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Chien-Chih Huang
Oregon State University

David P. Cann
Oregon State University

Xiaoli Tan
Iowa State University, xtan@iastate.edu

Naratip Vittayakorn
King Mongkut's Institute of Technology

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Phase transitions and ferroelectric properties in BiScO₃-Bi(Zn_{1/2}Ti_{1/2})O₃-BaTiO₃ solid solutions

Abstract

Ceramics solid solutions within the ternary perovskite system Bi(Zn_{1/2}Ti_{1/2})O₃-BiScO₃-BaTiO₃ were synthesized via solid-state processing techniques. The crystal structure of sintered ceramics was analyzed by x-ray diffraction. A stable perovskite phase was obtained for all compositions with a BaTiO₃ content greater than 50 mol %. Furthermore, a change in symmetry from pseudocubic to tetragonal was observed as the mole fraction of BaTiO₃ increased. Dielectric measurements show a dielectric anomaly associated with a phase transformation over the temperature range of 30 °C–210 °C for all compositions. Examination of the polarization hysteresis behavior revealed weakly nonlinear hysteresis loops. With these data, ferroelectric phase diagrams were derived showing the transition between the pseudocubic relaxor behavior to the tetragonal normal ferroelectric behavior. This transition was also correlated with changes in the diffuseness parameter.

Keywords

Dielectric oxides, Phase transitions, Ozone, Zinc, Solid solutions, X-ray diffraction, Relaxor ferroelectrics, Sintering, Dielectrics, Ferroelectric phase transitions

Disciplines

Materials Science and Engineering

Comments

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Chien-Chih Huang, David P. Cann, Xiaoli Tan, and Naratip Vittayakorn

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Phase transitions and ferroelectric properties in $\text{BiScO}_3\text{-Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BaTiO}_3$ solid solutions

Chien-Chih Huang^{a)} and David P. Cann

Materials Science, Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon 97331

Xiaoli Tan

Materials Science and Engineering Department, Iowa State University, Ames, Iowa 50011

Naratip Vittayakorn

Department of Chemistry, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand 10520

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Ceramics solid solutions within the ternary perovskite system $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BiScO}_3\text{-BaTiO}_3$ were synthesized via solid-state processing techniques. The crystal structure of sintered ceramics was analyzed by x-ray diffraction. A stable perovskite phase was obtained for all compositions with a BaTiO_3 content greater than 50 mol %. Furthermore, a change in symmetry from pseudocubic to tetragonal was observed as the mole fraction of BaTiO_3 increased. Dielectric measurements show a dielectric anomaly associated with a phase transformation over the temperature range of 30 °C–210 °C for all compositions. Examination of the polarization hysteresis behavior revealed weakly nonlinear hysteresis loops. With these data, ferroelectric phase diagrams were derived showing the transition between the pseudocubic relaxor behavior to the tetragonal normal ferroelectric behavior. This transition was also correlated with changes in the diffuseness parameter. © 2007 American Institute of Physics. [DOI: [10.1063/1.2769787](https://doi.org/10.1063/1.2769787)]

I. INTRODUCTION

Perovskite $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) ceramics are widely used for many industrial applications due to their superior performance in piezoelectric, dielectric, and pyroelectric applications. However, recently there have been environmental concerns about PZT related to the toxicity of lead oxides which are volatile during processing. Consequently, this has motivated the search for lead-free piezoelectric materials with piezoelectric properties comparable to PZT with a reduced environmental impact.

The origin of the enhanced piezoelectric response in perovskite PZT is the result of lone pair electrons in the Pb^{2+} hybrid orbitals¹ and the existence of a morphotropic phase boundary (MPB) between two ferroelectric phases.² Therefore, Bi^{3+} is an excellent candidate for the substitution of Pb in the PZT system since it has a similar electronic structure and there are already numerous Bi-based perovskite ceramics that can be used in solid solutions.^{3–8} Through systematic research, a number of MPB systems based on $\text{Bi}(M)\text{O}_3\text{-PbTiO}_3$ ($M=\text{Ti}^{4+}, \text{Sc}^{3+}, \text{Zn}^{2+}, \text{Nb}^{5+}, \dots$) have been discovered.^{6,8} Recently, BiScO_3 (BS) perovskite has drawn attention due to its high Curie temperature ($T_c=450$ °C) and its excellent piezoelectric properties at the MPB with PbTiO_3 .⁶ Another Bi-based perovskite, $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$, exhibits a high T_c with an enhanced tetragonality through solid solution with PbTiO_3 .^{8,9} However, both BiScO_3 and $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ are unstable in their pure form and can only be stabilized under high pressures^{10,11} or in solid solutions with other perovskite end members.^{6,8} In order to develop

lead-free piezoelectric materials, BaTiO_3 (BT) was used for this research in order to stabilize the BZT and BS perovskite phases in a solid solution.

