# Large piezoelectric effect in Pb-free Ba(Ti,Sn)O3-x(Ba,Ca)TiO3 ceramics

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# Large piezoelectric effect in Pb-free $Ba(Ti,Sn)O_3$-x$(Ba,Ca)TiO_3$ ceramics

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We designed a Pb-free pseudo-binary system, $Ba(Sn_{0.12}Ti_{0.88})O_3$-x$(Ba_{0.7}Ca_{0.3})O_3$ (BTS-*x*BCT), characterized by a phase boundary starting from a tricritical triple point of a paraelectric cubic phase, ferroelectric rhombohedral, and tetragonal phases. The optimal composition BTS-30BCT exhibits a high piezoelectric coefficient $d_{33} \sim 530$ pC/N at room temperature. In view of the recent report of high piezoelectricity in another Pb-free system BZT-BCT (Liu and Ren, Phys. Rev. Lett. **103**, 257602 (2009)), which possesses a similar tricritical triple point in the phase diagram, it seems that forming a suitable phase boundary starting from a tricritical triple point could be an effective way to develop high-performance Pb-free piezoelectrics. © *2011 American Institute of Physics*. [doi:10.1063/1.3640214]

Piezoelectric materials, which generate a voltage in response to mechanical strain (and vice versa), are central to a vast range of applications.[1,2] Among all known piezoelectric materials, the PZT (lead zirconate titanate) family ceramics have dominated almost all piezoelectric applications since 1950's.[1–5] However, their Pb toxicity has raised global environmental concerns and restrictions.[3–8] Therefore, there is an urgent demand for the Pb-free substitutes. Recently, several notable Pb-free piezoelectric ceramics have been reported to exhibit promising piezoelectric properties,[4–11] especially the $(K,Na)NbO_3$ based pseudo-ternary system[7] and the $BaTiO_3$ based pseudo-binary system.[9]

The common approach to generate high piezoelectricity is to place the material at the phase transition boundary between two ferroelectric phases[8] or even between one ferroelectric phase and one non-ferroelectric phase.[12] The instability of the polarization state at the phase transition regions allows a significant polarization variation under external stress or electric field. As a result, the properties of materials related to polarization change, such as dielectric permittivity and piezoelectric coefficients, can be enhanced significantly.

Very recent study further shows that besides the transition boundary between two phases, high piezoelectricity can also be ascribed to the fact that the phase boundary starts from a triple point of a paraelectric cubic phase (C), ferroelectric rhombohedral (R), and tetragonal (T) phases.[9–11] The newly reported system, $Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-*x*BCT) is characterized by such a phase boundary between R (BZT side) and T (BCT side) phases starting from a C-T-R triple point.[9–11] This triple point is further proved to be a tricritical point by the vanishing thermal hysteresis and highest transition permittivity peak at the point.[9] Such a phase boundary (tricritical triple point type) has a flattened energy landscape and consequently a low energy barrier for polarization rotation.[9–12] As a result, the piezoelectric coefficient $d_{33}$ of optimal composition reaches ~600 pC/N at the room temperature (RT).

However, up to now only the BZT-*x*BCT system[9–11] is reported to possess both tricritical triple point and high piezoelectricity. Thus, it is tempting to speculate that by designing a phase boundary starting from a tricritical triple point in the phase diagram, high piezoelectricity can be obtained. Then, it is interesting to see whether high $d_{33}$ can be indeed achieved in a wider range of systems following the same idea. In the present study, we thus designed a Pb-free system, $Ba(Sn_{0.12}Ti_{0.18})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$.

All the ceramic samples were fabricated by a conventional solid-state reaction method with starting chemicals of $BaCO_3$ (99.95%), $CaCO_3$ (99.9%), $SnO_2$(99.9%), and $TiO_2$ (99.9%). The calcining was performed at 1350 °C and sintering was done at 1450 °C in air. The dielectric properties were evaluated using a HIOKI3532 LCR meter at 1 kHz. Ferroelectric hysteresis loops were measured at 10 Hz. The piezoelectric constant $d_{33}$ was measured by a Berlingcourt-type $d_{33}$ meter for poled samples with a cylindrical shape. The unipolar electrostrain was measured with poled disk-shaped samples under an electric field of 500 V/mm using a MTI 2000 photonic sensor. The temperature dependence of properties was measured by using a resonance method.[11]

