Large Electrostrictive Strain in \((\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-\text{BaTiO}_3-\text{(Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3\) Solid Solutions

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Relaxor ferroelectrics \((0.94-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3-(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3\) \((0 \leq x \leq 0.5)\), were prepared by a solid-state reaction process, and their structures were characterized by the transmission electron microscopy and Raman spectroscopy. The BNT–BT–xSBT \((0 \leq x \leq 0.5)\) has a very high electrostrictive strain \(S = 0.152\%\) with hysteresis-free behavior, much more than the reported \(S\) in other ferroelectrics. \(S-P^2\) profiles perfectly follow the quadratic relation, which indicates a purely electrostrictive effect with a high electrostrictive coefficient \(Q_{11}\) of \(0.0297 \text{m}^4/\text{C}^2\). Even, its \(Q_{11}\) keeps at a high level in the temperature range from ambient temperature to \(180^\circ\text{C}\). The field-induced large electrostrictive strain of BNT–BT–0.3SBT was attributed to the existence of ferroelectric nanodomains.

I. Introduction

Electromechanical actuators directly transform input electrical energy into mechanical energy. Of the many types of actuator materials including magnetostrictive, photostrictive, and shape memory alloys, piezoelectric and electrostrictive ceramics are widely used in applications requiring high-generative force, high-frequency operation, accurate displacement, quick response time, or small device size. Electrostrictive production depends on the direction of the field regardless of its polarity, and this expansion relaxes back to zero when the field is removed. Electrostrictive materials can be categorized in a simplified version \(S = Q^e P^2\), where \(P\), \(S\), and \(Q\) are polarization, strain, and electrostrictive coefficients, respectively. More commonly, this effect is utilized in lead-containing relaxor materials owing to their high-level strain of 0.1% and \(Q\) value of \(\sim 10^{-2} \text{m}^4/\text{C}^2\). However, making lead-free electrostrictive materials is highly desirable due to the increasing concern for environmental safety, as the lead compounds are toxic.

In relaxor ferroelectrics, the electrostrictive strain can be kept at a relatively high level in a wide temperature range due to the diffused phase transition. Traditionally, the phase transition temperature of a relaxor ferroelectric at ambient temperature can enhance the electrostrictive property effectively. These days great interest has been devoted as complex dielectric behaviors with strong-frequency dispersion and large electric field–induced strains were observed in \((1-x)\) BNT–xBT based lead-free materials. The origin of the observed large strain in these systems was identified as a consequence of a drastic reduction in the remanent strain due to the presence of a “non-polar” phase at zero field, which enables each unipolar cycle to fully utilize the inherently large poling strain of BNT-based materials. Aksel \textit{et al.} demonstrated that the large-strain behavior is related with the nucleation of a mixture of nanodomains that disturbs the long-range ferroelectric order rather than a long-range phase transition.

It was reported that, in BNT–SBT, the formula scheme “a ferroelectric relaxor + a ferroelectric” for solid solutions leads to a high purely electrostrictive strain. To further improve the electrostrictive property, the \((\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3\) in lead-free BNT–BT ferroelectrics with pseudocubic crystal structure at RT is introduced, where \((\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3\) is reported as a new lead-free ferroelectric relaxor. In \((\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3\) strontium vacancies (\(\square\)) are created to balance the charge misfit due to the substitution of divalent Sr ions by trivalent Bi ions. The materials \((0.94-x)\) \((\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3-x(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3\), ceramics exhibit a very high electrostrictive strain at room temperature with hysteresis-free behavior. The electrostrictive strain \(S\) is up to 0.152% at \(-80 \text{kV/cm}\) at room temperature for the sample with \(x = 0.3\) and the calculated electrostrictive coefficient \(Q_{11}\) is \(0.0297 \text{m}^4/\text{C}^2\), about 1.7 times the value of the electrostrictive coefficient compared with traditional Pb-based electrostrictors. Meanwhile, this high electrostrictive coefficient keeps at a high level in the accessible temperature range from room temperature to \(180^\circ\text{C}\). The TEM and Raman revealed that the formation of nanodomains around room temperature at \(x = 0.3\) plays a key role in field-induced large electrostrictive strain.

