Journal

Rapid Communication

A Novel BiFeO₃–BaTiO₃–BaZrO₃ Lead-Free Relaxor Ferroelectric Ceramic with Low-Hysteresis and Frequency-Insensitive Large Strains

Donggeng Zheng and Ruzhong Zuo[†]

Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of
Technology, Hefei 230009, China

A novel $(0.67 - x)$BiFeO₃–0.33BaTiO₃–xBaZrO₃ lead-free relaxor ferroelectric ceramic was developed by a solid-state reaction method. Measurements of temperature-dependent dielectric permittivity and the polarization/strain hysteresis loops demonstrated an obvious evolution of dielectric relaxor behavior at room temperature (RT) from nonergodic to ergodic states. A significantly enhanced electrostrain of ~0.37% at 7 kV/mm with a relatively small hysteresis of ~39% and a low-frequency sensitivity was found at $x = 0.04$, showing large potential for actuator applications. This was basically attributed to a rapid response of forward and backward switching between ergodic and ferroelectric phases owing to similar free energies and large local random fields.

I. Introduction

ENVIRONMENTAL concerns have stimulated wide interests in making lead-free ferroelectric materials. One of these attempts is to develop new lead-free ceramics with large electromechanical strains for actuator applications. In terms of the relationship between electrostrain S and polarization P: $S = QP^2$, where Q is the electrostrictive coefficient, which is usually weakly dependent on the composition of perovskite-type materials, it seems better to seek ferroelectric materials with a large spontaneous polarization. This relationship is valid not only for electrostrictive materials, but also for relaxor ferroelectrics.[1] It is believed that the polar nanoregions (PNRs) play an important role in relaxor behavior. An ergodic relaxor can freeze into a nonergodic relaxor near a critical freezing temperature T_f.[2] Large electrostrains of 0.3%–0.4% were recently reported in $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT)-based lead-free relaxor ferroelectrics near T_f.[3–5] Unfortunately, their strains displayed serious hysteresis ($\geq 60\%$).[3–6] BiFeO₃ (BF) was recognized as a potential lead-free material owing to its excellent intrinsic polarization ($P > 100~\mu C/cm^2$).[7] A giant strain response (above 5%) was observed in BF thin films.[8] By comparison, BF ceramics generally exhibit low polarization and strain values owing to their poor electric insulation. Solid solution ceramics of $(1-x)$BF–xBaTiO₃ (BT) can exhibit a relatively large spontaneous polarization of 42 $\mu C/cm^2$ at $x = 0.33$.[9]

In this work, a new lead-free solid solution of BF–BT–BaZrO₃ (BZ) was constructed. Their dielectric, ferroelectric, and electromechanical strain properties were systematically explored.

II. Experimental Procedures

The $(0.67-x)$BF–0.33BT–xBZ ($x = 0$–0.08) ceramics were fabricated by a solid-state reaction method. High-purity ($\geq 99.0\%$) raw materials of Bi_2O_3, Fe_2O_3, $BaCO_3$, TiO_2, and ZrO_2 were mixed in alcohol, and then calcined at 700°C–800°C for 12 h. The as-pressed samples were sintered at 990°C for 2 h in alumina crucibles. The dielectric properties at various frequencies were measured using an LCR meter (Agilent E4980A, Santa Clara, California) in a tube furnace. The S–E loops were measured using a ferroelectric test system (Precision multiferroelectric; Radiant Technologies Inc, Albuquerque, New Mexico) connected with an accessory laser interferometer vibrometer (AE SP-S 120E, SIOS Meβtechnils, GmbH, llmenau, Germany).

III. Results and Discussion

The dielectric permittivity (ε_r) and loss tangent (tan δ) of BF–BT–xBZ ceramics are shown in Fig. 1(a). All samples exhibited typical frequency dispersion and diffuse phase transition behavior near the temperature (T_m) at dielectric maxima (ε_m). The diffuseness degree γ can be calculated from a modified Curie–Weiss law $1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma/C$ at $T > T_m$, and another parameter ΔT_{relax} was defined as the difference between two T_m values measured at 1000 and 1 kHz. A significant increase in both γ and ΔT_{relax} values was observed with increasing x [Fig. 1(b)]. The T_f value can be obtained by fitting the measured dielectric permittivity versus temperature curves to the Vogel–Fulcher relationship $f = f_o \cdot \exp(-E_a/(k(T_m - T_f))$, where E_a is the activation energy,[2] as shown in Fig. 1(c). Increase in the calculated E_a with x indicated progressively large dynamics and small size of PNRs.[10] In addition, the relaxor phase at room temperature (RT) transformed from a nonergodic state to an ergodic state. The decreased tan δ at elevated temperatures with increasing x indicated the improvement of the electric insulation.

