

Review

# Prospective of (BaCa)(ZrTi)O<sub>3</sub> Lead-free Piezoelectric Ceramics

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**Abstract:** Piezoelectric ceramics is a functional material that can convert mechanical energy into electrical energy and vice versa. It can find wide applications ranging from our daily life to high-end techniques and dominates a billion-dollar market. For half a century, the working horse of the field has been the polycrystalline PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> (PZT), which is now globally resisted for containing the toxic element lead. In 2009, our group discovered a non-Pb piezoelectric material, (BaCa)(ZrTi)O<sub>3</sub> ceramics (BZT-BCT), which exhibits an ultrahigh piezoelectric coefficient  $d_{33}$  of 560–620 pC/N. This result brought extensive interest in the research field and important consequences for the piezoelectric industry that has relied on PZT. In the present paper, we review the recent progress, both experimental and theoretical, in the BZT-BCT ceramics.

**Keywords:** piezoelectric; ceramic; lead-free

## 1. Introduction

Piezoelectricity refers to the phenomenon of interconversion between mechanical energy and electrical energy, which yields a mechanical-stress-induced polarization or an electrical-field-induced strain. Such ability of energy conversion enables piezoelectric materials to be widely used in devices such as sensors, actuators, transducers, etc. [1,2]. For more than half a century, Pb-based piezoelectric ceramics (e.g. PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>, PbMg<sub>x</sub>Nb<sub>1-x</sub>-PbTiO<sub>3</sub> and PbZn<sub>x</sub>Nb<sub>1-x</sub>-PbTiO<sub>3</sub>) have dominated the area of most applications. However, the use of Pb-based materials is restricted by increasingly tight regulations due to its high toxicity [3,4]. This arouses extensive investigations on the mechanism of high piezoelectricity in Pb-based materials and the exploration of Pb substitutes [5–8].

In 2009, a large piezoelectric performance with  $d_{33}$  of 620 pC/N was observed for 0.5Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub>-0.5(Ba<sub>0.7</sub>Ca<sub>0.3</sub>)TiO<sub>3</sub> composites (BZT-50BCT) [9]. Later, the modified BZT-BCT composite ceramics showed a higher  $T_c \sim 114$  °C than BZT-0.53BCT [10]. By optimizing the poling conditions, BZT-BCT ceramics combines a large piezoelectric performance with  $d_{33}$  of 630 pC/N and the planar electromechanical factor of 56% [11]. Yang et al. prepared the lead-free BZT-BCT ceramics by sol-gel technique [12], whose maximum permittivity was above 9000 with a maximum converse piezoelectric coefficient ( $d_{33}^*$ ) of 400 pm/V.

In this review, we summarize the recent progresses on BZT-BCT piezoelectric ceramics by different doping mechanisms that may offer some thoughts on the future improvement of BZT-BCT and even other piezoelectric ceramics. Further, the potential application of BZT-BCT ceramics are presented, including electrocaloric effect, fluorescence and energy storage. Based on the current achievements, we also propose some prospects, which may provide new directions on the development of BZT-BCT ceramics.

## 2. MPB Strategy

In both Pb-based and Pb-free piezoelectric systems, the common solution to promote piezoelectric performance is to place materials at their phase transition boundaries, either a paraelectric to ferroelectric phase boundary or multi ferroelectric phases coexisting boundary (including the most famous morphotropic phase boundary, i.e. MPB), since the instability of the polarization at phase boundaries allows a significant polarization variation under an external stress or electric field. Despite the intense interests in the phase coexisting strategy, the key to understanding the consequent high piezoelectricity in BZT-*x*BCT ceramics is still in dispute. For instance, we initially proposed the coexistence of tetragonal (T) and rhombohedral (R) symmetry at MPB, evidenced by the synchrotron X-ray diffraction (XRD) results from Ehmke [13] and transmission electron microscope (TEM) results from Gao [14]; however, soon after, the discovery of an intermediate orthorhombic (O) phase was found based on synchrotron XRD results from Keeble [15,16] and temperature spectrum of dielectric permittivity from Damjanovic [17].