Recently, Tinberg *et al.* reported ferroelectric thin films based on the $\text{BiScO}_3\text{-BaTiO}_3$ binary system.¹² Similar to the $\text{BiScO}_3\text{-PbTiO}_3$ system, when PbTiO_3 was replaced with BaTiO_3 , the perovskite structure was stabilized and a MPB was observed. Although there are no reports related to the $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BaTiO}_3$ system, an increased transition temperature can be expected for this system.

In this work, the phase equilibria and dielectric properties of the ternary solid solution $\text{BiScO}_3\text{-Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BaTiO}_3$ (BS-BZT-BT) were examined. This article may provide an alternative approach for lead-free piezoelectric materials development.

II. EXPERIMENTAL PROCEDURE

Solid solutions of $(1-x)(0.5\text{BiScO}_3\text{-}0.5\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3)\text{-xBaTiO}_3$ (BS-BZT-BT) were prepared by conventional ceramic processing. Reagent grade oxide powders of Bi_2O_3 ($\geq 99.9\%$), ZnO ($\geq 99\%$), TiO_2 ($\geq 99.9\%$), and BaCO_3 ($\geq 99.5\%$) were batched in stoichiometric amounts and ball-milled with ethanol and yttrium-stabilized zirconia media for 6 h. The dried powders were double calcined in open crucibles between 800 °C–950 °C for 24 h and followed by an additional milling and drying step. The calcined powders were mixed with 3 wt % polyvinyl alcohol (PVA) and then uniaxially cold-pressed at 150 MPa into 12.7 mm diameter pellets. Following binder burnout at 500 °C, the pellets were sintered in sealed crucibles between 850 °C–1200 °C for 2 h. For phase determination, x-ray

^{a)}Electronic mail: huangch@onid.orst.edu

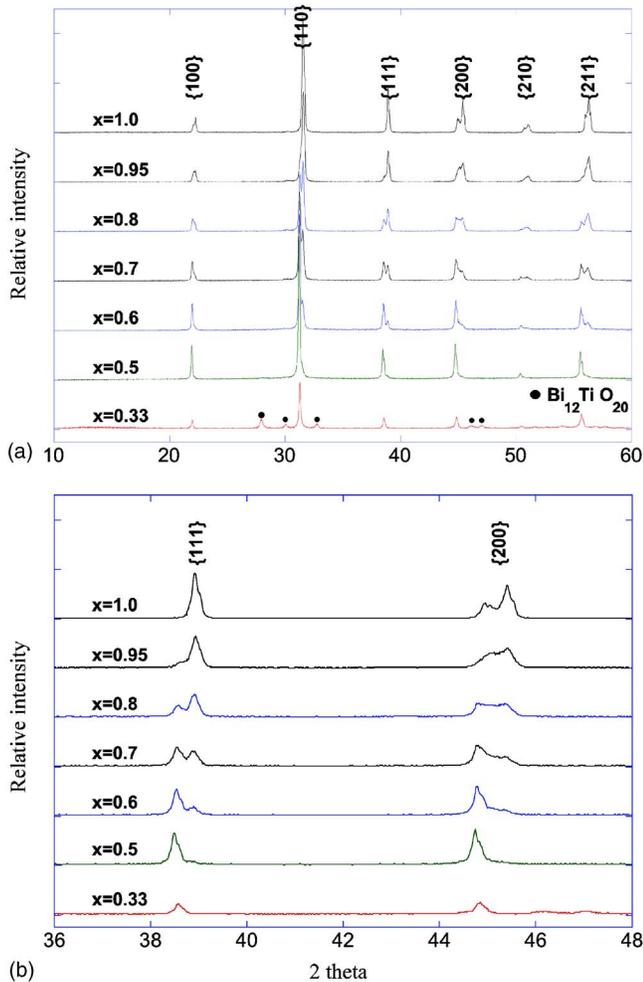


FIG. 1. (Color online) XRD diffraction pattern of calcined $(1-x)$ (BS-BZT)- x BT powders.

diffraction (XRD, Siemens D5000 diffractometer) was utilized in the 2θ scan range of $10\text{--}60^\circ$ for calcined powders and sintered pellets.

