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A comparison between tetragonal-rhombohedral and tetragonal-orthorhombic phase boundaries on piezoelectricity enhancement

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Abstract – We made a detailed comparison of physical properties between the tetragonal-rhombohedral (T-R) phase boundary (in the $Ba(SnTi)O_3-x(BaCa)TiO_3$ system) and the tetragonal-orthorhombic (T-O) phase boundary (in the $Ba(Sn_xTi_{1-x})O_3$ system). The contrasting results suggest that the T-R phase boundary enhances the piezoelectricity more significantly than the T-O phase boundary. Such difference is considered to stem from the dissimilar anisotropy for polarization rotation, the different elastic softening and the different domain wall contribution between T-R and T-O phase boundaries.

Piezoelectric materials polarize electrically in proportion to an applied stress; conversely, they undergo strains in proportion to an applied electric field [1,2]. Such electromechanical responses lead to many applications ranging from sensors to actuators [2–4]. High piezoelectric properties, which related to polarization change, are always expected [3–5]. In pursuing materials with high piezoelectric coefficients, one important approach is to utilize the instability of polarization state at phase transition boundaries, where a significant polarization variation under external stress or electric field can be achieved [6–8].

Two types of phase boundaries are widely utilized in searching for high piezoelectricity, *i.e.*, the tetragonal-orthorhombic (T-O) phase boundary and the tetragonal-rhombohedral (T-R) phase boundary [9,10]. The T-O phase boundary is known as a transition region between ferroelectric tetragonal and orthorhombic phases in the composition-temperature phase diagram. Such kind of phase boundary can be found in pure $BaTiO_3$ system and various $(K,Na)NbO_3$ based solid solutions [11,12]. Similarly, the T-R phase boundary is a transition region between ferroelectric tetragonal and rhombohedral phases. Almost all the high-performance Pb-based systems like PZT [13], PMN-PT [14] and PZN-PT [15] possess the T-R phase boundaries. Some newly reported Pb-free systems, such as $Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-xBCT) [16–19], $Ba(Sn_{0.12}Ti_{0.88})O_3-x(Ba_{0.7}Ca_{0.3})O_3$ (BTS-xBCT) [20], and $Ba(Hf_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ (BHT-xBCT) [21] are also characterized by such a T-R phase boundary between R (BZT, BTS, BHT side) and T (BCT side). Interestingly, in most cases the T-R transition system involves a cubic-tetragonal-rhombohedral (C-T-R) triple point, while the T-O transition system does not. For the T-R transition system, the R symmetry ($R3m$) and T symmetry ($P4mm$) do not have group sub-group relation, and the R and T phases share the same paraelectric cubic (C) phase in the compositional phase diagram [22,23]. Thus a C-T-R triple point can be found in T-R transition systems, like the newly reported $BaTiO_3$ based systems (it is a tricritical point simultaneously) [16–21] and the Pb-based PZT [13], PMN-PT [14], PZN-PT [15] systems (yet whether it is a tricritical point still needs experimental verification) [24]. For the T-O transition system, the O symmetry ($Amm2$) is the sub-group of T symmetry ($P4mm$) and the high-symmetry T phase is usually the parent of low symmetry O phase [3,4,23]. Thus such triple point is rare in T-O transition systems.

Both the T-O and T-R phase boundaries have been shown to induce the instability with respect to the

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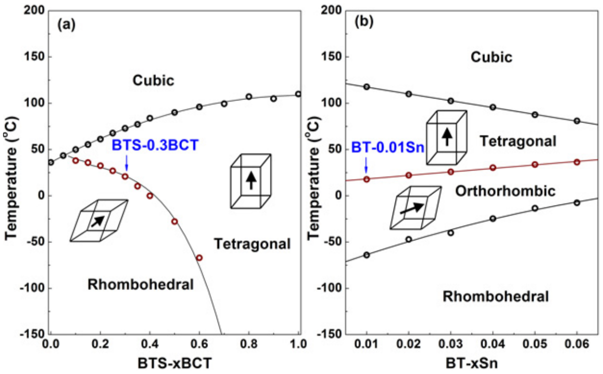