In addition, the phenomenological Landau–Devonshire model suggests that the reduction of polarization anisotropy is responsible for enhanced piezoelectric response approaching to MPB [18,19]. Acosta calculated the anisotropy energy of a sixth-order Landau potential formulated for the BZT-*x*BCT system and found that the anisotropy energy approaches zero near the O-R rather than the T-O phase boundary. They thus attributed the best piezoelectric property found at the T-O phase boundary to two other factors, i.e., higher degree of poling and increased elastic softening [20]. Ke used the energy barrier along the minimum energy pathway on the free energy surface for direct domain switching to quantitatively measure the degree of polarization anisotropy and suggested that the polarization anisotropy at the T-O phase boundary was the smallest [21].

In most MPB systems (e.g., PMN-PT and PZN-PT), MPB is temperature dependent, similar to the BZT-BCT system, but this does not render such systems useless. Many important applications of this system have been found. The widely used solution to achieve temperature stability is to choose a composition slightly away from the MPB, so that the properties are no longer sensitive over the ambient temperature range. However, this is at the expenses of a slight reduction of piezoelectric properties. It is the same situation in the BZT-BCT ceramics. As shown in Figure 1, by choosing BZT-45BCT, a composition slightly off MPB composition (50BCT),  $d_{33}$  becomes almost temperature independent in the room temperature range (20–40 °C). This temperature stability is achieved with some sacrifices of  $d_{33}$ , but the  $d_{33}$  (~360 pC/N) is still much higher than many other non-Pb piezoelectric materials.

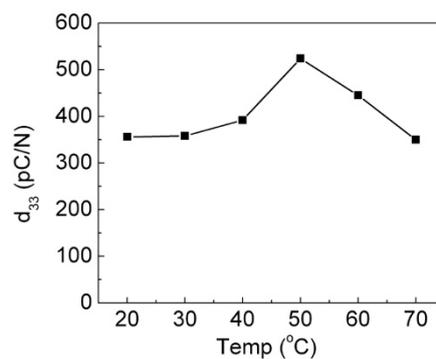


Figure 1. Temperature dependence of  $d_{33}$  of BZT-45BCT.

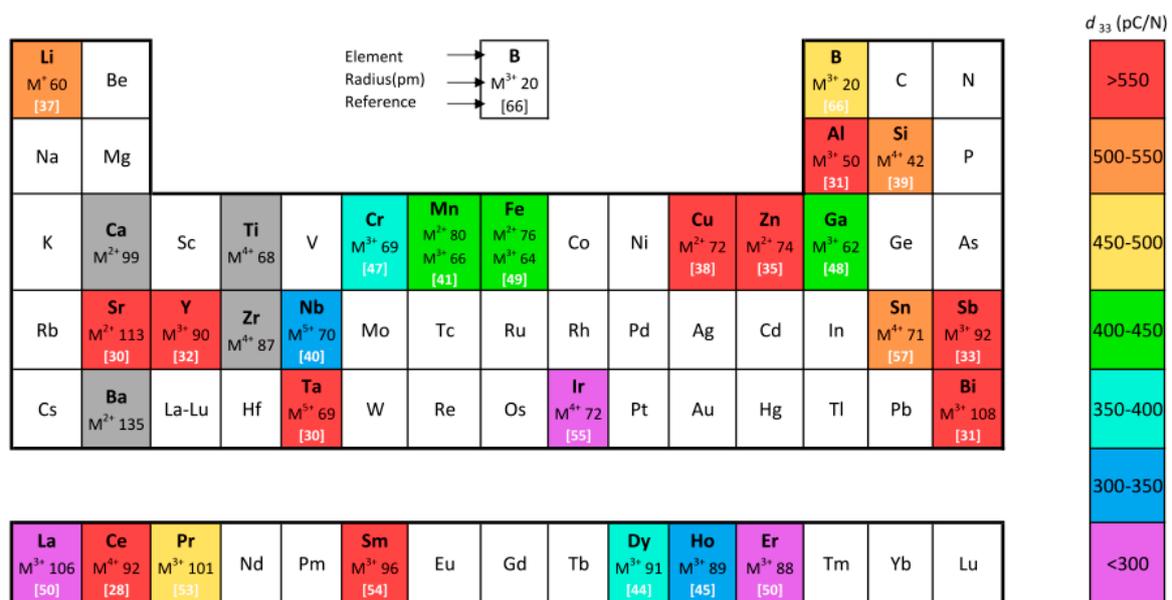
## 3. Approach to Tailor the Piezoelectric Performance of BZT-BCT