Prior to the electrical measurements, the pellets were polished to smooth and parallel surface. After polishing, a silver electrode paste (Heraeus C1000) was applied and then fired at 600°C . An Agilent 4284A LCR was used to measure the dielectric properties over a wide temperature range using a NorECS ProboStat high-temperature measurement cell. The polarization versus electric field hysteresis loops of selected compositions were recorded at room temperature and -50°C , respectively, with a RT66A standard ferroelectric test system (Radiant Technologies).

III. RESULTS AND DISCUSSION

A. Perovskite phase determination

Figure 1(a) displays the XRD patterns for calcined powders of $(1-x)$ (BS-BZT)- x BT. Perovskite phases were obtained for compositions containing at least 50 mol % BaTiO_3 . For compositions below this amount, a complex mixture of phases was observed. Based on the $\{111\}$ and $\{200\}$ peak splittings shown in Fig. 1(b), the composition with $x=0.5$ corresponds to a pure rhombohedral symmetry.

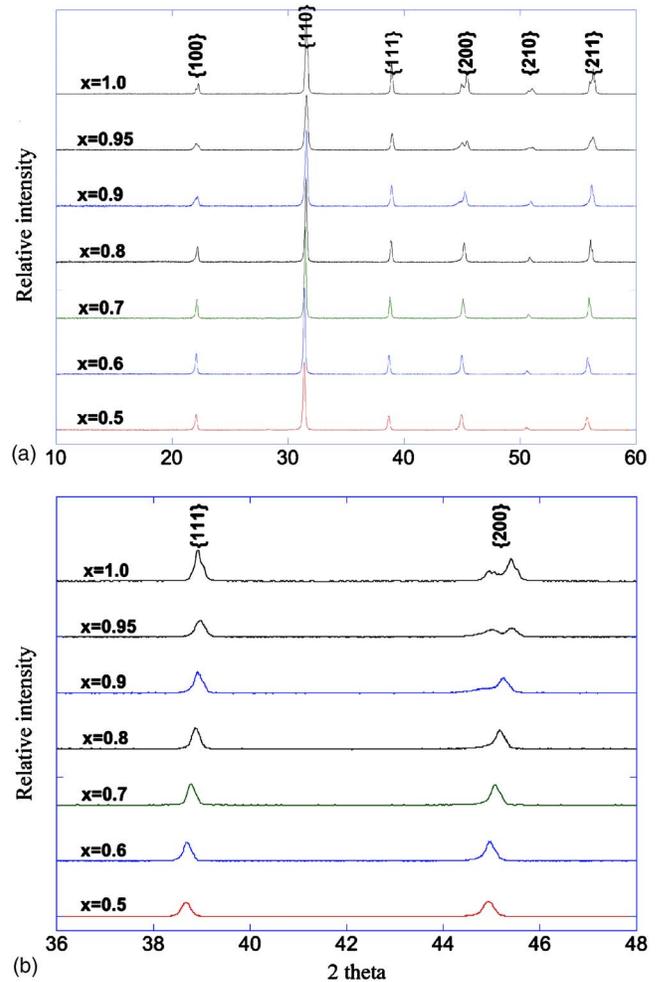


FIG. 2. (Color online) XRD diffraction pattern of sintered $(1-x)$ (BS-BZT)- x BT ceramics.

Compositions above $x=0.95$ stabilized in a pure tetragonal symmetry. The peaks between these two compositions indicated the coexistence of rhombohedral and tetragonal phases. The XRD patterns of sintered $(1-x)$ (BS-BZT)- x BT pellets shown in Fig. 2 confirm that the samples retained phase pure perovskite for all compositions with 50 mol % and above BaTiO_3 . In contrast to the calcined powders, in the sintered pellets the tetragonal perovskite phase was only present for compositions with $x=0.95$ to $x=1$. The remainder of the compositions $x \leq 0.9$ exhibited a rhombohedral symmetry. These results indicate that the MPB in this system may be located between $x=0.9$ and 0.95 . This shift in symmetry between the calcined and sintered samples may be due to a number of factors. The observation of the coexistence of two perovskite phases in calcined powders is likely the result of the relatively low processing temperature. The limited reaction kinetics may have resulted in an incomplete reaction between BT, BS, and BZT. In addition, both Bi_2O_3 and ZnO have some degree of volatility at this temperature that may have caused a slight change in composition. Upon sintering, homogenization occurred, leading to a clearly observed single-perovskite phase.