II. Experimental Procedure

Ceramic powders were fabricated by the mixed oxide route from high-purity raw powders being \(\text{BaCO}_3\) (99.0%), \(\text{Bi}_2\text{O}_3\) (99.9%), \(\text{TiO}_2\) (98%), \(\text{SrCO}_3\) (99%), and \(\text{Na}_2\text{CO}_3\) (99.8%). The powders were weighed and mixed by ball milling in isopropyl alcohol for 6 h. After drying, the mixtures were calcined in a covered alumina crucible at \(850^\circ\text{C}\) for 4 h. The calcined powders were ball milled again for 4 h, then compacted into pellets of 12 mm in diameter at a pressure of 140 MPa and sintered in air at \(1125^\circ\text{C}-1200^\circ\text{C}\) for 4 h. The resulted pellets were polished to a final thickness of 1 mm for property investigations. Silver electrodes were coated on both the polished surfaces and fired at 850°C for 20 min for electric test.

Phase structure of the powders ground from the sintered samples was investigated by X-ray diffraction (XRD;
XRD-7000; Shimadzu, Kyoto, Japan) with CuKα radiation in 20 range 20°–80° at room temperature. The surface morphologies of the ceramics were observed using a SEM (JSM-5610; JEOL, Tokyo, Japan). The dependence of the electric polarization (P) and the longitudinal strain (S) on an external electric field (E) were measured at 1 Hz using a ferroelectric test unit (TF-2000; aix-ACCT, Aachen, Germany) for 20°C–160°C (Temperature controller; aix-ACCT). The dielectric properties were measured using a precision impedance analyzer (4294A; Agilent, Santa Clara, CA). Raman spectra were obtained with an instrument (LabRAM HR800; Horiba Jobin Yvon, Lyon, France) in a backward scattering geometry (the exciting source was the 514.5 nm line from an argon ion laser). For the Raman study, the sintered pellets were polished on one side using diamond paste and then cleaned thoroughly with acetone. The samples were subsequently annealed at 400°C for 8 h to remove any residual surface stresses left after the polishing. The variable temperature Raman spectra of the ceramics were stabilized at the desired temperature for 5 min prior to the spectrum measurement. TEM specimens were prepared from the as-sintered pellets through standard procedures including grinding, cutting, dimpling, and ion milling. The dimpled disks were annealed at 300°C accelerating voltage. 160°C for 2 h to minimize the residual stresses before Ar-ion mill to electron transparency. Lattice images were obtained by using a TEM (Tecnai F30; FEI, Hillsboro, OR) operated at 300 kV accelerating voltage.

III. Results and Discussion

The XRD analyses of the powders ground from sintered BNT–BT–xSBT ceramic samples with x = 0–0.5 revealed a single perovskite structure without apparent secondary phases, as provided in Fig. 1. The pseudocubic structures for all the composition range were studied, as no peak splitting other than K_a1 and K_a2 was detected, supporting the fact that there is no obvious long-range noncubic distortion. The inset shows the SEM micrographs of BNT–BT–0.3SBT ceramics. It can be noticed that the ceramics are dense and have uniform structure.

Ferroelectric hysteresis loops (polarization P versus electric field E) of the samples were measured at ambient temperature at 1 Hz plotted in Fig. 2(a). The polarization hysteresis loop of x = 0 displays a well-saturated typical ferroelectric behavior with the maximum and remanent polarizations of 43 and 33 μC/cm², respectively. It is noted that the remanent polarization of 33 μC/cm² drops drastically down to 2.6 μC/cm² at a substitution of 10 mol% SBT. It implies that the ferroelectric order is disturbed with the addition of SBT, leaving a “non-polar” phase at zero electric field. Due to their comparable free energies, nonpolar phase can transform reversibly into a ferroelectric phase by an external electric field. For the samples with x = 0.3, only a very slim P–E profile is observed, which is slimmer than that of other lead-free or lead-containing electrostrictors. The currently observed P–E loop can be due to a normal relaxor for BNT–BT–0.3SBT. The P–E profile is almost linear in the samples with x = 0.5, indicating a paraelectric behavior.