The chemical modification is the most efficient and widely accepted way to tailor the piezoelectric performance of piezoceramics. Table 1 summarizes the most attractive achievements of both pure BZT-BCT ceramic and doped ceramics. Based on the mechanism of chemical modification, the composition optimization can be categorized into improving microstructure by sintering aids and

substitution doping, and the most improved piezoelectric performances of each doping element can be found in Figure 2.

**Table 1.** Piezoelectric performance of the BZT-BCT based ceramics.

Compositions	$d_{33}$ (pC/N)	$k_p$	$\epsilon_r$	$T_c$ (°C)	Reference
BZT-50BCT	650	53%	4500	85	[22]
	630	56%		90	[11]
	620		3060	93	[23]
	572	57%	4821	94.8	[24]
	546	65%	4050		[25]
	464		2938		[26]
BZT-50BCT-0.08 wt% ZnO	603				[27]
BZT-50BCT-0.04 wt% CeO <sub>2</sub>	600	51%	4843		[28]
BZT-50BCT-0.1 wt% CeO <sub>2</sub>	565	52%	3860		[29]
BZT-50BCT-0.2 wt% Sr(Cu <sub>1/3</sub> Ta <sub>2/3</sub> )O <sub>3</sub>	577	#####		97	[30]
99.2 mol% (BZT-50BCT)-0.8 mol% BiAlO <sub>3</sub>	568	54%	3375	72	[31]
BZT-50BCT-0.06 wt% Y <sub>2</sub> O <sub>3</sub>	560	53%		95	[32]
BZT-50BCT-0.1% Sb <sub>2</sub> O <sub>3</sub>	556	52%	3985		[33]
(Ba <sub>0.82</sub> Sr <sub>0.03</sub> Ca <sub>0.15</sub> )(Zr <sub>0.1</sub> Ti <sub>0.9</sub> )O <sub>3</sub>	534	#####		84	[34]
BZT-50BCT-0.06 mol% ZnO	521	#####			[35]
BZT-50BCT-1 mol% Sn-1 mol% Sr	514	#####			[36]
BZT-50BCT-0.3 wt% Li <sub>2</sub> CO <sub>3</sub>	512	49%	4394	79.6	[37]
BZT-50BCT-0.04 wt% CuO	510	45%	3762	95	[38]
BZT-50BCT-0.5 mol% SiO <sub>2</sub>	500				[39]



**Figure 2.** Piezoelectric coefficient ( $d_{33}$ ) of the point-defects modified BZT-BCT ceramics.

### 3.1. Substitution Doping

Ferroelectrics are rarely used in a chemically pure form and doping is always employed with the goal of tailoring the properties for specific applications. Different doping usually brings about different consequence, such as acceptor doping to obtain low dielectric losses and donor doping to achieve high piezoelectric coefficients. For the equivalent doping, it is usually employed to modify

the Curie temperature and introduce the compositional disorder, which may also greatly affect the piezoelectric performance. As shown in Figure 2, the radius of  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  are 135 pm and 99 pm, respectively, while  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  are 68 pm and 87 pm, respectively. Usually, large ions will occupy the A-site, and small ions will occupy the B-site, and intermediate ions will occupy both sites with different ratios of the perovskite structure.

### 3.1.1. Acceptor Doping

An acceptor dopant has a lower oxidation number than that of the host cation. This will create oxygen vacancies owing to the charge compensation, and the oxygen vacancies can contribute to the mass transport and improve the density during sintering process [27,35,40].