The lattice parameters were calculated from XRD patterns shown in Table I. Although Bi^{3+} is slightly smaller than

TABLE I. Room-temperature structure and dielectric data for all compositions at 10 KHz.

x mol % BT	0.5	0.6	0.7	0.8	0.9	0.92	0.95	1
Structure			Rhombohedral				Tetragonal	
lattice parameter (Å)	4.046	4.040	4.030	4.022	4.014	4.009	a : 3.997 c : 4.023	a : 3.992 c : 4.034
T_m (°C)	208	161	118	76	45	33	111	134
ϵ_m at T_m	1100	1170	1240	1360	2570	3960	3520	9740
δ	587.5	210.3	143.1	70	61.4	57.3	16.3	3.4
γ	1.99	1.74	1.65	1.67	1.66	1.44	1.38	1.11

Ba²⁺ based on 12-fold coordination, the unit cell volume increased with decreasing BaTiO₃ content due to substitution of larger size *B*-site cations Zn²⁺(0.88 Å) and Sc³⁺(0.885 Å) for Ti⁴⁺(0.745 Å). Comparing the tetragonal structure for $x=1$ and $x=0.95$, the results show that the $c:a$ ratio increased with BaTiO₃ content. This may be due to the phase transition for $x=0.95$ that occurs close to room temperature, which results in the formation of a pseudocubic phase.

B. Dielectric behavior of BS-BZT-BT

The dielectric constant and dielectric loss were measured from 100 Hz to 100 KHz as a function of temperature. The room-temperature dielectric properties for all of the compositions in this study are listed in Table I. Figure 3 shows the

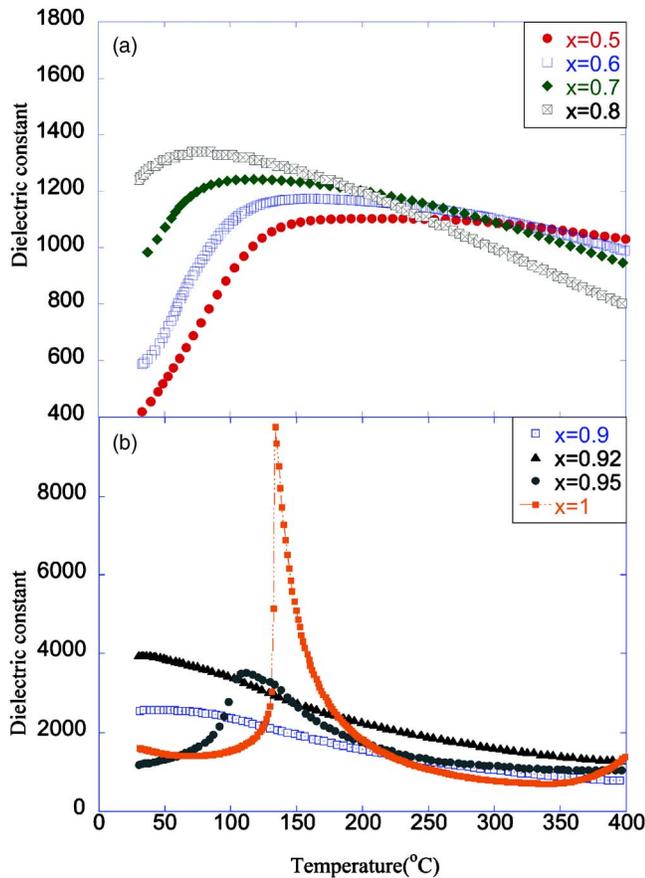


FIG. 3. (Color online) Dielectric constant of $(1-x)(\text{BS-BZT})-x\text{BT}$ as a function of temperature at measuring frequency of 10 kHz.