Fig. 1: (Colour on-line) (a) The phase diagram of BTS-xBCT system as proposed in ref. [20], showing a T-R phase boundary. (b) The phase diagram of BT-xSn system, showing a T-O phase boundary.

polarization rotation from Landau theory [5,17] and consequently to enhance the piezoelectric properties [6–10,17–21]. However, it seems that the systems possessing T-R phase boundary show higher piezoelectric properties (typically have $d_{33} \sim 300$–$600\,\mathrm{pC/N}$) than those possessing T-O phase boundary ($d_{33} \sim 50$–$300\,\mathrm{pC/N}$ in most cases) [10,17]. It is then of interest to clarify why there exists such obvious difference between these two kinds of phase boundaries in enhancing piezoelectricity, since both of them can facilitate polarization change by phase instability.

Therefore, in the present study, we try to pursue the reason for such divergence on piezoelectricity enhancement. In order to make a meaningful comparison, it is better that the T-O and T-R transition occurs in similar systems and at a similar temperature. We chose a T-R phase boundary in the newly reported BTS-xBCT system (fig. 1(a)) [20] and a T-O phase boundary in the terminal compound $\mathrm{Ba(Sn}_x\mathrm{Ti}_{1-x})\mathrm{O}_3$ (hereafter abbreviated as BT-xSn) (fig. 1(b)) [25]. The BT-0.01Sn has a T-O transition at 23.8 °C, being close to the T-R transition temperature (22.9 °C) in BTS-0.3BCT. We found that the T-R and T-O phase boundaries indeed yield quite different piezoelectricity. By comparing the physical properties related with polarization change, elastic softening and microstructures between BTS-0.3BCT and BT-0.01Sn, the possible origin of such contrasting behaviors in enhancing piezoelectricity have been discussed.

All samples were fabricated by a conventional solid-state reaction method with starting chemicals of $\mathrm{BaCO_3}$ (99.95%), $\mathrm{CaCO_3}$ (99.9%), $\mathrm{SnO_2}$ (99.9%) and $\mathrm{TiO_2}$ (99.9%). The BTS-xBCT samples were calcined at 1350 °C, and sintered at 1450 °C in air. The BT-xSn samples were calcined at 1150 °C and sintered at 1400 °C in air. The dielectric properties were evaluated by HIOKI3532 LCR meter at 1 kHz and ferroelectric hysteresis loops were measured with a ferroelectric tester at 10 Hz. The piezoelectric constant d_{33} was measured by commercial Berlingcourt-type d_{33} meter for poled samples with cylindrical shape. The unipolar electro-strain was measured with poled disk-shaped samples by MTI 2000 photonic sensor under an electric field of 500 V/mm. Samples for the elastic constant component S_{33}^{E} measurement were poled under an electric field of 800 V/mm and the frequency spectra were measured by a HIOKI 3532–50 LCR meter. Multi-frequency dynamic mechanical analysis (DMA) measurement was carried out by TA Q800 to record the elastic modulus as a function of temperature at 0.2, 1, 4, 10 Hz. Samples were measured in a three-point bending mode with constant displacement amplitude of $5\,\mu\mathrm{m}$ and the cooling rate was 2 K/min. Transmission electron microscopy (TEM) observation was done to identify the microscopic structures.

Figure 1 shows that, at room temperature (23 °C), the BTS-0.3BCT sample locates right at its T-R phase boundary, while the BT-0.01Sn sample is at its T-O phase boundary. However, the piezoelectric coefficient d_{33} of BT-0.01Sn shows a value of 145 pC/N at room temperature, which is much lower than that of BTS-0.3BCT (530 pC/N) [20]. Such a contrast between T-O and T-R phase boundaries is consistent with the report in the literature [10]. In order to clarify why there exists such large divergence between these two kinds of phase boundaries on enhancing piezoelectricity, we then made a detailed comparison by measuring the physical properties related with polarization change, elastic softening and microstructures.

