Composition-induced antiferroelectric phase and giant strain in lead-free 
(Na$_{y}$Bi$_{z}$)Ti$_{1-x}$O$_{3(1-x)}$-xBaTiO$_{3}$ ceramics

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(Na$_{y}$Bi$_{z}$)Ti$_{1-x}$O$_{3(1-x)}$-xBaTiO$_{3}$ ceramics with an excess in Bi$^{3+}$ and/or a deficiency in Na$^{+}$ were prepared and investigated. It is found that an antiferroelectric phase can be induced through a modulation of the mole ratio of Na$^{+}$ and Bi$^{3+}$. A phase boundary between ferroelectric and antiferroelectric phases can be observed at ambient temperature. A modulated phase, which is the origin of relaxor antiferroelectric behavior, should be attributed to a compositional modulation. The antiferroelectric phase can be induced to the ferroelectric phase by an applied electric field. The stability of the induced ferroelectric phase strongly depends on the mole ratio of Na$^{+}$ and Bi$^{3+}$. A recoverable giant strain of 0.48% comparable to PbZrO$_{3}$-based antiferroelectrics as well as electrostrictive coefficients (0.026 C$^{4}$ m$^{-2}$) much higher than lead-based relaxor ferroelectrics with low-temperature dependence was achieved in (Na$_{y}$Bi$_{z}$)Ti$_{1-x}$O$_{3(1-x)}$-xBaTiO$_{3}$ antiferroelectrics. Our results show there is a high possibility that the novel lead-free antiferroelectrics will replace the PbZrO$_{3}$-based ones.

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I. INTRODUCTION

Antiferroelectrics (AFE’s) have many potential applications in high-energy storage capacitors, high-strain actuators, pyroelectric sensors [for compositions near ferroelectric (FE) and AFE phase boundary], explosive electrical transducers, and electrical refrigeration.$^{1-11}$ Especially with the development of microelectronic devices, AFE thin films have huge applications in microelectromechanical systems (MEMS) and decoupling capacitors in high-speed dynamic random access memory (DRAM) devices.$^{12-14}$ However, there are only a few functional oxides that exhibit antipolar cation displacements that can be fabricated at ambient pressures. And until now, only PbZrO$_{3}$-based compounds have ever shown the ability to switch between an antipolar (AFE) and polar (FE) state under electric field, giving rise to large strain and/or charge. Thus, PbZrO$_{3}$-based AFE materials have been extensively studied over the past several decades.$^{1-14}$ However, a restriction of PbO use in electronic devices is now demanded by environmental legislation in the European Union and part of Asia.$^{15}$ The discovery of a new kind of PbO-free AFE compound is therefore extremely urgent from the fundamental scientific perspective and from a device application standpoint.

