$–$x$PbTiO$_3$ with $x=0.2$ to 0.49 are RFE and the composition of $x=0.49$ has a $T_m$ of $\sim 300$ °C at 10 kHz, which is the highest $T_m$ among all Pb(Bi$_{1/2}$Bi$_1$)$_2$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 xBiScO$_3$–(1–x)PbTiO$_3$ in the range of 0.5 $\leq x \leq 0.6$ are RFE with $T_m$ up to $\sim 323$ °C (100 kHz) at $x=0.5$.$^{18}$ The solid solution of xPbTiO$_3$–(1–$x$)Bi(Mg$_{1/2}$Ti$_{1/2}$)$_2$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 memory$^{22}$ and high-temperature piezoelectric applications.$^{23,24}$ Moreover, they are environment friendly lead-free piezoelectric materials. Their general formula is (Bi$_2$O$_3$)$_{2n}$($A_{m-2n}$B$_n$O$_{3m}$)$^{2n+}$, 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 (Bi$_2$O$_3$)$_{2n}$ 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 $A_2/am$, the polarization along the c-axis is cancelled because of mirror symmetry.\(^5\) However, in odd-layer compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$, monoclinic, space group $P_{c}$) a small degree of spontaneous polarization along the c-axis can be observed besides the major polarization along the a-axis.\(^28-30\) Some Aurivillius phase compounds show interesting relaxor and multiferroic properties when Ba/lanthanides\(^31,32\) and Fe (Ref. 33) are on the A- and B-site in the general formula, respectively. BaBi$_4$Ti$_4$O$_{15}$ is reported to show RFE behavior with $T_m$ = $400 \ ^\circ C$ at 1 MHz.\(^34\)

Mixed-layer Aurivillius phase compounds were first discovered by Kikuchi et al.\(^35,36\) 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.\(^37\) 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\(^38\) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$–$\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics\(^39\) 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, BaBi$_4$Ti$_3$Nb$_2$O$_{21}$ (BBTN), with the highest value of $T_m$ ($636 \ ^\circ C$ at 100 kHz) of all of the known RFEs is reported. It is an intergrowth of BaBi$_4$Nb$_2$O$_9$ (BBN, $n=2$)–$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT, $n=3$). Although this compound was reported by Kikuchi et al.,\(^35\) 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 component is ferroelectric (BIT) (Ref. 40) and the other is relaxor (BBN).\(^31\) 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 for 4 h for BBN and BIT, and 1050 °C for 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., C2011004DG). The temperature dependence of the dielectric constants $\varepsilon_r$ 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.\(^41\) 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.\(^40\) The piezoelectric constant, $d_{33}$, was measured using a piezo $d_{33}$ meter (Z1-3B, 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.\(^36,42,43\) The XRD pattern of BBTN is not a simple mixture of BBN and BIT, 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 2m+1) highest diffraction peak in Aurivillius phase.\(^44\) 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 $T_m$ ($\approx$ 280 ± 5 °C at 100 kHz) and $T_m$
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\(_3\)B\(_2\))O\(_3\), 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, BIT, the temperature dependences of dielectric constants and losses of the three ceramics at two frequencies (100 kHz and 1 MHz) are shown in Fig. 4. At 200–300 °C, the BBN ceramics demonstrate strong frequency dispersion of permittivity and loss, whereas the BBTN ceramics have much broader, frequency independent, dielectric permittivity peaks, as shown in Fig. 4(a). The \(\varepsilon_r\) values of BBTN ceramics are almost comparable to those of BBN ceramics. In comparison, BIT ceramics show a frequency independent dielectric anomaly at 675 °C. A frequency dependent loss peak can be found in BIT ceramics between 300 and 600 °C, as shown in Fig. 4(b). This can be attributed to oxygen vacancy hopping.\textsuperscript{48,49} The higher losses of BIT result from its high electrical conductivity.\textsuperscript{40} BBTN ceramics have a frequency dependent dielectric anomaly at about 636 °C (100 kHz) [Fig. 4(b)]. The \(\varepsilon_r\) values of BBTN ceramics are much smaller than those of BIT ceramics. A diffuse phase transition is always expected in the ceramics of Ba-bearing Aurivillius phase compounds,\textsuperscript{31} as is the case for BBTN ceramics. Compared with the \(T_c\) (675 °C) of BIT, the \(T_m2\) (636 °C at
100 kHz) of BBTN ceramics is shifted toward a lower temperature. The fact that $T_c$ (or $T_m$) of Aurivillius intergrowth phase materials is between those of its two constitutes has been reported in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$–$\text{Bi}_3\text{Ti}_3\text{O}_9$ (intergrowth 2+3, $T_c=830 \, ^\circ\text{C}$) (Ref. 47) and $\text{Bi}_3\text{Ti}_{1.5}\text{W}_{0.5}\text{O}_9$–$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (intergrowth 2+3, $T_c=730 \, ^\circ\text{C}$). 46