Firstly, we compared the physical properties associated with polarization change between T-R (BTS-0.3BCT) and T-O (BT-0.01Sn) phase boundaries, shown in fig. 2. The dielectric permittivity *vs.* temperature and dielectric loss *vs.* temperature curves of BTS-0.3BCT are shown in fig. 1(a), and those of BT-0.01Sn are presented in fig. 2(b). It is found that the dielectric permittivity of BTS-0.3BCT is about twice that of BT-0.01Sn, indicating the T-R phase boundary is much "softer" than the T-O phase boundary with respect to polarization change under small electric field. Figure 2(c) shows the polarization (P)-electric field (E) hysteresis loops of the two systems. One can see that their coercive field E_{c}, spontaneous polarization P_{m} and remnant polarization P_{r} are almost the same. Such similar ferroelectric properties indicate that the two phase boundaries respond equally to large electric field. The most contrasting results are shown in fig. 2(d): BTS-0.3BCT (after poling) exhibits almost three times larger electro-strain (0.041%) than BT-0.01Sn (0.012%), under the same electric field of 500V/mm. The larger electro-strain reveals that the crystal lattice at T-R phase boundary can respond to the external electric field more easily than that at T-O phase boundary. We will show later that such large difference in lattice softening contribute to the contrasting piezoelectric performances of these two systems.

Secondly, we compared the elastic modulus of the two samples. The elastic modulus *vs.* temperature curves of BTS-0.3BCT and BT-0.01Sn are presented in fig. 3. In

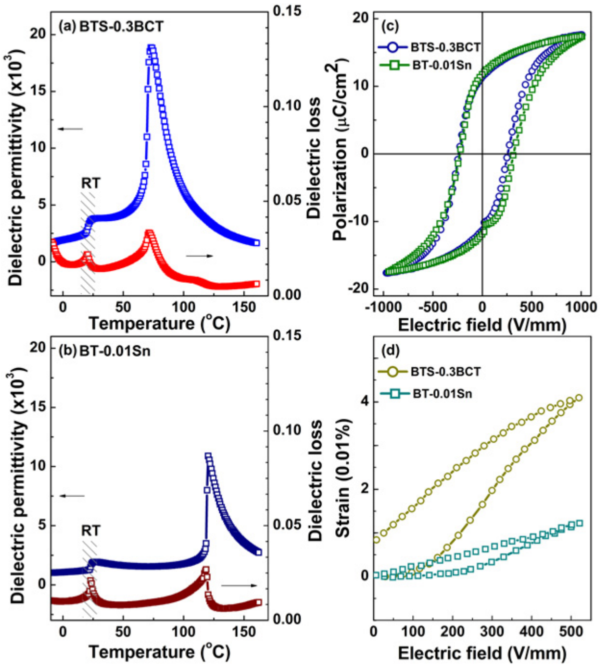

Fig. 2: (Colour on-line) (a) and (b) Dielectric permittivity and dielectric loss *vs.* temperature curves for BTS-0.3BCT and BT-0.01Sn, respectively. For comparison the two figures are in the same scale. RT represents the room temperature (23 °C). (c) Room temperature P-E hysteresis loops of BTS-0.3BCT and BT-0.01Sn. (d) Room temperature electric field induced strain of BTS-0.3BCT and BT-0.01Sn.

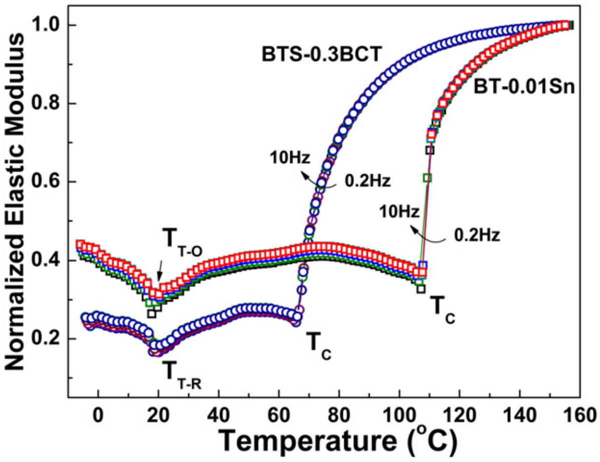

Fig. 3: (Colour on-line) Elastic modulus of BTS-0.3BCT and BT-0.01Sn, which are normalized by their corresponding elastic modulus at 150 °C, respectively. The elastic modulus is recorded for multi-frequencies, 0.2 Hz, 1 Hz, 4 Hz, 10 Hz.