permittivity versus temperature at 10 KHz for $(1-x)$ (BS-BZT)- $x\text{BT}$ from $x=0.5$ to 1.0. It was observed that the maximum permittivity, ϵ_m , increased with increasing BaTiO₃ content. However, temperature at which maximum permittivity appeared, T_m , exhibited a more complex trend. It is very clear from the data that, while pure BaTiO₃ exhibited a strong first-order phase transition, the addition of BS+BZT caused a shift toward relaxor ferroelectric behavior. It is well known that perovskite BaTiO₃ has three phase transitions within a wide range of temperature.¹³ According to our XRD data in Fig. 2, when mixed with more than 10 mol % BS-BZT, all three transition temperatures merged into one diffuse transition which is also reflected in the XRD data. This kind of phenomenon has also been noted when BaTiO₃ was mixed with BaZrO₃.¹⁴ In Table I, the data clearly show that T_m decreased with increasing BaTiO₃ content for $x \leq 0.9$. On the contrary, T_m increased with BaTiO₃ content for $x \geq 0.95$.

For a diffuse phase transition, the degree of diffuseness can be obtained from the parameter δ_r derived via the following expression:¹⁵

$$\frac{\epsilon'_m}{\epsilon'(f,T)} = 1 + \frac{[T - T_m(f)]^\gamma}{2\delta_r^2} \quad (1 \leq \gamma \leq 2). \quad (1)$$

The parameter of γ is degree of dielectric relaxation, where $\gamma=1$ corresponds to a normal first-order ferroelectric phase transition. Larger values of γ express more relaxor-ferroelectric behavior of transition. The value of δ_r represents degree of diffuseness for transition peaks. Both γ and δ_r were determined from the slope and intercept of $\ln(\epsilon'_m/\epsilon')$ vs $\ln(T-T_m)$. According to Table I, a greater percentage of BS and BZT resulted in a higher degree of diffuseness and stronger relaxor behavior. This can be explained by the increased cation disorder due to the substitution on the *A*-site by Bi and on the *B*-site by Sc and Zn.

The dielectric property as a function of frequency for $(1-x)(\text{BS-BZT})-x\text{BT}$ is shown in Fig. 4. A strong frequency dependence characteristic of a relaxor ferroelectric was observed. The peaks appearing around 600 °C for $x=0.8$ are likely the result of oxygen vacancies.¹⁶ Moreover, these compositions possess a stable dielectric constant of approximately 1000 and low loss tangent ($\tan \delta < 0.01$) up to high temperatures ($T < 400$ °C). It may have great potential for high-temperature applications.

The polarization versus electric field measurements at 4 Hz for $x=0.5$ and $x=0.7$ are shown in Fig. 5. The samples used in this study were sintered without being covered,