Figures 2(a) and (b) demonstrated non-first-cycle S–E loops for BF–BT–xBZ ceramics. The $x = 0$ sample showed a butterfly bipolar strain loop and a almost linear unipolar strain curve, because of an irreversible nonergodic-to-ferroelectric phase transformation. The negative strains were formed because the ferroelectric domain reorientation was involved. It can be seen from Fig. 2(c) that the substitution of BZ induced a pronounced increase in S_{pos} up to ~0.37% at $x = 0.04$ and simultaneously led to a almost zero S_{neg}. The electric field induced large strain in relaxor ferroelectrics was generally ascribed to reversible ergodic–ferroelectric phase transformation.[3,4] From Fig. 2(b), one can calculate the normalized strain d_{33}^* ($= S_{max}/E_{max}$) and corresponding strain hysteresis (Hys. $= W_{max}/S_{max}$), as plotted in Fig. 2(d). The largest hysteresis for the $x = 0.04$ composition could be considered as a result of the time effect of forward and backward switching of ergodic and ferroelectric phase transi-
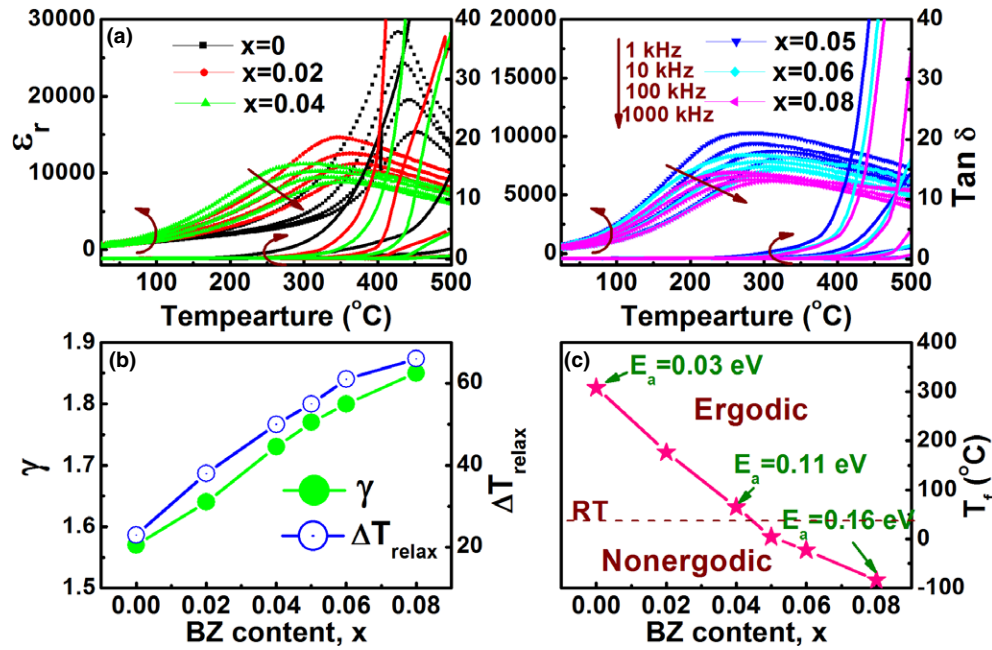
S. Zhang—contributing editor

Fig. 1. (a) Dielectric permittivity and loss tan δ as a function of temperature and frequency for BF–BT–xBZ ceramics, (b) ΔT_{relax} and γ values, and (c) T_f values with varying x.
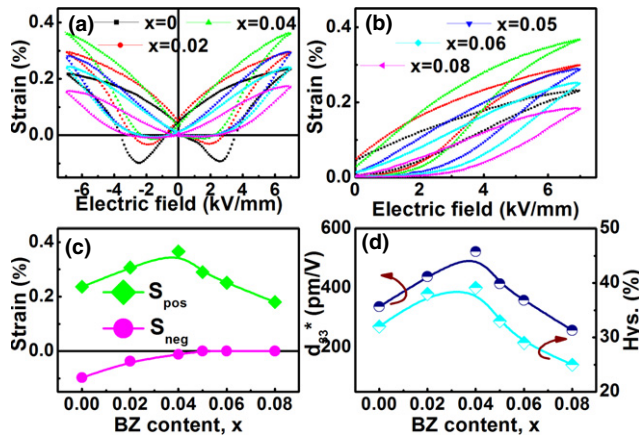