order to compare the lattice softening during the transitions, the elastic modulus of the two systems is normalized by their own elastic modulus value at 150 °C, respectively. As can be seen in fig. 3, the phase transitions, including cubic to tetragonal, T-O and T-R, are all characterized by a dip of elastic modulus. The elastic modulus of BTS-0.3BCT at T-R phase boundary drops about 75%, while that of BT-0.01Sn at T-O phase boundary drops about 60%, comparing with the elastic modulus of paraelectric phase. It seems the elastic softening in BTS-0.3BCT is more significant than that in BT-0.01Sn. We further determined the elastic compliance component S_{33}^{E} by the resonant method (see details in refs. [16,26]), which contributes to the piezoelectric coefficient d_{33} directly [26]. The S_{33}^{E} of BTS-0.3BCT and BT-0.01Sn at room temperature is $14.7 \times 10^{-12}\,\mathrm{m^2/N}$ and $13.0 \times 10^{-12}\,\mathrm{m^2/N}$, respectively. These results suggests the crystal lattice at T-R phase boundary is elastically softer than that at T-O phase boundary, which indispensably contributes to the higher piezoelectricity at T-R phase boundary.

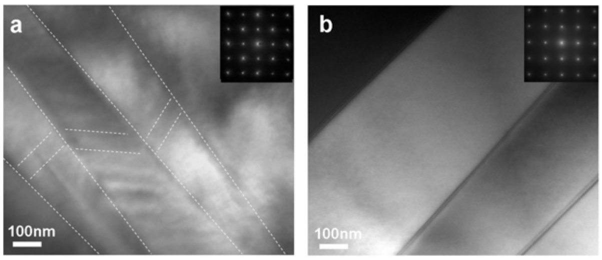

Fig. 4: Bright field domain morphology of (a) BTS-0.3BCT and (b) BT-0.01Sn, obtained from the [100] incidence.

Thirdly, we compared the microstructures of the two samples by TEM. Figure 4(a) reveals one typical domain morphology of BTS-0.3BCT, obtained from the [100] incidence. It is characterized by a number of microdomains with an average width of 40–50 nm. Such morphology is similar to the so-called hierarchical domain structure, and has been observed in several Pb-based systems within T-R phase boundary, such as PMN-PT [27], La-doped PZT [28] and also the newly reported Pb-free system BZT-xBCT [29]. Figure 4(b) shows the typical domain morphology of BT-0.01Sn obtained from the [100] incidence as well. Being different from BTS-0.3BCT, it is composed of large ferroelectric domains and the domain width is around 350 nm. Such domain morphology is similar to the typical ones in ferroelectric materials, such as $BaTiO_3$ [30]. In addition, we found that the domains in BTS-0.3BCT are easily broken up by the electron beam during TEM observation; on the contrary, the domains in BT-0.01Sn are much more stable under the electron beam of TEM.

Several typical properties of BTS-0.3BCT and BT-0.01Sn ceramics are summarized in table 1. BTS-0.3BCT exhibits much higher dielectric permittivity (ϵ) and piezoelectric coefficient (d_{33} and $\mathrm{d}S/\mathrm{d}E$). Moreover, the crystal lattice of BTS-0.3BCT is elastically softer (S_{33}^{E}). Ferroelectric properties under high external field (the coercive field E_{c}, spontaneous polarization P_{m} and remnant polarization P_{r}) are almost the same for the two systems. As will be discussed in the following, such a detailed comparison will enable us to clarify why T-R phase boundary exhibits higher piezoelectric performance than T-O phase boundary.