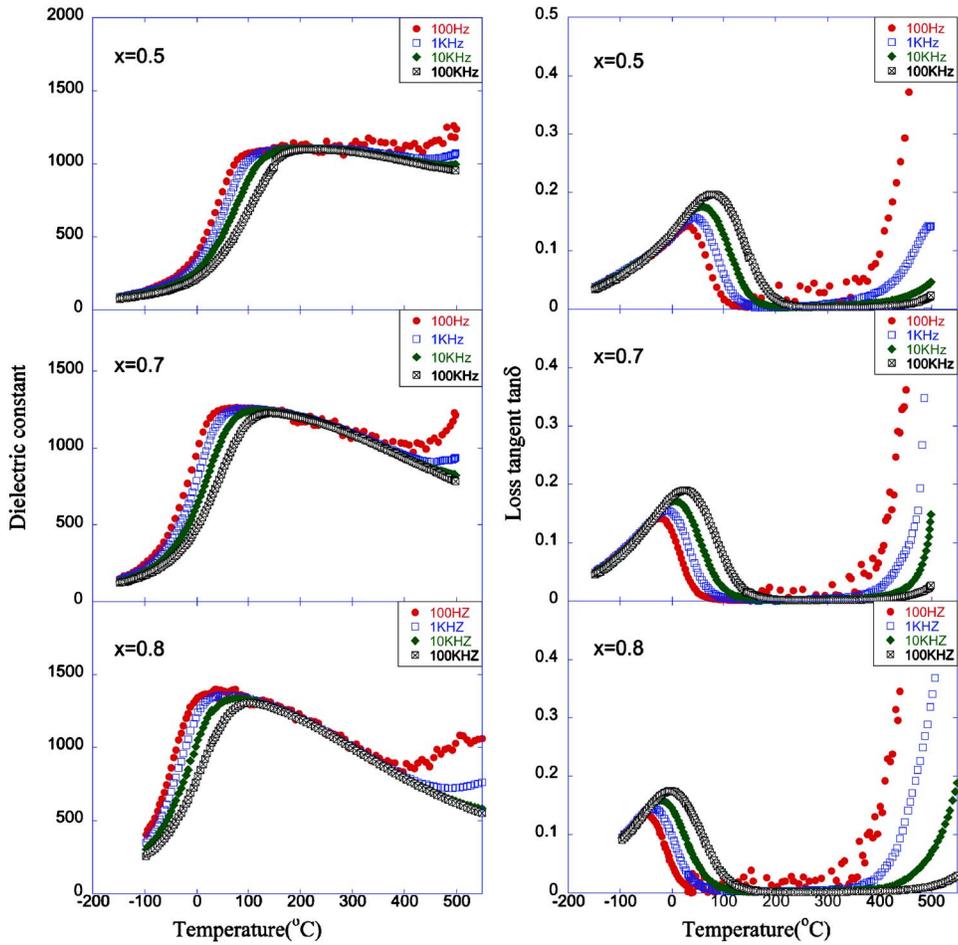


FIG. 4. (Color online) Dielectric constant and loss tangent of $(1-x)$ (BS-BZT)- x BT with $x=0.5, 0.7,$ and 0.8 as a function of temperature.

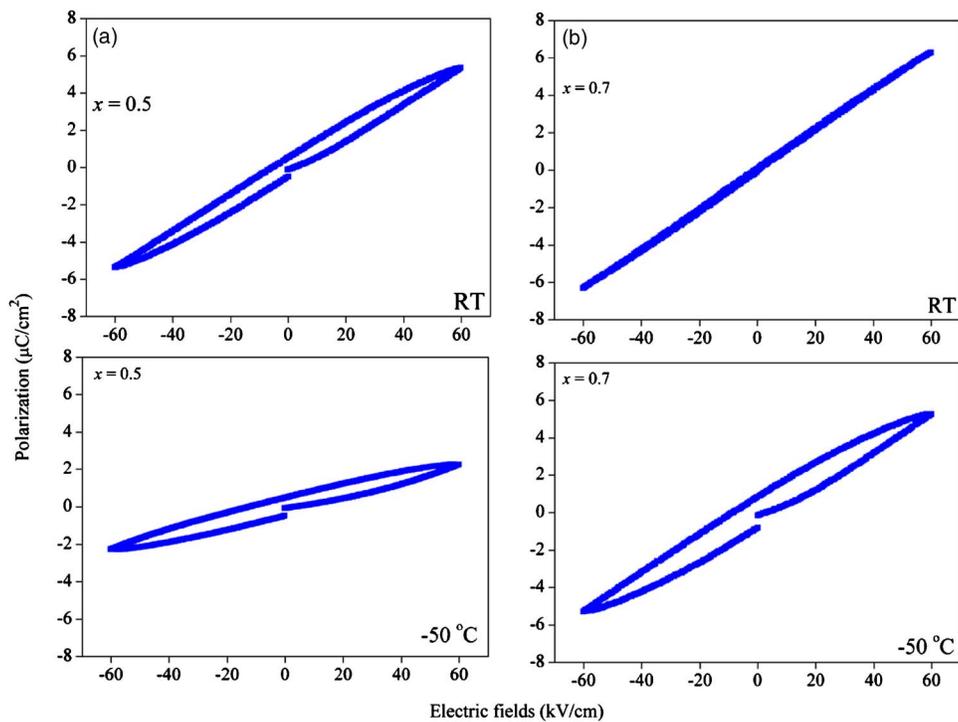


FIG. 5. (Color online) Polarization data on $(1-x)$ (BS-BZT)- x BT ceramics at 4 Hz for (a) $x=0.5$ and (b) $x=0.7$.