$\text{Zn}^{2+}$  has a radius of 74 pm and prefers to replace smaller ions in B-site. JG Wu pointed out that the  $\text{Zn}^{2+}$  substitution into the  $(\text{Ti}, \text{Zr})^{4+}$  site results in both structure disorder and lattice distortion. The presence of oxygen vacancies helps the mass transport during sintering, which is responsible for the enhanced grain growth as the ZnO content increases. Besides, the tricritical point of these ceramics was shifted to room temperature while the Curie temperature decreased simultaneously by the introduction of ZnO. Macroscopically, the BZT-BCT ceramics have  $\epsilon_r \sim 4500$  and  $\tan\delta < 1.5\%$ . BZT-BCT ceramic with 0.06 mol.% ZnO demonstrates an enhanced electrical behavior with  $d_{33} \sim 521$  pC/N,  $k_p \sim 47.8\%$ , and  $2P_r \sim 19.37 \mu\text{C}/\text{cm}^2$ , owing to the room-temperature tricritical point induced by doping with ZnO [35]. Similar results were also reported by Zhao [27]. In Zhao's work, the BZT-BCT ceramics with 0.08 wt% ZnO show maximum remnant polarization and spontaneous polarization ( $P_r = 10.14 \mu\text{C}/\text{cm}^2$ ,  $P_s = 19.68 \mu\text{C}/\text{cm}^2$ ). At the same time, the giant piezoelectric coefficient of  $d_{33} = 603$  pC/N and high planar electromechanical coupling factor of  $k_p = 0.56$  were also obtained for the samples. Besides, they revealed that further raising ZnO content would cause partial  $\text{Zn}^{2+}$  ions occupying A-site, resulting in decrease in lattice parameters. Consequently, excessive  $\text{Zn}^{2+}$  are effective in reducing the poling state and in depressing the domain switching of BCZT- $x$ Zn ceramics; thus, they degrade the dielectric, ferroelectric and piezoelectric properties.

Mn as an interesting impurity exhibits multivalence states ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$ ), and has been extensively used to substitute the A- and/or B-site ions of ferroelectrics for tailoring electrical properties [41]. Typically, it manifests itself as  $\text{Mn}^{2+}$  when sintering at high temperature above 850 °C. Meng et al. reported that the addition of 0.25 mol%  $\text{MnO}_2$  promotes grain growth, improves the ferroelectricity of the ceramics and strengthens ferroelectric tetragonal-ferroelectric orthorhombic phase transition near 40 °C [42]. Such ceramics exhibit the optimum piezoelectric properties ( $d_{33} = 306$  pC/N and  $k_p = 42.2\%$ , respectively). Excess  $\text{MnO}_2$  inhibits the grain growth and degrades the ferroelectric and piezoelectric properties of the ceramics. Wu et al. reported similar results: the 0.15 wt% MnO doped BZT-BCT ceramics have optimum electrical properties:  $d_{33} = 382$  pC/N,  $k_p = 44.5\%$ ,  $\epsilon_r = 2611$ , and  $\tan\delta = 0.63\%$ . Besides, they also observed the double hysteresis loop when MnO dopant exceeds 0.3 wt%, which indicates the reversible domain switching dominating by the acceptor defect dipoles [43].

### 3.1.2. Donor Doping

A donor dopant has a higher oxidation number than that of the host cation. This will create cationic vacancies, either A-site or B-site vacancies in the perovskite structure. The donor dopant may effectively reduce the Curie temperature and facilitate the domain switching behavior, characterized as slim hysteresis loops with small coercive field and hysteresis loss.

Li et al. reported that, with the introduction of the donor Dy at A-site, the BZT-BCT ceramics possessed improved temperature stability. Besides the high piezoelectric coefficient of  $d_{33} = 366$  pC/N and planar electromechanical coupling factor of  $k_p = 43.0\%$ , the Dy-doped BZT-BCT ceramics exhibited stable electromechanical coupling coefficients over a common usage temperature range of 20–100 °C [44]. They also revealed similar results in Ho-doped BZT-BCT ceramics [45].

