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Citation: *Journal of Applied Physics* **107**, 104111 (2010); doi: 10.1063/1.3380847

View online: <http://dx.doi.org/10.1063/1.3380847>

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

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(Received 6 October 2009; accepted 7 March 2010; published online 21 May 2010)

Intergrowth $\text{BaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ($\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$) 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 $\sim 280^\circ\text{C}$, 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 $\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$ ceramics. The piezoelectric response remained even after annealing at temperatures above 636°C .

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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,^{3,4} 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 ($\epsilon_{r\text{max}}$) increases and the magnitude of $\epsilon_{r\text{max}}$ decreases.³ 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 $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$, ($\text{B}_1 = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Sc}^{3+}, \dots$, $\text{B}_2 = \text{Nb}^{5+}, \text{Ta}^{5+}, \text{W}^{6+}, \dots$) or lanthanum-substituted $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PLZT).³ Among lead-based perovskite compounds, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ 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 be-

havior in the phase diagram of $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3\text{-PbTiO}_3$ solid solutions.¹⁴ Compositions of $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3\text{-PbTiO}_3$ that are rich in $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ and close to the MPB usually display RFE behaviors. Solid solution of $(1-x)\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}x\text{PbTiO}_3$ with $x=0.2$ to 0.49 are RFE and the composition of $x=0.49$ has a T_m of $\sim 300^\circ\text{C}$ at 10 kHz, which is the highest T_m among all $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3\text{-PbTiO}_3$ 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 $x\text{BiScO}_3\text{-(}1-x\text{)PbTiO}_3$ in the range of $0.5 \leq x \leq 0.6$ are RFE with T_m up to $\sim 323^\circ\text{C}$ (100 kHz) at $x=0.5$.¹⁸ The solid solution of $x\text{PbTiO}_3\text{-(}1-x\text{)Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ with $x=0.30\text{-}0.35$ exhibit RFE behavior with $T_m \approx 400^\circ\text{C}$ at 100 kHz.²⁰ In tungsten bronzes, $\text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ with $x=0.25$ exhibit RFE response with $T_m = 389^\circ\text{C}$ at 100 kHz.²¹ Rutile-based FeTiTaO_6 is reported to be RFE with $T_m = 550\text{ K}$ 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 $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, 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 $(\text{Bi}_2\text{O}_2)^{2+}$ 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

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a-axis. Based on their orthorhombic space group $A2_1am$, the polarization along the *c*-axis is cancelled because of mirror symmetry.²⁷ 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. $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ is reported to show RFE behavior with $T_m = 400^\circ\text{C}$ at 1 MHz.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 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ceramics³⁸ 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, $\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$ (BBTN), with the highest value of T_m (636°C at 100 kHz) of all of the known RFEs is reported. It is an intergrowth of $\text{BaBi}_2\text{Nb}_2\text{O}_9$ (BBN, $m=2$)– $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT, $m=3$). Although this compound was reported by Kikuchi *et al.*,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 BaCO_3 of 99.0% purity, Bi_2O_3 of 99.975% purity, TiO_2 of 99.6% purity, and Nb_2O_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 $\text{Cu } K_\alpha$ 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

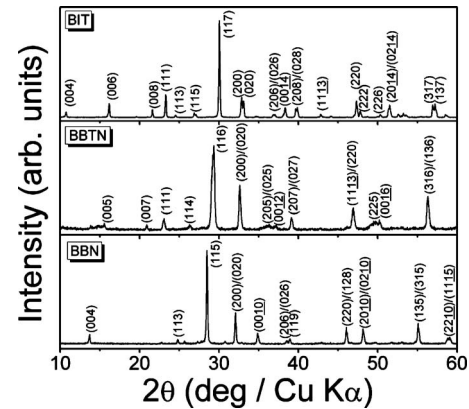


FIG. 1. XRD patterns of BIT, BBTN, and BBN calcined powder.

were performed on Pt-electroded samples (Gwent Electronic Materials Ltd., C2011004D5). The temperature dependence of the dielectric constants ϵ_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 (ZJ-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, $\sim 2\ \mu\text{m}$ long, and $0.5\ \mu\text{m}$ 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} ($\approx 280 \pm 5^\circ\text{C}$ at 100 kHz) and T_{m2}