The system we designed is a solid solution of two terminal compounds, $Ba(Sn_{0.12}Ti_{0.88})O_3$ (abbreviated as BTS) and $(Ba_{0.7}Ca_{0.3})TiO_3$ (abbreviated as BCT). The x-ray diffraction profiles of BTS-*x*BCT system at RT are presented in Fig. 1(a). All the samples show a $BaTiO_3$-like perovskite structure, and the two terminal compounds (BTS and BCT) are characterized by R structure[13,14] and T structure[15] respectively.

The lattice parameters ($a$ and $c$) and tetragonality ($=c/a-1$) as a function of the concentration ($x$) of tetragonal terminal BCT are shown in Fig. 1(b). With decreasing $x$, the tetragonal lattice parameters $a_T$ and $c_T$ gradually converge to one pseudo-cubic lattice parameter $a_{PC}$ and the tetragonality decreases to nearly zero at $x = 30$; this indicates that there is a compositional structure change at $x = 30$. Such a crystal structure evolution with composition is analogous to that of PMN-PT system at morphotropic phase boundary between local R symmetry and T symmetry.[16]

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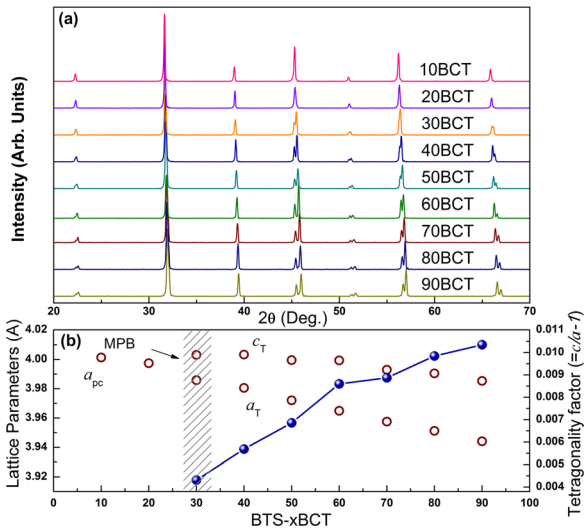


FIG. 1. (Color online) (a) X-ray profile of BTS-$x$BCT (x = 10, 20, 30, 40, 50, 60, 70, 80, 90). (b) Lattice parameters and tetragonality factor ($c/a - 1$). Phase boundary region is indicated by the shaded area.

The phase diagram of BTS-$x$BCT system is shown in Fig. 2(a). The transition temperatures were determined by dielectric permittivity ($\varepsilon$) versus temperature (T) curves and a few typical ones are shown in Figs. 2(b)–2(e). The phase diagram is characterized by a phase boundary separating R phase (BTS side) and T phase (BCT side). Notably, this phase boundary starts form a C-R-T triple point locating at $x = 8$ and at $T = 47\,^{\circ}\mathrm{C}$. As shown in Fig. 2(f), the thermal hysteresis of R-T transition decreases sharply towards the triple point and is nearly vanishing at this point. Meanwhile, the thermal hysteresis of C-T and C-R transition also shows similar behavior but the changes are less. Such facts suggest this triple point is a tricritical point corresponding to a crossover from a discontinuous to a continuous transition.[9,17] Figures 2(b)–2(e) shows that the 5BCT, a near-tricritical composition, exhibits the highest permittivity peak at $T_C$. The anomaly further supports that the point is a tricritical triple point. Thus, the BTS-$x$BCT system possesses a similar phase boundary with BZT-$x$BCT system.[9] Therefore, the equally excellent piezoelectric performance is expected in the present system.