As another common donor dopant to A-site,  $\text{La}^{3+}$  is often employed to enhance the electrical or mechanical responses under small AC field while reducing the loss in ferroelectric ceramics. Sun et al. reported that a small amount of  $\text{La}^{3+}$  (~0.15%) resulted in an increase of  $d_{33}$  at 50 °C due to the coexistence of orthorhombic and tetragonal phases. Besides, the 0.15 mol% La doped BZT-BCT ceramics turned to the semi-conductor and showed positive temperature coefficient (PTC) behavior [46]. Other donor dopants such as  $\text{Cr}^{3+}$  and  $\text{Ga}^{3+}$  also showed excellent improvements of  $d_{33}$  [47,48].

Besides the mono-element doped ceramics, compound doped BZT-BCT are also investigated. Wu et al. investigated the  $\text{BiFeO}_3$  doped BZT-BCT ceramics [49]. Here,  $\text{Bi}^{3+}$  acted as the donor dopant at A-site while  $\text{Fe}^{3+}$  as the acceptor at B-site. By addition of  $\text{BiFeO}_3$ , the grain size becomes smaller, and these ceramics become denser. The 0.2 mol%  $\text{BiFeO}_3$  doped BZT-BCT ceramics demonstrated an improved piezoelectric behavior ( $d_{33} \sim 405$  pC/N and  $k_p \sim 0.44$ ). Tian et al. added  $\text{Er}^{3+}$  and  $\text{La}^{3+}$  into the BZT-BCT ceramics and found  $\text{Er}^{3+}$  first substituted A sites and then B sites in the matrix of  $\text{ABO}_3$  structure. The elevated piezoelectric constant ( $d_{33} \sim 200$  pC/N) and receded mechanical quality factor ( $Q_m \sim 70$ ) at with 0.12%  $\text{La}^{3+}$  doping and 0.2%  $\text{Er}^{3+}$  doping showed “softening effect” by donor doping [50].

Extensive studies with other donor dopants were also carried on the BZT-BCT ceramics [30,51–54], as shown in Figure 2.

### 3.1.3. Equivalent Doping

Researchers have tried other doping with equivalent valence as the A-site or B-site to achieve MPB in the  $\text{BaTiO}_3$  ceramics [55–60]. Zhou et al. designed a new Pb-free piezoelectric system  $\text{Ba}(\text{Hf}_{0.2}\text{Ti}_{0.8})\text{O}_3-(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ , which yields high piezoelectricity with  $d_{33} \sim 550$  pC/N, comparable to that of the best Pb-based material PZT-5H ( $d_{33} \sim 590$  pC/N). Besides, their study suggests the non-isotropy of polarization at triple point by precise detection of transitional thermal hysteresis. Previously, the isotropy at triple point was always taken as the basic assumption in related modeling work and understanding [56]. Xue et al. designed a similar Pb-free pseudo-binary system,  $\text{Ba}(\text{Sn}_{0.12}\text{Ti}_{0.88})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{O}_3$ , characterized by a phase boundary starting from a critical triple point of a paraelectric cubic phase, ferroelectric rhombohedral, and tetragonal phases [57]. The optimal composition BTS-30BCT exhibits a high piezoelectric coefficient  $d_{33} = 530$  pC/N at room temperature.

For the equivalent doping of A-site, one of the most typical substitution is  $\text{Sr}^{2+}$ , which can contribute to the microstructure by increasing grain size and density, and at the same time decrease  $T_c$  [34,36,58,59]. As a result of fine microstructure and lower  $T_c$ , excellent piezoelectric properties with large  $d_{33}$  of 534 pC/N was exhibited in Bai and Li's work when 0.03 mol  $\text{Sr}^{2+}$  was doped [34].  $\text{Sn}^{4+}$  is another commonly used element locating at B-site to enhance the piezoelectric properties of lead-free piezoelectric ceramics, especially in BT based ceramics [57,60]. In Ding and Liu's work, the co-doping of  $\text{Sn}^{4+}$  and  $\text{Sr}^{2+}$  could lead to good piezoelectrical properties of  $d_{33} = 514$  pC/N and  $k_p = 52.62\%$ , although smaller grain size was obtained comparing with pure BZT-BCT ceramics, which is different from many other dopants that usually enhance the grain growth with low content [36].