Table 1: Typical ferroelectric, dielectric, piezoelectric and elastic properties of BTS-0.3BCT and BT-0.01Sn.

Material	$T_{\text{T-O}}/T_{\text{T-R}}$ (°C)	ϵ (ϵ_0)	$P_{\max}$ (μC/cm^2)	P_{r} (μC/cm^2)	E_{c} (V/mm)	d_{33} (pC/N)	dS/dE (pC/N)	$\epsilon_{\max}$ (ϵ_0)	S_{33}^{E} (m^2/N)
BT-0.01Sn	23.8	1900	17.8	10.8	280	145	244	10900	13.0×10^{-12}
BTS-0.3BCT	22.9	3800	18.0	10.6	248	530	820	18800	14.7×10^{-12}

The reason why the present BTS-0.3BCT exhibits much better piezoelectric properties than the BT-0.01Sn can be understood through both the intrinsic effect (polarization rotation and polarization extension) [8,16,17] and the extrinsic effect (contribution from domain wall and interphase boundary motion) [31]. From recent theoretical models [17,32–36], the symmetry-adapted Landau polynomial with respect to the magnitude of polarization P and its direction (unit vector $\mathbf{n}$), is given by

$$F(x,T,n,P)=A(x,T)P^2+B(x,n)P^4+C(x,n)P^6. \quad (1)$$

The T-R phase boundary in BTS-xBCT system starts from a tricritical triple point [20]. It is known that at the tricritical triple point the phase transition becomes continuous [17,37]. The continuous nature of the transition at tricritical triple point requires the fourth-order term coefficient $B(x,\ n)$ equal to zero, which results in a vanishing energy barrier for polarization rotation between the $\langle 001\rangle_{\text{T}}$ state and the $\langle 111\rangle_{\text{R}}$ state. Further deviation from the triple point along the T-R phase boundary line to room temperature results in very weak polarization anisotropy and thus only slight increase of the energy barrier between $\langle 001\rangle_{\text{T}}$ and $\langle 111\rangle_{\text{R}}$ polarization states. Such weak anisotropy and low energy barrier still enables an easy polarization rotation and thus gives rise to high dielectric and piezoelectric properties. On the other hand, eq. (1) is also valid for the T-O phase boundary as the polarization direction vector $\mathbf{n}$ could be either $\langle 001\rangle_{\text{T}}$ or $\langle 110\rangle_{\text{O}}$. Thermodynamically the T-O phase transition is a discontinuous first-order transition, where the fourth order-term coefficient $B(x,\ n)$ is not equal to zero. This results in a fairly larger energy barrier (compared with that of T-R phase boundary) between the two polarization states (T and O) at the phase boundary. As a result, the piezoelectric enhancement is not as large as that at T-R phase boundary. It should be noted that the T-O phase boundary definitely enhance piezoelectric properties by the instability with respect to polarization rotation [5], but the property enhancement is not as significant as that at T-R phase boundary.

The significantly lower anisotropy at T-R phase boundary compared with that at T-O phase boundary is supported by two set of experimental results. One is the different domain morphology between BTS-0.3BCT (T-R) and BT-xBS (T-O) in fig. 4. Nearly vanishing polarization anisotropy makes the domain wall energy rather low. As a result, the domain size is minimized and the domains are unstable under the electron beam of TEM. On the contrary, the larger polarization anisotropy makes the domain wall energy larger and gives rises to big ferroelectric domains, which are more stable under electron beam of TEM [29]. The other is the contrasting enhancement of dielectric permittivity at T-O and T-R phase boundaries. As shown in table 1, the room temperature permittivity of BTS-0.3BCT is twice that of BT-0.01Sn. The nearly vanishing anisotropy in a certain energy profile plane (determined by axis $\langle 111\rangle_{\text{R}}$ and $\langle 001\rangle_{\text{T}}$) makes the polarization change quite easy. As a consequence, the dielectric permittivity is enhanced significantly. In contrast, the large anisotropy makes the polarization change difficult and then the dielectric permittivity cannot be much enhanced. The piezoelectric strain coefficient, d_{ij}, can be derived using the following equation:

$$d_{ij}=(k_{ij}^2\varepsilon_{ii}s_{jj})^{0.5}, \quad (2)$$

where k_{ij} is the electromechanical coupling factor, ϵ_{ii} is the component of dielectric permittivity, and s_{jj} is the component of elastic compliance [26]. Thus the twice difference in dielectric permittivity between T-R and T-O phase boundaries will result in obviously different piezoelectric performance.

As the BTS-0.3BCT has a lower T_{c} than BT-0.01Sn, the polarization extension will also contribute to the dielectric permittivity, due to the proximity of T-R phase boundary to the Curie temperature. However, the polarization extension does not determine the difference between BTS-0.3BCT and BT-0.01Sn dominantly. One may compare the dielectric permittivity at the same temperature deviation from T_{c} for the two systems: the dielectric permittivity at 23 °C (about $T_{\text{c}}-40\,^\circ$C) for BTS-0.3BCT (3800) is still twice that at 80 °C (about $T_{\text{c}}-40\,^\circ$C) for BT-0.01Sn (1600).

Besides the intrinsic effect (polarization rotation and polarization extension) discussed above, the contribution from domain wall motion also plays an important role. As shown in fig. 4, BTS-0.3BCT (T-R) involves more complex domain structure and smaller domain size, comparing with BT-0.01Sn (T-O). According to the classical domain theory, domain size (D) reflects the domain wall energy (F_{DW}) through $D\propto\sqrt{F_{\text{DW}}}$ [23]. Thus, BTS-0.3BCT has smaller domain wall energy than BT-0.01Sn. As a result, the domain wall at T-R phase boundary in BTS-0.3BCT can respond to the external electric field more easily than that at T-O phase boundary in BT-0.01Sn. This will also give rise to the contrasting piezoelectric properties between T-R and T-O phase boundaries.

In addition, although the present T-R phase boundary does not involve the monoclinic (M) phase [20], investigations on PMN-PT, PZN-PT, PZT have shown the presence of M symmetry linked T and R at the phase boundary [38,39]. The low-symmetry M phase at the T-R phase boundary can enable the polarization vector rotate more easily within the monoclinic plane and also result in a more complex domain structure than that at the T-O phase boundary [40]. This will lead to superior piezoelectric properties at the T-R phase boundary than the T-O phase boundary [31]. Therefore, the existence of low symmetry M phase at T-R phase boundary can also contribute to the divergence between these two phase boundaries.

Recent theoretical studies based on Landau-Devonshire modeling [32,35,36] have shown that the elastic softening of the material in a certain direction will enhance the piezoelectricity as well. An elastically softer system corresponds to a larger elastic compliance. As shown in table 1, the elastic compliance S_{33}^{E} for T-R phase boundary composition is larger than that of T-O phase boundary. According to eq. (2), the larger elastic compliance S_{33}^{E} will enable higher piezoelectric coefficient d_{33}. Thus, the crystal lattice softening also contributes the high piezoelectric performance of T-R phase boundary as well.

It should be noted that, despite the obvious difference in piezoelectric properties, the ferroelectric properties (E_{c}, P_{m} and P_{r}) at T-R phase boundary are not much superior to those at T-O phase boundary. One possible reason is that although the energy barrier for polarization rotation at T-R phase boundary is significantly smaller than that at T-O phase boundary with respect to a small exciting field, their difference is negligible when under large electrical field during ferroelectric testing.

In summary, the reason why T-R phase boundary is superior to T-O phase boundary in piezoelectricity enhancement mainly stems from the lower polarization anisotropy, higher domain wall contribution and stronger lattice softening at T-R phase boundary compared with those at T-O phase boundary. These factors take effects simultaneously to give rise to the divergence between T-R and T-O phase boundary.

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