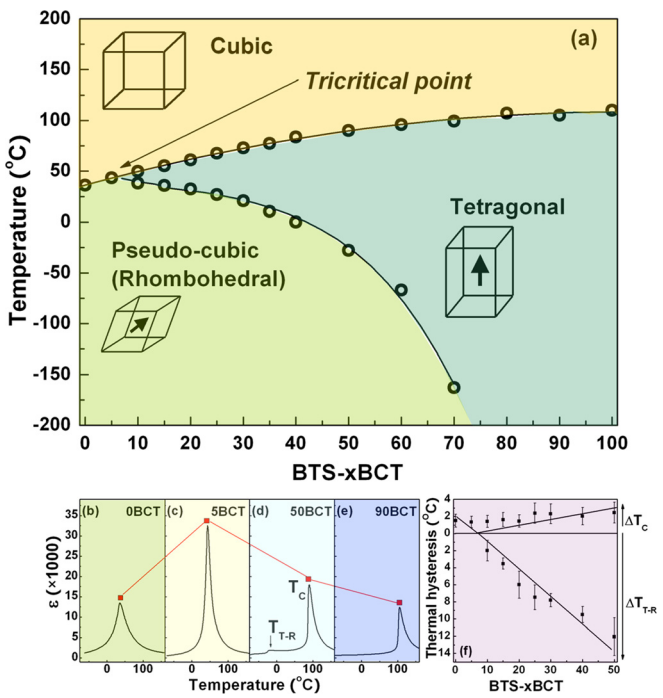


FIG. 2. (Color online) (a) Temperature-composition phase diagram of BTS-$x$BCT. (b)-(e) Typical dielectric permittivity vs. temperature curves for BTS-xBCT ($x = 0$, 5, 50, 90). (f) At triple point (about BTS-8BCT), the transition thermal hysteresis of the three transitions vanishes.

Figure 3 reveals the composition dependence of properties of this BTS-$x$BCT system at RT (25 °C). Figures 3(a)–3(d) show the saturation polarization $Pm$, remnant polarization $Pr$, coercive field $E_C$, and permittivity $\varepsilon$ of different compositions, respectively. It is found that all the properties show anomaly around the optimal composition 30BCT, such as the highest value of $Pm$, $Pr$ and $\varepsilon$, and also fairly low $E_C$. The permittivity value of BTS-30BCT is about 3800, comparable with that of soft PZT materials (2000–3500).[18] Figures 3(e) and 3(f) show the results of piezoelectric properties. The $d_{33}$ shows a maximum of 530 pC/N at 30BCT and lowers with deviating from the 30BCT. But it still maintains 441/378 pC/N for 25BCT/35BCT, respectively. The $dS/dE$ has a highest value of 820 pm/V at 30BCT as well and is comparable with that of the soft PZT ceramics (900 pm/V). The property anomaly is analogous to that found in Pb-free BZT-BCT system[9] and Pb-based PZT,[1] PMN-PT,[19] PZN-PT (Ref. 20) systems.

The intrinsic polarization rotation and extension and extrinsic domain wall contribution to the high performance are considered.[9,12] The continuous nature of the transition at the tricritical triple point requires that the free energy landscape will be flattened with respect to polarization states.[9] Further deviation from the triple point along the phase boundary to RT results in very weak polarization anisotropy. Such weak anisotropy favors polarization rotation and enhancement of the transverse susceptibility and shear piezoelectric coefficients.[9,12] In addition, because of the low $T_C$ of BTS-30BCT, the polarization extension, which favors enhancement of the

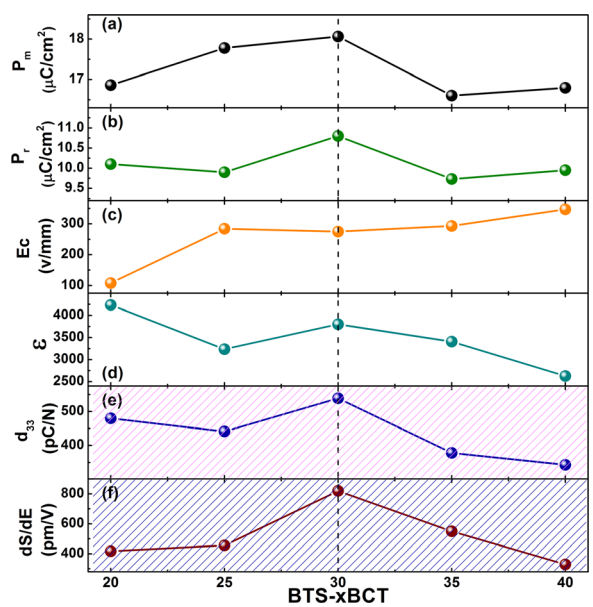


FIG. 3. (Color online) Composition dependence of (a) saturation polarization $Pm$, (b) remnant polarization $Pr$, (c) coercive field $E_C$, (d) permittivity $\varepsilon$, (e) piezoelectric coefficient $d_{33}$, and (f) converse piezoelectric coefficient dS/dE.