### 3.2. Grain Size Effect and Sintering Aids

It is well known that grain size can have a significant influence on the properties of ferroelectric ceramics. For BZT-BCT based ceramics, the benefits to  $d_{33}$  from large grain size are extremely obvious, as shown in Figure 2. Elements acting as sintering aids such as Ce, Cu, Si, Li, etc. present brilliant performance. As the grain size decreased to the micron level, the permittivity at room temperature increased. The increase in permittivity can be understood in terms of the twinning behavior of polycrystals with decreasing grain size [61].

Hao et al. fabricated various BZT-50BCT ceramics with different grain size ranging from 0.4 to 32  $\mu\text{m}$ . As grain size decreases, the diffuse phase transition behavior is enhanced. As the grains grow up to more than 10  $\mu\text{m}$ , samples exhibit good piezoelectric properties with  $k_p > 0.48$ ,

$k_t > 0.46$ ,  $d_{33} > 470$  pC/N, and  $d_{33}^* > 950$  pm/V. Besides, the increasing grain size effectively enhances the resistance to thermal depolarization [62].

In application, sintering aids are usually employed to enlarge the grain size and modify the microstructure to lower the sintering temperature and at the same time enhance the performance [28,29,37,63,64]. SiO<sub>2</sub>, Li<sup>+</sup>, and CuO are widely used as the sintering aid of ceramics and exhibited good contributions in BZT-BCT system. In Chen's work, the dopant of Li<sup>+</sup> reduced the sintering temperature of BZT-50BCT from 1540°C to 1400°C and piezoelectric performance with  $d_{33} = 512$  pC/N and  $k_p = 49\%$  were obtained [37]. In the work of co-doping of CeO<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub>, adding of Li<sub>2</sub>CO<sub>3</sub> could largely decrease the sintering temperature from 1450°C to 1050°C comparing with the composition of CeO<sub>2</sub> dopant only [29]. Liu systematically studied the effect of SiO<sub>2</sub> dopant on the dielectric, ferroelectric and piezoelectric properties of the BZT-50BCT ceramics sintered at different temperatures and the results show that doping of SiO<sub>2</sub> could enhance  $P_r$  and  $d_{33}$  while reducing  $E_c$ . They obtained  $d_{33}$  of 500 pC/N [39,65]. CuO was also found to be effective on decreasing sintering temperature and modifying the microstructure of BZT-BCT ceramics, thus enhanced piezoelectric properties were achieved due to the large grain size caused by CuO [30,46,54]. The co-doping of CuO and B<sub>2</sub>O<sub>3</sub> can largely benefit the morphology and enhance the piezoelectric properties [66]. Besides, some other substitution doping elements can also contribute to the sintering process at the same time such as Zn and Mn. In Wu's work, the grain size of ZnO doped BZT-BCT ceramic increased and surface morphologies became denser with the help of ZnO [35]. Similarly, MnO could also help sintering process greatly and benefit the piezoelectric performance [43,67].

#### 4. For other Applications

It is well accepted that the easy polarization extension and rotation mechanism (low energy barriers for polarization variation) are the two most important intrinsic factors contributing to the enhanced physical properties [68,69]. Besides the good piezoelectric performance, BZT-BCT also exhibits other good properties due to its easy polarization rotation and easy domain wall motion.

##### 4.1. Electrocaloric Effect

Electrocaloric effect (ECE) is a phenomenon that the change in adiabatic temperature and/or entropy of a dielectric material is induced by the application and removal of an electric field due to the change in the dipolar state of the material. In general, the ECE is parameterized by the adiabatic temperature change ( $\Delta T$ ), and the electrocaloric efficiency ( $\Delta T/\Delta E$ ). The main technical challenge in lead-free ferroelectric bulk materials is to generate a giant electrocaloric temperature change  $\Delta T$  under a relatively low electric field [70].