The $(1-x)$(Na$_{0.85}$Bi$_{0.5}$)TiO$_{3}$-xBaTiO$_{3}$ [abbreviated as NBT-BT 100(1-x)/100x hereafter] system is made up of well-known lead-free piezoelectric materials.$^{15-19}$ They show AFE behavior at a temperature depending on the BT content. For pure NBT, the depolarization temperature ($T_d$), that is, the transition temperature from the FE to the AFE phase, is at about 190 °C. For compositions at the morphotropic phase boundary (MPB) ($x \approx 0.06-0.08$), $T_d$ decreases to about 100 °C. When the BT content is increased further, the $T_d$ will increase again. With regard to the origin of AFE behavior in the NBT system, Doercet et al. reported that the low-temperature FE rhombohedral to higher-temperature tetragonal phase transition in NBT is a two-step phase-transition process via an AFE-like, intermediate modulated phase, which is typically revealed from the occurrence of $G \pm 1/2(110)_{p}$ superstructure spots and their elongation along $(001)_{p}$ over the 200–320 °C temperature range.$^{20,21}$ The formation of this modulated phase was proposed to be responsible for the AFE and relaxor-like behavior in NBT observed over the 200–320 °C temperature range.$^{20,21}$ Very recently, Ma et al. proposed an additional phase region exhibiting $P4bm$ non-1-domain ($0.07 < x < 0.09$). A new concept “relaxor AFE” was used to describe the unique short-range AFE order.$^{22}$ Obviously, the origin of AFE behavior is still the point at issue. In previous studies,$^{15-19}$ the mole ratio of Na$^{+}$ and Bi$^{3+}$ was always considered to be 1 due to the contrasting valence of the two involved cations (+1 for Na and +3 for Bi). However, it is in fact hard to keep the 1:1 ratio due to volatilization of Bi$_2$O$_3$ and Na$_2$O during sintering, which can lead to the variation of piezoelectric properties and depolarization temperatures in the published data.$^{15-19}$ Therefore, the effect of Na$^{+}$ or Bi$^{3+}$ nonstoichiometry on the structure and properties should not be ignored. There have been several previous studies concerning the nonstoichiometry issue of NBT-BT ceramics$^{23-26}$ involving Na$^{+}$ or Bi$^{3+}$ nonstoichiometry. They found that $T_d$ will decrease with an excess in Bi$^{3+}$ or a deficiency in Na$^{+}$.$^{23,26}$ The specimens with high excess Bi$^{3+}$ in NBT-BT 93/7 ceramics present shrunk and deformed hysteresis loops at room temperature. Xu et al. attributed the observed behavior to the generation of AFE microregions in the macroscopic FE matrices.$^{23}$ It is evident that the appearance of the AFE phase is strongly related to the mole ratio of Na$^{+}$ and Bi$^{3+}$. We therefore conducted a systematic investigation on NBT-BT ceramics with a deficiency in Na$^{+}$ and/or an excess in Bi$^{3+}$.

In this paper, it is found that the AFE phase can be induced at ambient temperature through a compositional modulation of Na$^{+}$ and Bi$^{3+}$ in a lead-free (Na$_{y}$Bi$_{z}$)Ti$_{1-x}$O$_{3(1-x)}$-xBaTiO$_{3}$ (abbreviated as N$^{100}_{100}$B$_{100}$T$_{100}$ hereafter) system at ambient temperature. The AFE ceramics show the ability to switch between an antipolar (AFE) and a polar (FE) state under electric field as occurs in PbZrO$_{3}$-based ceramics. The stability...
of the induced FE phase strongly depends on the mole ratio of Na$^{+}$ and Bi$^{3+}$. Giant electric-induced strain and a notably larger electrostrictive coefficient were thereby achieved.

II. EXPERIMENTAL

Ceramics with nominal composition $N_{100} B_{100} T_{(100(1-x))}$-100$_{x}$BT ($x = 0, 0.06, 0.07, 0.08, 0.12, \text{and} 0.15$, $y = 0.395–0.500$, $z = 0.400–0.515$) were synthesized using the solid-state reaction method. High-purity $Na_2CO_3$, $Bi_2O_3$, $BaCO_3$, and nano-$TiO_2$ ($\sim 20 \text{ nm}$) were used as starting materials. Mixtures of these starting materials in the appropriate ratio were first ball-milled for 12 h using ethanol as a medium followed by an initial calcination at 800 °C for 2 h. The calcined powder was then ball-milled again for 12 h and dried, followed by the addition of poly(vinylalcohol) as a binder. The resultant powder was then granulated and pressed into pellets with a diameter of 13 mm under a uniaxial pressure of 200 MPa. Finally, these pellets were sintered in air at 1150 °C for 2 h in a covered alumina crucible.

X-ray diffraction (XRD) measurements were performed on as-sintered ceramics surfaces with a BRUKER-AXS x-ray diffractometer with monochromatic Cu $K\alpha$ radiation in the step scanning mode with increments of 0.05°. For transmission electron microscopy (TEM) observation, as-sintered samples were mechanically polished down to 5 μm and then Ar-ion...
milled to electron transparency. TEM studies were carried out on a JEM-2010/INCA OXFORD microscope operated at 200 kV.