Fig. 2. (a) Bipolar and (b) unipolar S–E loops at 1 Hz for BF–BT–xBZ ceramics, (c) positive strain (S_{pos}) and negative strain (S_{neg}), and (d) $d_{33}*$ and hysteresis degree as a function of x.

tion.[11] Relatively small size of PNRs in this material would make its response to fields fast. The maximum $d_{33}*$ could reach ~528 pm/V with a strain hysteresis of ~39%, which is far lower than those of BNT-based relaxor ferroelectrics (usually Hys. > 60%).[3–6] A comparison among several typical lead-free ferroelectrics was made in Table I. Although the $(Na_{0.5}K_{0.5})NbO_3$ (NKN) and BT-based lead-free ceramics were reported to have low hysteresis, yet their strain values and $d_{33}*$ values are relatively small.[12,13]

Figure 3 shows the effect of electric field and frequency on strains for the $x = 0.04$ sample. The threshold driving field E_{ef} of the ergodic to ferroelectric phase transition was estimated by making the derivative of lower half unipolar S–E curves (dS/dE) [see Fig. 3(a)]. The maximum strain hysteresis just appeared at the field where the maximum dS/dE was reached (E_{ef}), which is slightly lower than the field value of the maximum $d_{33}*$ [Fig. 3(c)]. This result further indicated that the main contributions of strain and strain hysteresis should originate from the ergodic and ferroelectric phase transition at lower electric fields, instead of further domain switching at large fields. As shown in Table I, the $x = 0.04$ sample possessed a relatively low E_{ef} value than BNT-based systems. In addition, it can be seen from Fig. 3(d) that the $d_{33}*$ slightly decreased, and the hysteresis degree and E_{ef} values slightly increased with increasing frequency (0.2–100 Hz). When the measuring frequency increases, the domain wall motion lags and then its contribution to strains also drops. Because of extremely large dynamics and small size (i.e., large random fields) of ergodic PNRs in BF–BT–xBZ ($x = 0.04$) relaxor ferroelectrics, the response of domain wall motion to electric field is very fast, such that both $d_{33}*$ and E_{ef}, and their strain hysteresis almost are frequency independent.

IV. Conclusions

In summary, an obvious evolution of dielectric relaxor behavior was found in a new lead-free BF–BT–xBZ relaxor ferroelectric ceramic, as confirmed by the temperature-dependent

Table I. Comparison of Ferroelectric and Strain Properties of BF–BT–xBZ ($x = 0.04$) Ceramics with Some Lead-Free Ferroelectric Ceramics

Compounds	E (kV/mm)	P_{max} (μC/cm²)	S_{max} (%)	$d_{33}*$ (pm/V)	Hys. (%)	E_{ef} (kV/mm)	Ref.
NKNS–LT–BZ	4	~21	~0.2	~500	~14.1	—	[12]
BZT	4	~19	~0.18	~450	~5.2	~	[13]
BNT–BAT	8	~37	~0.36	~448	~71.9	~5.6	[3]
BNT–BNN	7	~34	~0.3	~420	~64.2	~5.1	[4]
BNT–BKT–Nb	7	~42	~0.42	~600	~65.1	~4.7	[5]
BNT–BT–NKN	8	~44	~0.45	~562	~69.3	~4.1	[6]
BF–BT–xBZ	7	~40	~0.37	~528	~39.1	~3.7	This study

$(Na,K)(Nb,Sb)O_3$: NKNS; $LiTaO_3$: LT; $Ba(Al_{1/2}Ta_{1/2})O_3$: BAT; $Ba(Ni_{1/2}Nb_{1/2})O_3$: BNN; $(Bi_{0.5}K_{0.5})TiO_3$: BKT.
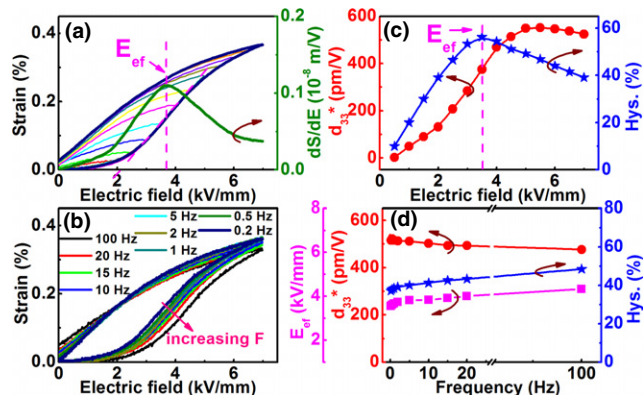
Fig. 3. (a) Unipolar S–E loops under different electric fields at 1 Hz for the $x = 0.04$ sample together with the dS/dE value during loading. (b) Frequency dependence of unipolar strain. (c) d_{33}^* and the strain hysteresis degree with electric fields. (d) d_{33}^*, the strain hysteresis degree and E_{ef} values with frequency.

dielectric permittivity and the ferroelectric polarization/strain hysteresis loops. A significantly enhanced electrostrain of ~0.37% under 7 kV/mm (normalized strain, ~528 pm/V) together with a relatively small hysteresis of ~39% and a low-frequency sensitivity was produced in the $x = 0.04$ sample, as compared with the previously reported BNT-based lead-free relaxor ferroelectrics.