Electric field-driven strains (S) at ambient temperature are shown in Fig. 2(b). Typical butterfly-type strain loop, whose maximum strain level is 0.37% and negative strain is 0.012%, was observed for the samples x = 0 with predominantly ferroelectric behavior. In contrast, x = 0.1, 0.3, and 0.5 show a drastic deviation from the typical ferroelectric behavior. Notice that the negative strain closely related to the domain back switching during bipolar cycles was disappeared

![Fig. 1](image1.png)

![Fig. 2](image2.png)

Fig. 1. X-ray diffraction patterns of BNT–BT–xSBT with x = 0–0.5, the inset shows the SEM images of the surface of BNT–BT–0.3SBT.

Fig. 2. (a) Polarization (P) versus electric field (E), and (b) strain (S) versus electric field (E) at 1 Hz for the samples with x = 0, 0.1, 0.3, and 0.5 at ambient temperature. (c) Strain (S) versus the square polarization (P²) for the samples with x = 0.1 and 0.3 at ~80 kV/cm at ambient temperature.
with \( x = 0.1 \). For \( x = 0.3 \) the \( S-E \) curves show almost hysteresis free with strain value in the range 0.152% at \( \sim 80 \) kV/cm and a quadratic variation \( P^2 \) with \( E \). This strain level is comparable with other lead-containing electrostrictors. The composition with \( x = 0.5 \) also shows a quadratic variation \( P^2 \) with \( E \), whereas the strain level decreased drastically.

Electrostriction can be particularly large in the following situations: (i) ferroelectric materials just above their \( T_C \), where an electric field can enforce the energetically unstable ferroelectric phase. \(^{17,18,23}\) The phase transition temperature of a relaxor ferroelectric is close to ambient temperature. Therefore, we adjust the composition and dopants in BNT–6BT-based lead-free ferroelectrics to produce a relaxor phase which can be induced to the FE at ambient temperature, and produce prominent lead-free electrostrictors. Figure 2(c) displays the plots of \( S-P^2 \) with the composition of \( x = 0.1 \) and 0.3. Evidently, the \( S-P^2 \) curves for the composition with \( x = 0.3 \) is linear, whereas that of \( x = 0.1 \) is slightly deviated from linear relationship. That means the sample with \( x = 0.3 \) is a pure relaxor without any macrodomain. In the meantime, the sample with \( x = 0.1 \) is a predominant relaxor with some distribution of macrodomain. The averaged electrostrictive coefficient \( (Q) \) for \( x = 0.1 \) and \( x = 0.3 \) are calculated to 0.0233 m\(^2\)C\(^{-2}\) and 0.0295 m\(^2\)C\(^{-2}\), respectively. The \( Q \) values of our materials are notably larger than other lead-containing and lead-free electrostrictors. \(^{17,18,23,24}\)

The temperature dependence of \( P-E \) loops at \( \sim 60 \) kV/cm of \( x = 0.3 \) is shown in Fig. 3(a). The inset of Fig. 3(a) shows the maximum polarization \( (P_{\text{max}}) \) of different temperature. The \( P_{\text{max}} \) changed from 19.5 to 16 \( \mu \)C/cm\(^2\) in the temperature range \( 30^\circ \)-\( 180^\circ \)C. In addition, the dissipated energy, that is, the area of the \( P-E \) curves, is determined to be \( 0.084 \times 10^4 \) J/m\(^3\) for \( x = 0.3 \) at ambient temperature. This value is lower than that of other reported electrostrictive materials. \(^{17,18,23,24}\) Figure 3(b) displays the temperature dependence of \( S \) and \( Q_{11} \) at \( \sim 60 \) kV/cm which exhibit an excellent thermal stability. \( Q_{11} \) increases little, with variation less than 5% in the temperature range \( 30^\circ \)-\( 180^\circ \)C. It is noted that the \( S \) and \( Q_{11} \) remain high in a wide range from room temperature up to \( 180^\circ \)C and exhibit better thermal stability than other electrostrictors.