For electrical characterization, the resultant samples were coated with silver paste on their surfaces and heat treated at 500 °C for 5 min to ensure good electrical contact. The polarization-field (P-E) and strain-field (S-E) hysteresis loops as well as the associated switching current (I-V) behavior were investigated by using an aixACCT FE test unit in conjunction with a laser interferometer. The samples were immersed in silicone oil to prevent arcing during the measurement. After unipolar strain characterization at room temperature, the dielectric properties were measured by using a computer-controlled Agilent 4294A impedance analyzer.

III. RESULTS AND DISCUSSION

The present study started with a series of N100,B100,T100(1−x)−100xBT ceramics. The XRD patterns of N100,B100,T100−N100,B100,T93−7BT, and N100,B100,T85−15BT are shown in Figs. 1(a)–1(c), respectively. Indexation is with respect to the underlying parent perovskite substructure (labeled with the subscript p, which denotes parent in what follows). Almost all the resultant ceramics can be identified as having a perovskite type structure except that of the N15.5B31.5T100 ceramics. For pure N100,B100,T100 ceramics, they all show rhombohedral symmetry, but an asymmetry of the (200)p peak was found for ceramics with a higher excess in Bi3+ and/or a higher deficiency in Na+ (indicative of pseudorhombohedral symmetry). For N100,B100,T100(1−x)−100xBT ceramics with x = 0.06, 0.07, and 0.08, no significant change in phase structure was found for ceramics with an excess in Bi3+ and/or a deficiency in Na+. Noticeable broadening of the (111)p peak and splitting of the (200)p peak were detected for all samples. This means that the ceramics with an excess in Bi3+ and/or a deficiency in Na+ still show the coexistence of rhombohedral and tetragonal phases, that is, they are still in the MPB region. For N100,B100,T100(1−x)−100xBT ceramics with x = 0.12 and 0.15, the (111)p peak is not split while the (200)p peak clearly splits, which is indicative of tetragonal symmetry. The specimens with an excess in Bi3+ and/or a deficiency in Na+ still maintain tetragonal symmetry. But note that the relative intensity of the (002)p peak become weaker and shifts to a higher angle.