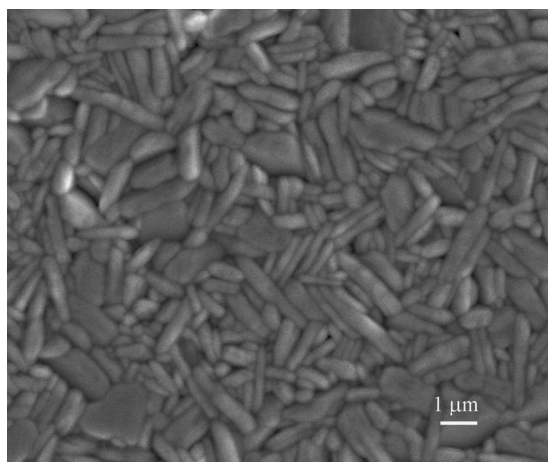


FIG. 2. SEM micrographs of BBTN ceramics.

($\approx 636 \pm 5$ °C at 100 kHz). In addition, both dielectric peaks are broad. Kikuchi *et al.*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_{m1}) of the first anomaly of ϵ_r is frequency independent, while T_{m2} of the second anomaly of ϵ_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 $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$, 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.⁴⁵ Two mechanisms are proposed to explain the two dielectric anomalies for intergrowth Aurivillius phase materials. Based on the dielectric properties of intergrowth $\text{Bi}_3\text{Ti}_{1.5}\text{W}_{0.5}\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=2$ and 3) ceramics, Luo *et al.*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.*⁴⁷ suggested from their study of intergrowth $\text{Bi}_3\text{TiNbO}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=2$ and 3) ceramics that the higher transition temperature corresponds to the Curie point,

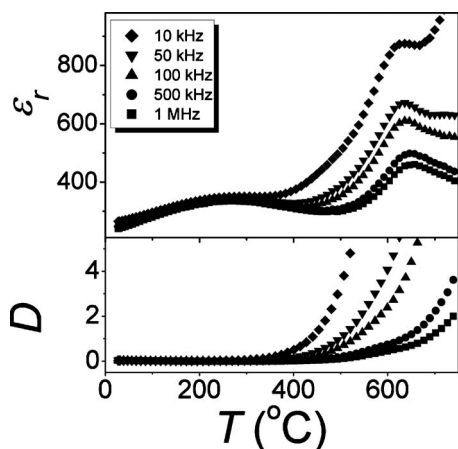
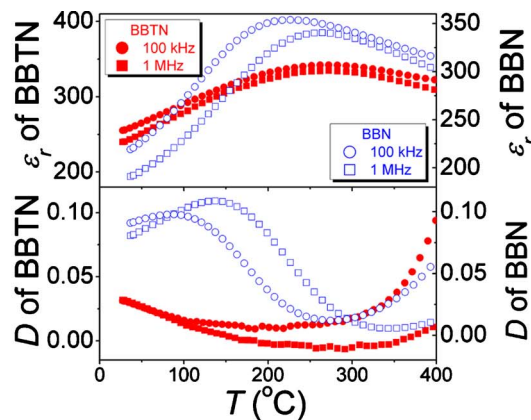
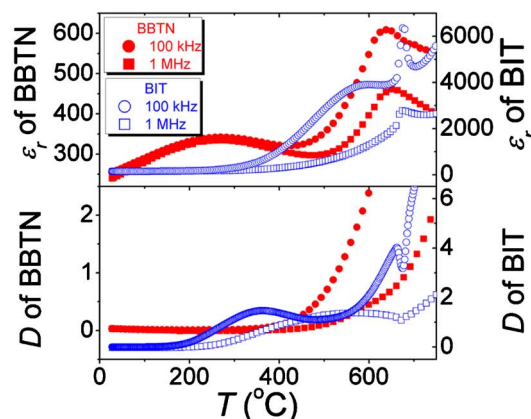


FIG. 3. Temperature dependence of dielectric constant ϵ_r and loss factor D for BBTN ceramics.