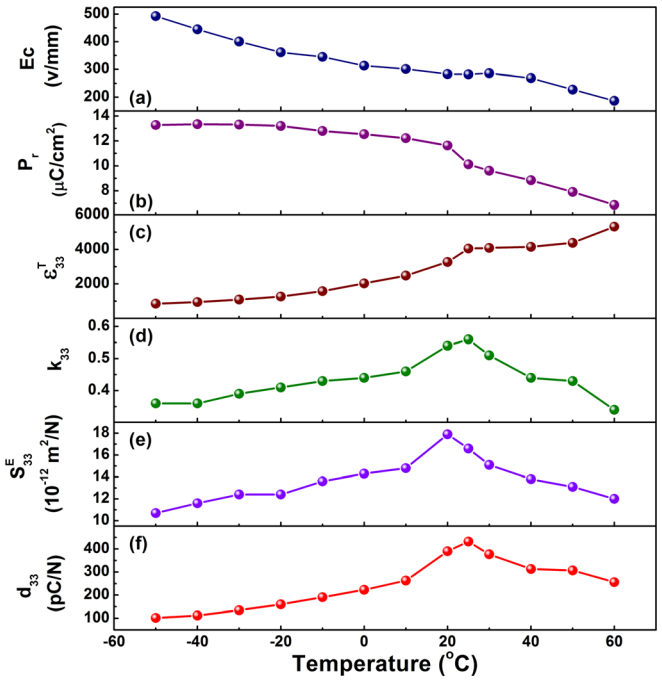


FIG. 4. (Color online) The temperature dependence of (a) coercive field $E_C$, (b) remnant polarization $Pr$, (c) permittivity $\varepsilon_{33}^T$, (d) electromechanical coupling factor $k_{33}$, (e) elastic compliance constant $s_{33}^E$ and (f) piezoelectric coefficient $d_{33}$ of BTS-30BCT ceramic.

longitudinal piezoelectric coefficient and longitudinal susceptibility, will also contribute. On the other hand, the domain wall motion becomes easier at the phase boundary, due to both the proximity of phase boundary to the Curie temperature and the flattened energy profile.[9–11,21–23] Thus, the domain wall motions will also contribute to the piezoelectricity, as manifested by the quite large dS/dE value.

Figure 4 reveals the temperature dependence of some important properties of the BTS-30BCT ceramic from −50 °C to 60 °C. The coercive field $E_C$ [Fig. 4(a)] and the remnant polarization $Pr$ [Fig. 4(b)] increase while the permittivity $\varepsilon_{33}^T$ [Fig. 4(c)] decreases with decreasing temperature, but they all show anomaly around RT. The electromechanical coupling factor $k_{33}$ [Fig. 4(d)], the elastic compliance constant $s_{33}^E$ [Fig. 4(e)], and the piezoelectric constant $d_{33}$ [Fig. 4(f)] are optimal around RT and they decrease with deviation from RT (the phase boundary regime). (The $d_{33}$ obtained by resonance method is usually smaller than the value by $d_{33}$ meter due to the difference in measurement frequency.)[11,18] Similar evolution of these functional properties with temperature have also been observed in BZT-$x$BCT system.[11] Although high piezoelectricity can be obtained in both BTS-$x$BCT and BZT-$x$BCT systems at RT, the temperature sensitivity will largely restrict their applications. Comparing with the best performed PZT system, the reason of such high temperature sensitivity lies in that the phase boundaries in these two Pb-free systems are obviously tilted.