The temperature dependence of the relative dielectric permittivity \( (\varepsilon') \) and loss tangent (\( \tan \delta \)) for BNT–BT–xSBT samples (\( x = 0, 0.1, 0.3 \) and 0.5) are shown in Fig. 4. The inset shows \( \Delta \varepsilon' \) \( (\varepsilon'_{1KHz}-\varepsilon'_{100KHz}) \) and \( \varepsilon'_{100KHz} \) is permittivity at 1 kHz and \( \varepsilon'_{1KHz} \) is permittivity at 100 kHz.) of samples with \( x = 0-0.5 \) at ambient temperature. For all the samples, two peaks are observed. One is the absolute maximum dielectric peak \( (T_m) \) without significant frequency dispersion, which is due to the “paraelectric-relaxor” phase transition. Another is a further, frequency-dependent, anomaly of the permittivity at lower temperatures \( (T_{R-T}) \), with very pronounced frequency dispersion. Recently, it has been proposed in 0.94 \( (\text{Bi}_0.9\text{Na}_{0.1})_2\text{TiO}_3 \)-0.06BaTiO\(_3\) that \( T_m \) is related to a relaxation of tetragonal polar nanoregions (PNRs) emerged from rhombohedral PNRs, and \( T_{R-T} \) is ascribed to the thermal evolutions of discrete PNRs, which has nothing to do with any measurable structural transition. \(^{25}\) With increasing SBT concentration, the \( T_{R-T} \) is shifted to a lower temperature compared with that of BNT–6BT and finally almost disappeared at \( x = 0.5 \). In the meantime, the intensity of frequency dispersion increases, with \( \Delta \varepsilon' \) increase from 260 for \( x = 0 \) to 600 for \( x = 0.3 \), which results in high permittivity at RT about 2323 compared with 1695 and 1431 of \( x = 0 \) and 0.1, respectively. It is suggested that the cation disordered between A-site is enhanced by increasing SBT and thus very intensive phase transition diffuseness, which were also found in other BNT-based solid solutions. \(^{1,2,20,27}\)

Figure 5 displays TEM micrographs and electron diffraction patterns from the same area in a grain with representative features for the composition \( x = 0.1 \) and \( x = 0.3 \). In Fig. 5(b) the grain morphology is visible. With increasing \( x \), areas of 200 nm (marked with arrows) with lamellar domain contrast were frequently observed. Figures 5(b) and (c) are the SAED patterns taken along the [100] and [110] zone axes, in which the 1/2 \( \text{ooe} \) in-phase and 1/2 \( \text{ooo} \) antiphase (where “o” and “e” indicate an index with odd and even numbers, respectively) reflection are observed (marked by rings and arrows, respectively) besides the fundamental perovskite reflections. It has been noted that these superlattice reflections originate from slight deviations from the ideal perovskite structure, which could have intensity contributions from: (i) oxygen octahedral tilts; (ii) chemical ordering of the A-site cations; and/or (iii) antiparallel displacements of cations. In NBT, it is believed that oxygen octahedral tilting is the dominate source of the intensity. \(^{30-34}\) These 1/2 \( \text{ooe} \) in-phase and 1/2 \( \text{ooo} \) antiphase indicate the presence of the in-phase octahedral tilting \( (\text{ooe}^\text{ooe}) \) and antiphase octahedral tilting \( (\text{ooe}^\text{ooo}) \), which can be used to identify local rhombohedral \( (R) \) and tetragonal \( (T) \) phase regions. In Fig. 5(d), the grain contrast was homogeneous implying the presence of nanoscale features. The inset shows the larger version of nanodomains of \( x = 0.3 \), which shows that the size of domain is 50 nm, and this is much smaller than that in the \( x = 0.1 \) sample. Such observation has been reported in the TEM study of relaxor ceramics. \(^{15,32-34}\) We observe that the intensity of the 1/2 \( \text{ooe} \) and 1/2 \( \text{ooo} \) of \( x = 0.3 \) is weaker than that in the \( x = 0.1 \). It suggests that the doped SBT destabilize the tetragonal and rhombohedral phase at room temperature, that is, the structure is more cubic than other BNT-based materials.