The P-E behavior for the N100,B100,T93−7BT ceramics are shown in Fig. 2(a). For N56.5B46.5T93−7BT samples, P-E loops appear to exhibit a typical P-E ferroelectric hysteresis loop character. With a smaller excess in Bi3+, pinched P-E hysteresis loops were observed in the specimens at ambient temperature (100y/100z: 43.5/47.5 and 42/48). Our findings demonstrate that the AFE polarization phase only exists in N100,B100,T93−7BT specimens with a higher excess in Bi3+ and/or a deficiency in Na+. The AFE phase can be induced to the FE phase. However, the induced FE phase is unstable, as is that in PbZrO3. They will return to the AFE phase after removing the electric field. Therefore, the appearance of pinched hysteresis loops clearly shows that a metastable FE phase can coexist with the AFE phase in the poled samples. Note that the appearance of the metastable FE phase has two possible explanations. One is that the metastable FE phase...
coexists with the AFE phase in the unpoled $N_{100}B_{100}T_{93.7}$BT samples. The other is that the AFE phase only exists in the unpoled $N_{100}B_{100}T_{93.7}$BT samples, the metastable FE phase is induced from the AFE phase, and the induced FE phase will partially return to the AFE phase after removing the electric field. To clarify this point, electron diffraction (ED) patterns at the $\langle 310 \rangle_p$ zone axis for $N_{47.5}B_{47.5}T_{93.7}$BT with typical FE hysteresis loop character and $N_{43.5}B_{47.5}T_{93.7}$BT with typical AFE hysteresis loop character were investigated, as shown in Figs. 3(a) and 3(b), respectively. The ED patterns display $G \pm 1/2(111)_p^*$ superstructure reflections ($R$ type) from the rhombohedral phase as well as $G \pm 1/2(110)_p^*$ reflections ($T$ type) from the tetragonal phase, which means a coexistence of rhombohedral and tetragonal phases. A strong stretching of the $G \pm 1/2(110)_p^*$ reflections and diffuse streak lines parallel to $\langle 001 \rangle_p^*$ were found at room temperature in all two samples. This can only be clearly observed in the temperature range between 200 and 320 °C in pure NBT ceramics (cf. with Fig. 4 in Ref. 20). In this temperature range, a periodic distribution of $Pnma$ orthorhombic perovskite sheets, with their own octahedral tilting system, developed as an intergrowth within the $R3C$ rhombohedral matrix, in which the formation of $Pnma$ sheets can be easily achieved as it represents natural $\{100\}_p$ twin planes separating two
R3C FE domains related by a pseudomerohedral twinning law.\textsuperscript{20} A modulated phase is formed of \textit{Pnma} orthorhombic sheets, appearing within the R3C parental matrix and exhibiting \textit{a}’\textsuperscript{4}\textit{a}’\textsuperscript{5}\textit{a}’\textsuperscript{6} octahedral tilting system.\textsuperscript{20} Similarly, such a modulated phase, which was proposed to be the origin of relaxor AFE behavior in pure NBT by Dorcet \textit{et al.},\textsuperscript{20} should also exist in N\textsubscript{100}B\textsubscript{100}T\textsubscript{100}−\textsubscript{xy}BT ceramics at ambient temperature. It is also observed that the \textit{G} \textsuperscript{+} 1/2(110)\textsuperscript{p} spots are more stretched in unpoled N\textsubscript{45.5}B\textsubscript{47.5}T\textsubscript{39.7}−7BT samples than those of N\textsubscript{46.5}B\textsubscript{46.5}T\textsubscript{93}−7BT samples. We then may propose that the amount of modulated phase is correlated with the stretching degree of the \textit{G} \textsuperscript{+} 1/2(110)\textsuperscript{p} spots. The stretching degree may increase with more excess in Bi\textsuperscript{3+} and deficiency in Na\textsuperscript{+}. The TEM results from representative grains in these two ceramics are shown in Figs. 3(c) and 3(d), respectively. Nanodomains were observed as the results of Ma \textit{et al.} very recently.\textsuperscript{22} The MPB region may be an AFE phase region. The AFE phase can be induced to the FE phase and the induced FE phase can exist stably after removing the electric field in N\textsubscript{46.5}B\textsubscript{46.5}T\textsubscript{93}−7BT samples as occurs in (Ph,La)(Zr,Ti)O\textsubscript{3}\textsuperscript{11,12}. However, the induced FE phase will partially return to the AFE phase after removing the electric field in N\textsubscript{46.5}B\textsubscript{47.5}T\textsubscript{93}−7BT samples. The above results demonstrate that the stability of the induced FE phase for ceramics in the MPB region can be tailored through the compositional modulation of Na\textsuperscript{+} and Bi\textsuperscript{3+}. In addition to the AFE phase that exists in the MPB region, we found that pinched as well as double hysteresis loops can also be observed for compositions away from the MPB region with a higher excess in Bi\textsuperscript{3+} and/or a deficiency in Na\textsuperscript{+} with \textit{x} = 0, 0.12, and 0.15. The hysteresis loops and associated \textit{I-V} curves for N\textsubscript{50}B\textsubscript{50}T\textsubscript{0} are shown in Fig. 