Then, it is meaningful to discuss how to shape the phase boundary into a vertical one with good temperature reliability. Comparing with the phase boundary in BZT-$x$BCT system,[9] the one in BTS-$x$BCT system is more curved. It is found that the same T terminal BCT of the two systems has $T_C$ of 120 °C. The R terminal BZT has $T_C$ about 50 °C, while the BTS has $T_C$ around 30 °C. Apparently, the $T_C$ of BZT terminal is closer to the $T_C$ of BCT terminal, giving rise to a comparatively vertical phase boundary. It, thus, seems that comparable $T_C$ of T and R terminals would lead to a vertical phase boundary. On the other hand, our preliminary data have shown that while keeping the T terminal unchanged, just by increasing the Sn content from 12% to 16% in R terminal, the phase boundary becomes more vertical.[24] It is noted that with increasing Sn content in BTS terminal, the tetragonal and orthorhombic phases are suppressed and the R phase stability increases.[13,14] Thus, increasing the stability of R terminal, to make equal competition between R and T terminals, may be also important for shaping the phase boundary to be vertical. However, increasing the R phase stability in $BaTiO_3$ based systems by doping Sn or Zr often sacrifices the $T_C$, so there exists a balance between the two aspects for the shape of the phase boundary. Based on the recent experimental results, only the above two factors are briefly discussed. However, further systematic investigations are still required to clarify the key factors determining the shape of the phase boundary and to engineer a vertical phase boundary for practical applications.

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[1]B. Jaffe, *Piezoelectric Ceramics* (Academic, India, 1971).
[2]K. Uchino, *Ferroelectric Device* (Marcel Dekker, New York, 2000).
[3]N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolitchnov, A. K. Taganstev, D. V. Taylor, T. Yamada, and S. Streiffer, J. Appl. Phys. **100**, 051606 (2006).
[4]T. R. Shrout and S. Zhang, J. Electroceram. **19**, 113 (2007).
[5]T. Takenaka, H. Nagata, and Y. Hiruma, Jpn. J. Appl. Phys. **47**, 3787 (2008).
[6]T. Takenaka, K. Maruyama, and K. Sakata, Jpn. J. Appl. Phys. **30**, 2236 (1991).
[7]Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Nature **432**, 84 (2004).
[8]J. Rödel, W. Jo, K. T. P. Seifert, E.-M. Anton, T. Granzow, and D. Damjanovic, J. Am. Ceram. Soc. **92**, 1153 (2009).
[9]W. Liu and X. Ren, Phys. Rev. Lett. **103**, 257602 (2009).
[10]H. Bao, C. Zhou, D. Xue, J. Gao and X. Ren, J. Phys. D: **43**, 465401 (2010).
[11]D. Xue, Y. Zhou, H. Bao, C. Zhou, J. Gao, and X. Ren, J. Appl. Phys. **109**, 054110 (2011).
[12]D. Damjanovic, Appl. Phys. Lett. **97**, 062906 (2010).
[13]N. Baskaran and H. Chang, J. Mater. Sci.: Mater. Electron. **12**, 527 (2001).
[14]C. Lei, A. A. Bokov, and Z. G. Ye, J. Appl. Phys. **101**, 084105 (2007).
[15]T. Mitsui and W. B. Westphal, Phys. Rev. **124**, 1354 (1961).
[16]T. Y. Koo and S. W. Cheong, Appl. Phys. Lett. **80**, 4205 (2002).
[17]E. K. H. Salje, *Phase Transitions in Ferroelastic and Co-Elastic Crystals* (Cambridge University Press, Cambridge, 1990).
[18]S. J. Zhang, E. F. Alberta, R. E. Eitel, C. A. Randall, and T. R. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **52**, 2131 (2005).
[19]B. Noheda, D. E. Cox, G. Shirane, J. Gao, and Z. G. Ye, Phys. Rev. B **66**, 054104 (2002).
[20]D. E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, and Y. Yamada, Appl. Phys. Lett. **79**, 400 (2001).
[21]S. Zhang, R. Xia, T. R. Shrout, G. Zang and J. Wang, J. Appl. Phys. **100**, 104108 (2006).
[22]H. Guo, A. A. Bokov, and Z.-G. Ye, Phys. Rev. B **81**, 024114 (2010).
[23]F. Li, S. Zhang, Z. Xu, X. Wei, J. Luo, and T. R. Shrout, Appl. Phys. Lett. **96**, 192903 (2010).
[24]D. Xue, Y. Zhou, and X. Ren (unpublished)