Acknowledgments

References

[1] J. Fu and R. Z. Zuo, "Giant Electrostrains Accompanying the Evolution of a Relaxor Behavior in Bi(Mg,Ti)O$_3$–PbZrO$_3$–PbTiO$_3$ Ferroelectric Ceramics," *Acta Mater.*, **261**, 3687–94 (2013).

[2] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, "Freezing of the Polarization Fluctuations in Lead Magnesium Niobate Relaxors," *J. Appl. Phys.*, **68**, 2916–21 (1990).

[3] W. F. Bai, Y. L. Bian, J. H. Hao, B. Shen, and J. W. Zhai, "The Composition and Temperature-Dependent Structure Evolution and Large Strain Response in $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$xBa(Al_{0.5}Ta_{0.5})O_3$ Ceramics," *J. Am. Ceram. Soc.*, **96** [1] 246–52 (2013).

[4] F. Li, R. Z. Zuo, D. G. Zheng, and L. T. Li, "Phase-Composition-Dependent Piezoelectric and Electromechanical Strain Properties in $(Bi_{1/2}Na_{1/2})TiO_3$–$Ba(Ni_{1/2}Nb_{1/2})O_3$ Lead-Free Ceramics," *J. Am. Ceram. Soc.*, **98** [3] 811–8 (2015).

[5] K.-N. Pham, A. Hussain, C. W. Ahn, I. W. Kim, S. J. Jeong, and J.-S. Lee, "Giant Strain in Nb-Doped $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ Lead-Free Electromechanical Ceramics," *Mater. Lett.*, **64**, 2219–22 (2010).

[6] S. T. Zhang, A. B. Kounga, E. Aulbach, H. Ehrenberg, and J. Rödel, "Giant Strain in Lead-Free Piezoceramics $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$–$K_{0.5}Na_{0.5}NbO_3$ System," *Appl. Phys. Lett.*, **91**, 112906, 3pp (2007).

[7] D. Lebeugle, D. Colson, A. Forget, and M. Viret, "Very Large Spontaneous Electric Polarization in BiFeO$_3$ Single Crystals at Room Temperature and Its Evolution Under Cycling Fields," *Appl. Phys. Lett.*, **91**, 022907, 3pp (2007).

[8] J. X. Zhang, et al., "Large Field-Induced Strains in a Lead-Free Piezoelectric Material," *Nat. Nanotechnol.*, **6**, 98–102 (2011).

[9] T. Ozaki, et al., "Ferroelectric Properties and Nano-Scaled Domain Structures in $(1-x)BiFeO_3$–$XBaTiO_3$ $(0.33<x<0.50)$," *Ferroelectrics*, **385**, 155–61 (2009).

[10] H. Ogihara, C. A. Randall, and S. Trolier-McKinstry, "Weakly Coupled Relaxor Behavior of BaTiO$_3$–BiScO$_3$ Ceramics," *J. Am. Ceram. Soc.*, **92**, 110–8 (2009).

[11] E. Sapper, N. Novak, W. Jo, T. Granzow, and J. Rödel, "Electric-Field-Temperature Phase Diagram of the Ferroelectric Relaxor System $(1-x)Bi_{1/2}Na_{1/2}TiO_3$–$XBaTiO_3$ Doped with Manganese," *J. Appl. Phys.*, **115**, 194104, 7pp (2014).

[12] J. Fu, et al., "Electric Field Induced Intermediate Phase and Polarization Rotation Path in Alkaline Niobate Based Piezoceramics Close to the Rhombohedral and Tetragonal Phase Boundary," *Appl. Phys. Lett.*, **100**, 22902, 5pp (2012).

[13] Z. Yu, C. Ang, R. Guo, and A. S. Bhalla, "Piezoelectric and Strain Properties of Ba(Ti$_{1-x}$Zr$_x$)O$_3$ Ceramics," *J. Appl. Phys.*, **92**, 1489–93 (2002). □