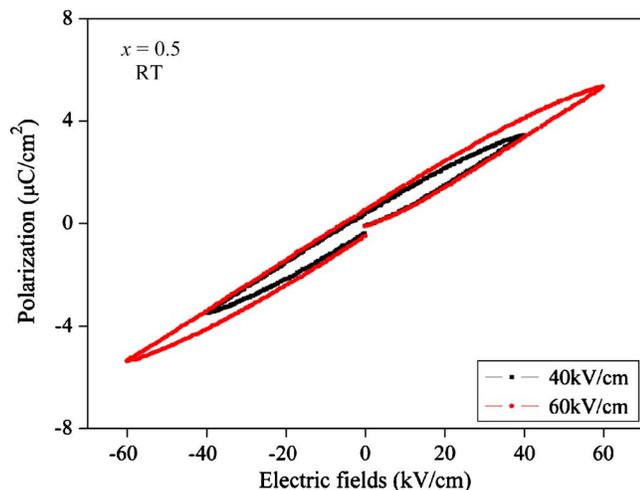


FIG. 6. (Color online) The P - E hysteresis loop measured from the ceramic of $x=0.5$ at 4 Hz at room temperature.

which, due to the loss of Zn and Bi, resulted in a slight downward shift in T_{\max} (i.e., on the order of 10°C – 20°C). The loop from the ceramic of $x=0.5$ exhibits a weak nonlinearity at room temperature, which is not unexpected given that the measurements were taken at a temperature in the vicinity of T_m . At $T=-50^{\circ}\text{C}$ the slope of the loop decreased as expected due to the decrease in dielectric permittivity below T_m . Figure 6 displays room-temperature P - E data for $x=0.5$ as a function of electric field. As the E -field increases, a clear elliptical rotation is observed which is another indication of nonlinear behavior. The $x=0.7$ sample exhibited a narrow, weakly nonlinear loop at room temperature which broadened at lower temperatures corresponding to the increased $\tan \delta$ below the transition temperature (Fig. 4). It is interesting to note that even at relatively high fields up to 60 kV/cm all the loops were weakly nonlinear with relatively low polarization values.

C. Phase transformations in the $(1-x)(\text{BS-BZT})$ - $x\text{BT}$ system

Figure 7 presents data on the phase transformation in the $(1-x)(\text{BS-BZT})$ - $x\text{BT}$ system obtained from the dielectric data. Starting from pure BaTiO_3 the phase transition decreases as the (BS-BZT) content increases to a minimum of 33°C at $x=0.92$. At higher (BS-BZT) concentrations the transition temperature then increases up to $x=0.5$. Also plotted in Fig. 7 is the diffuseness parameter δ as a function of composition. Pure BaTiO_3 exhibits a sharp first-order phase transition, but as the (BS-BZT) content increases a quasilinear increase in δ is observed owing to increased relaxor behavior.

IV. CONCLUSION

Single-phase perovskite was obtained for $(1-x)(\text{BS-BZT})$ - $x\text{BT}$ for compositions containing at least

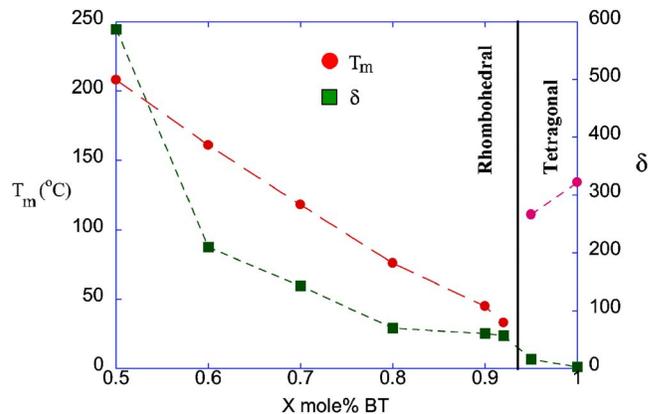


FIG. 7. (Color online) T_{\max} and diffuseness δ as a function of BaTiO_3 content.

50 mol % BaTiO_3 . The XRD data revealed that a MPB may exist between 5–10 mol % BS-BZT added to BaTiO_3 . The dielectric characterization revealed that as BS-BZT was added to BaTiO_3 the phase transition became very diffuse. The relaxor ferroelectric behavior was likely due to complex cation ordering on the A -site and on the B -site. Due to the diffuseness of the phase transition, the compositions in this study exhibited a very stable dielectric constant greater than 1000 and low loss tangents (<0.01) over a wide range of temperature ($T < 400^{\circ}\text{C}$).

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