(a)



(b)

FIG. 4. (Color online) Comparison of dielectric properties of BBTN ceramics with those of two constituent oxides: (a) BBN and (b) BIT.

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 compounds, BBN and 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 ϵ_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.^{48,49} The higher losses of BIT result from its high electrical conductivity.⁴⁰ BBTN ceramics have a frequency dependent dielectric anomaly at about 636 °C (100 kHz) [Fig. 4(b)]. The ϵ_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,³¹ as is the case for BBTN ceramics. Compared with the T_c (675 °C) of BIT, the T_{m2} (636 °C at

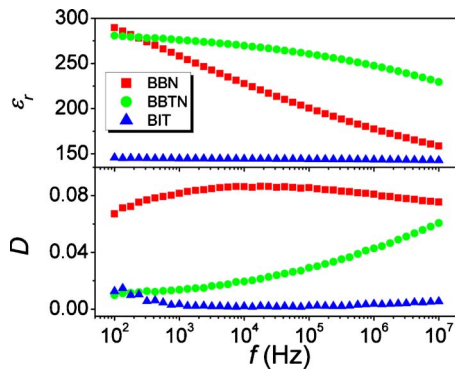


FIG. 5. (Color online) Frequency dependences of dielectric constant and loss of BBN, BBTN, and BIT at room temperature.

100 kHz) of BBTN ceramics is shifted toward a lower temperature. The fact that T_c (or T_{m2}) of Aurivillius intergrowth phase materials is between those of its two constituents has been reported in $\text{Bi}_3\text{NbTiO}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ (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 $f=1.68 \times 10^4$ 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

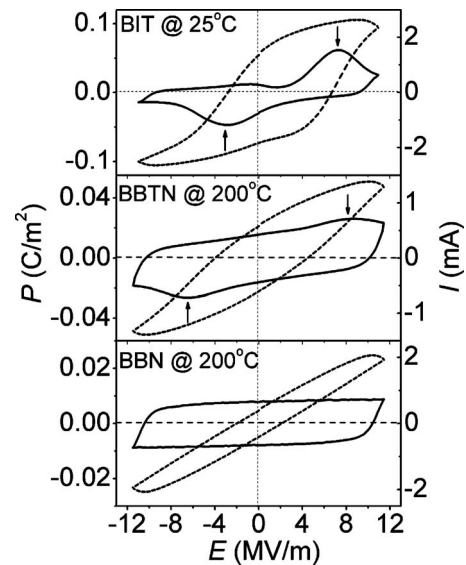


FIG. 6. P - E and I - E loops measured with 100 Hz at 25°C for BIT, 200°C for BBTN and BBN ceramics. Dashed and solid lines show P - E and I - E loops, respectively.

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 $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ($\text{Bi}_3\text{TiNbO}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$) ceramics.⁵¹ This was ascribed to the existence of poled $\text{Bi}_3\text{TiNbO}_9$ ($T_c=935^\circ\text{C}$) clusters in $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$. 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 .⁴⁴ The weak piezoelectric activity of BBTN 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.⁵²

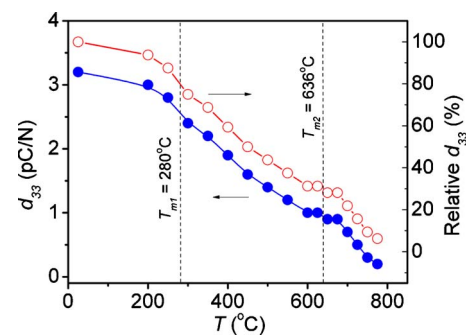


FIG. 7. (Color online) Effect of thermal depoling on piezoelectric properties of BBTN ceramics.

IV. CONCLUSION

In summary, intergrowth $\text{BaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ($\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$) 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 $\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$ are greatly different from its two constituent oxides, $\text{BaBi}_2\text{Nb}_2\text{O}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The dielectric spectrum of $\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$ 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 $\text{BaBi}_6\text{Ti}_3\text{Nb}_2\text{O}_{21}$ 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.

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