The Raman spectra of BNT–BT–xSBT \( (x = 0-0.3) \) from 50 to 1000 cm\(^{-1}\) at room temperature are shown in Fig. 6(a). The overall spectral signature demonstrates a relatively broad feature; which is in good agreement with previous reports. \(^{35-38}\) This can be attributed to the A-site disorder and the overlapping of Raman modes due to the lattice anharmonicity. Raman spectra of BNT–BT–xSBT ceramics show that most of the bands undergo constant shifting and broadening as the SBT concentration increases. Wavenumbers <\( \approx \)200 cm\(^{-1}\) modes can be associated with vibrations of the perovskite A-site, thus involving Bi, Na, Ba, and Sr cations. The mode at \( \approx 125 \) cm\(^{-1}\) (marked by dotted arrow) has previously been assigned as belonging to \( A_1 \) symmetry and, more recently, associated with Na–O vibrations, and the other modes to vibrations involving the Bi–O bond \( (75 \text{ cm}^{-1}) \). \(^{21,39}\) With increasing SBT substitution, we observed an increase in FWHM of mode 75 cm\(^{-1}\) and a sudden drop in the wavenumber and
intensity of mode at 125 cm\(^{-1}\), which can be interpreted as a weakening of the A–O bonds. As a result of this change in the bond situation, a higher polarizability of the unit cells, resulting in the possible formation of nanodomains, which could be revealed in the TEM, is conceivable. A more disordered lattice was obtained due to the presence of nanodomains produced by bond weakening (i.e., a more cubic lattice). Conveniently, electrostrictive effects tend to be more pronounced in perovskites with a structure close to cubic, thus explaining the electrostrictive behavior of the material. In fact, the appearance of additional modes (marked by black arrow) in the spectral profiles gives an indication that the rhombohedral phase changes to cubic through an intermediate noncubic phase. The mode at \(\approx 260\) cm\(^{-1}\) has been assigned as an \(A_1\) mode closely related to the strength of the Ti–O bond. The splitting of this peak(s) (marked by red arrow) at room temperature with increasing SBT reveals a change in symmetry, to a structure whose irreducible representation has a higher number of Raman active modes. The mixed-phase nature is signaled most clearly by the shoulders on both sides of the 260 cm\(^{-1}\) feature. The high-frequency bands above 450 cm\(^{-1}\) have all been associated with TiO\(_6\) vibrations, namely, the breathing and stretching modes of the oxygen octahedra.

Fig. 4. Temperature dependence of the relative dielectric permittivity (\(\varepsilon'\)) and loss tangent (\(\tan \delta\)) for the BNT–BT–\(x\)SBT at different frequencies. The inset of \(x = 0.3\) shows \(\Delta \varepsilon' (\varepsilon'_{1kHz} - \varepsilon'_{100kHz})\) of samples with \(x = 0, 0.1, 0.3,\) and 0.5 at ambient temperature.

Fig. 5. (a) Bright-field TEM image, which shows grainy morphology ferroelectric domains for \(x = 0.1\). (b, c) SAED patterns of \(x = 0.1\) along the [100] and [110] zone axis. (d) Bright-field TEM image, which shows nanosized ferroelectric domains for \(x = 0.3\), the inset shows the larger version of nanodomains of \(x = 0.3\). (e, f) SAED patterns of \(x = 0.3\) along the [100] and [110] zone axis, where 1/2 000 superlattice reflections are marked by arrows, 1/2 001 ones by rings.
Both dielectric and ferroelectric properties of BNT-BT-SBT systems were investigated. With the increase in SBT, the relaxor-like frequency dispersion became stronger near $T_{R-T}$ with the shift of $T_{R-T}$ to ambient temperature. A very high electrostrictive strain (−0.152%) with a high electrostrictive coefficient $Q_{T1}$ of 0.0297 m$^2$/C$^2$ is observed at samples with $x = 0.3$. Meanwhile, the $Q_{T1}$ maintains it at a high level from ambient temperature to 180°C. The TEM and Raman spectroscopy revealed that the existence of nanodomains around room temperature at $x = 0.3$ plays a key role in field-induced large electrostrictive strain.

**IV. Conclusion**

Variable temperature Raman spectra (−160°C to 0°C) in the range from 50 to 1000 cm$^{-1}$ are shown in Fig. 6(b). With increasing temperature, temperature-induced broadening occurs. The 260 cm$^{-1}$ peak splitting persisted till −160°C somewhat similar to that previously reported by Luo et al., which could also support the idea that higher structural disorder exists in the Ti-O bond of the TiO$\_6$ octahedra with increasing temperature; such behavior may be associated with the nucleation of nanodomains within the ferroelectric matrix. The inset of Fig. 6(b) shows the details of the temperature dependence of the position of both the Bi-O and Ti-O modes. The inset shows the temperature dependence of the position of both the Bi-O and Ti-O modes.

**References**

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