2(b); AFE behavior can be clearly seen in the corresponding switching current curve. The hysteresis loops for N\textsubscript{100}B\textsubscript{100}T\textsubscript{35}−15BT samples are shown in Fig. 2(c); a double hysteresis loop can be clearly observed for N\textsubscript{33.3}B\textsubscript{33.3}T\textsubscript{33.3}−15BT samples. The N\textsubscript{50}B\textsubscript{50}T\textsubscript{0} and N\textsubscript{25}B\textsubscript{25}T\textsubscript{25}−15BT samples are well accepted as a rhombohedral FE phase with R\textit{3c} space group and a tetragonal FE phase with \textit{P4mm} space group, respectively. Therefore, a pure AFE phase or the coexistence of FE and AFE phases in the ground state is proposed for compositions away from the MPB region with a higher excess in Bi\textsuperscript{3+} and/or a deficiency in Na\textsuperscript{+}, that is, there are phase boundaries between FE and AFE phases in the compositions away from the MPB region. ED patterns at the (310)\textsubscript{p} zone axis for the two unpoled samples also show a strong stretching of the \textit{G} \textsuperscript{+} 1/2(110)\textsuperscript{p} reflections and diffuse streak lines parallel to (001)\textsuperscript{p} at room temperature. Then we speculated that a modulated phase, which has been proposed to be the origin of relaxor AFE behavior, can be developed not only within the R\textit{3c} parent matrix but also within the \textit{P4mm} parent matrix. Dorcet \textit{et al.} proposed that the modulated phase better corresponds to a strain modulation rather than to a compositional modulation.\textsuperscript{20} Our results show that the modulated phase may be due to a compositional modulation, although such a phenomenon seems impossible due to the contrasting valence of the two involved cations (+1 for Na and +3 for Bi). To further investigate the phase-transition behavior, the temperature dependence of the relative dielectric permittivity \textit{\varepsilon}\textsubscript{r} and loss tangent tan \textit{\delta} for poled N\textsubscript{100}B\textsubscript{100}T\textsubscript{0}−\textsubscript{xy} samples was measured. Figures 4(a)−4(e) show the temperature dependence of the relative dielectric permittivity \textit{\varepsilon}\textsubscript{r} and loss tangent tan \textit{\delta} for poled N\textsubscript{100}B\textsubscript{100}T\textsubscript{94}−6BT samples. For N\textsubscript{47}B\textsubscript{47}T\textsubscript{94}−6BT, N\textsubscript{45.5}B\textsubscript{47.5}T\textsubscript{94}−6BT, and N\textsubscript{44}B\textsubscript{47}T\textsubscript{93}−7BT samples, the inflection point of tan \textit{\delta} observed at lower temperature is \textit{T}\textsubscript{d}, corresponding to the FE-AFE phase transition. Note that \textit{T}\textsubscript{d} decreases for specimens with more excess in Bi\textsuperscript{3+} and/or more deficiency in Na\textsuperscript{+}. The \textit{T}\textsubscript{d} for N\textsubscript{47}B\textsubscript{47}T\textsubscript{94}−6BT, N\textsubscript{45.5}B\textsubscript{47.5}T\textsubscript{94}−6BT, and N\textsubscript{44}B\textsubscript{47}T\textsubscript{93}−7BT samples are 88, 66, and 38°C (1 kHz), respectively. The frequency dispersion in \textit{\varepsilon}\textsubscript{r} and tan \textit{\delta} is weaker at temperatures below \textit{T}\textsubscript{d} but becomes significant above \textit{T}\textsubscript{d}. The frequency dispersion in \textit{\varepsilon}\textsubscript{r} and tan \textit{\delta} is a minimum at a temperature below \textit{T}\textsubscript{d} for N\textsubscript{47}B\textsubscript{47}T\textsubscript{94}−6BT and gradually becomes stronger for specimens with more excess in Bi\textsuperscript{3+} and/or more deficiency in Na\textsuperscript{+}. These results further confirm that the stability of the induced FE phase strongly depends on the mole ratio of Bi\textsuperscript{3+} and Na\textsuperscript{+}. With further increase in temperature, the frequency dispersion becomes weaker or even vanishes before reaching \textit{T}\textsubscript{m} (the temperature where \textit{\varepsilon}\textsubscript{r} reaches a maximum) with more excess in Bi\textsuperscript{3+} and/or more deficiency in Na\textsuperscript{+}. In contrast to the above three compositions, for N\textsubscript{42}B\textsubscript{42}T\textsubscript{94}−6BT and N\textsubscript{12.5}B\textsubscript{48}T\textsubscript{94}−6BT samples, no sharp anomaly exists in either the \textit{\varepsilon}\textsubscript{r} versus \textit{T} or the tan \textit{\delta} versus \textit{T} curve at lower temperature, that is, we cannot observe the \textit{T}\textsubscript{d} anymore. The frequency-dependent \textit{\varepsilon}\textsubscript{r} and tan \textit{\delta} show typical relaxor characteristics until the relaxor behavior vanishes at a temperature higher than 150°C. This dielectric behavior coincides well with short-range AFE order. The dielectric behaviors of other ceramics were also measured. Similar dielectric dispersion behaviors were observed in all the samples.