Figure 5 shows the variation of dielectric constant and loss values as a function of frequency ranging from 100 Hz to 10 MHz at room temperature for BBN, BBTN, and BIT ceramics. Compared to the normal ferroelectric behavior of BIT, both BBN and BBTN show much stronger frequency dependence of dielectric constant and loss, as is the case for a typical relaxor.50 The dielectric constants of BBN and 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 $f=1.68 \times 10^4 \, \text{Hz}$. 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 ($>10^7 \, \text{Hz}$). The dielectric loss of BIT slightly drops from $10^2$ to $10^3 \, \text{Hz}$ and then remains almost constant above $10^3 \, \text{Hz}$.

**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 \, ^\circ\text{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 \, ^\circ\text{C}, as shown in Fig. 6. The piezoelectric constant $d_{33}$ of BBTN was $3.2 \pm 0.2 \, \text{pC/N}$ after poling at 200 \, ^\circ\text{C}$ and BIT was $4.5 \pm 0.2 \, \text{pC/N}$ 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 $T_m$ and $T_c$. The BBTN ceramics still showed weak piezoelectric response after annealing at temperatures above $T_m$. Finally, after annealing at 775 \, ^\circ\text{C}$, the BBTN ceramics exhibited no piezoelectric response. The existence of weak piezoelectric response above $T_c$ has been reported in mixed-layer $\text{Bi}_3\text{Ti}_4\text{NbO}_{31}$ ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$–$\text{Bi}_3\text{Ti}_3\text{O}_9$) ceramics.51 This was ascribed to the existence of poled $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($T_c=935 \, ^\circ\text{C}$) clusters in $\text{Bi}_3\text{Ti}_4\text{NbO}_{31}$. 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 \, ^\circ\text{C}.44 The weak piezoelectric activity of BIT ceramic above $T_m$ suggests that spontaneous polarization of BBTN ceramics is not suddenly lost at $T_m$ but decays more gradually to zero, which is consistent with it being a RFE.52

**FIG. 5.** (Color online) Frequency dependences of dielectric constant and loss of BBN, BBTN, and BIT at room temperature.

**FIG. 6.** $P-E$ and $I-E$ loops measured with 100 Hz at 25 \, ^\circ\text{C}$ for BIT, 200 \, ^\circ\text{C}$ for BBTN and BBN ceramics. Dashed and solid lines show $P-E$ and $I-E$ loops, respectively.

**FIG. 7.** (Color online) Effect of thermal depoling on piezoelectric properties of BBTN ceramics.
IV. CONCLUSION

In summary, intergrowth BaBi$_2$Nb$_2$O$_9$–Bi$_4$Ti$_3$O$_{12}$ (BaBi$_2$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$_2$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$_2$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$_2$Ti$_3$Nb$_2$O$_{21}$ ceramics. The weak piezoelectric response above 636 °C temperature indicates the existence of spontaneous polarization of BBTN ceramics above $T_m$, which is consistent with it being a RFE.

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