It is well known that a large electric-field-induced strain can be achieved associated with the AFE-FE phase transition. We also measured the electric-field-induced strain for the N\textsubscript{100}B\textsubscript{100}T\textsubscript{100}−\textsubscript{xy} ceramics. Typical strain field (\textit{S-E}) curves of AFE’s were observed in N\textsubscript{100}B\textsubscript{100}T\textsubscript{100}−\textsubscript{xy} ceramics with a higher excess in Bi\textsuperscript{3+} and/or a deficiency in Na\textsuperscript{+} (without negative strain). A giant recoverable strain of 0.48% under 70 kV/cm was achieved in the N\textsubscript{44}B\textsubscript{45}T\textsubscript{94}−6BT sample (Fig. 5). This value

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{(Color online) Bipolar strains of N\textsubscript{44}B\textsubscript{45}T\textsubscript{94}−6BT samples measured under an electrical field with a frequency of 1 Hz.}
\end{figure}
is higher than all the recently reported NBT-based ceramics and even higher than the strain obtained with established FE Pb(Zr,Ti)O$_3$ ceramics.\textsuperscript{27–32} A strain of 0.23% with small hysteresis under 70 kV/cm at room temperature was obtained in the N$_{42}$B$_{48}$T$_{93}$-7BT sample (Fig. 6). This value is comparable to strains obtained in Pb-based AFE’s. Figure 7 shows the plots of $S$ and $P^2$ derived from the room temperature $S$-$E$ curve of Fig. 6. The slope of this curve corresponds to the electrostriction coefficient.\textsuperscript{28} Clearly, the $S$-$P^2$ curves deviate slightly from linear relations, which means the contribution of electrostriction strain should be predominant. The averaged electrostrictive coefficient ($Q$) is calculated to be of 0.026 m$^4$ C$^{-2}$. This value is comparable to the recently reported NBT-BT-(Na,K)NaO$_3$ ceramics and much higher than the lead-based electrostrictive material [for Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$-PbTiO$_3$, $Q$ is reported to be about 0.017 m$^4$ C$^{-2}$ (Ref. 33)]. Moreover, a strain of 0.21% with no hysteresis is still available when the temperature is up to 150 °C (Fig. 6). All these results demonstrate that N$_{42}$B$_{48}$T$_{93}$-7BT ceramics are suitable for high-precision positioning devices and actuators. New insight has also been provided into ways to further optimize lead-free AFE electrostrictors.

### IV. CONCLUSIONS

The ground state is an AFE phase at ambient temperature for unpoled compositions in the MPB region. The ground state of the ceramics shows the coexistence of AFE and FE phases or a pure AFE phase for unpoled compositions away from the MPB region with a high excess in Bi$^{3+}$ and/or a high deficiency in Na$^+$, that is, there are phase boundaries between FE and AFE phases at ambient temperature at these compositions. The AFE N$_{100}$B$_{100}$T$_{100(1-x)-100x}$-BT ceramics shows the ability to switch between an antipolar (AFE) and a polar (FE) state as occurs in PbZrO$_3$-based ceramics. The stability of the induced FE phase strongly depends on the mole ratio of Na$^+$ and Bi$^{3+}$. A recoverable giant strain of 0.48% or electrostrictive coefficients as high as 0.026 m$^4$ C$^{-2}$ (about 1.5 times the value of traditional Pb-based electrostrictors) has been observed in N$_{100}$B$_{100}$T$_{100(1-x)-100x}$-BT AFE ceramics. Our results show that these lead-free AFE’s have huge application potential for use as sensors and actuators.

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