BZT-BCT has attracted much attention due to its relatively low coercive field and large polarization. Besides, the low Curie temperature also benefits the applications at room temperature. Sanliarp et al. reported that 0.65BZT-0.35BCT ceramics exhibited a  $\Delta T$  of 0.33 °C and  $\Delta T/\Delta E$  of 0.165 K mm kV<sup>-1</sup> at 65 °C under an electric field change  $\Delta E = 20$  kV/cm [71]. G. Singha et al. reported large ECE in BZT-BCT ceramics [72]. They revealed that BZT-0.8BCT possessed an electro-caloric coefficient as high as 0.253 K mm/kV near tetragonal-to-cubic phase transition. They ascribed the high ECE to the higher polarization flexibility. Wang et al. performed direct measurements for BZT-BCT ceramics in non-adiabatic and non-equilibrium conditions. They found that BZT-0.7BCT showed the maximal ECE temperature change ( $\Delta T_{ECE}$ ) of 0.55 K was recorded for an applied field of 40 kV/cm at  $T = 85$  °C [73]. Besides the good performance, they also revealed a very large discrepancy between the indirectly estimated and the directly measured  $\Delta T_{ECE}$ . This was attributed to non-adiabatic conditions of the experiment resulting in a heat exchange with the environment.

##### 4.2. Fluorescence

In recent years, ferroelectrics doped with rare earth elements have attracted great attention owing to their excellent multifunctional properties [74,75]. Multi-property coupling among the presence

of an electric field, mechanical stress and photons can introduce many applications as piezoelectric ceramics, mechano-luminescence and electro-luminescence materials. Peng Du et al. investigated the fluorescence intensity ratio of green up conversion emissions at 525 and 550 nm in the temperature range of 200–443 K for Er-doped BZT-BCT ceramics. The maximum sensing sensitivity and temperature resolution were found to be  $0.0044 \text{ K}^{-1}$  and 0.4 K, respectively, suggesting that Er-doped 0.5BZT-0.5BCT ferroelectric ceramic possesses potential application in optical temperature sensing [52,76].

Jiang Wu et al. reported that 0.5 mol%  $\text{Er}^{3+}$  BZT-BCT ceramics, synthesized via a sol-gel synthesis route and a ceramic sintering process, possessed excellent photoluminescence performance, which is sensitive to compositional changes [52]. The morphotropic phase boundary composition exhibited the maximum photoluminescence peak intensity at 550 nm.

### 4.3. Energy Storage

In theory, the energy density  $J$  corresponds to relative permittivity and dielectric breakdown strength (BDS) according to the definition  $J = 1/2\varepsilon_0\varepsilon_r E_{\text{max}}^2$ . For high energy storage density, ferroelectrics are expected to possess large saturated polarization, small remnant polarization and high BDS. BZT-BCT ceramics have evoked much interest. For certain compositions, this system exhibits large permittivity of 8400, triple that of pure  $\text{BaTiO}_3$  ceramics. For the  $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ -rich compositions, this system gradually transforms to the relaxor ferroelectrics, which exhibit diffusion phase transition with broadened permittivity peaks and slim ferroelectric hysteresis loops of large maximum polarization and small remnant polarization. These characteristics may favor the high energy density applications. Venkata et al. reported a significant increase in the permittivity with relatively low dielectric losses in the Zr-rich BZT-BCT ceramics [77].  $x\text{BZT-BCT}$  ( $x = 0.10, 0.15, 0.20$ ) ceramics exhibited the electric breakdown strength as 134–170 kV/cm and high permittivity of 5200–8400. The consequent energy storage density can even reach  $0.98 \text{ J/cm}^3$ . Besides the pure ceramics form, the addition of glass may effectively enhance the BDS and consequently promote energy storage density [77]. Liu et al. employed glass addition  $\text{BaO-SrO-TiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-BaF}_2$  into BZT-0.15BCT ceramics, which exhibited a large permittivity of 3458 at 25 °C under 1 kHz, slim hysteresis loop with the maximum polarization of  $12.53 \mu\text{C/cm}^2$  and a remnant polarization of  $4.05 \mu\text{C/cm}^2$  [78]. Microstructural observation indicated that the average grain size reduced significantly with increasing the glass concentration. Macroscopically, the glass ceramics exhibited diffusion phase transition with reduced peak permittivity but broad peak with relatively large permittivity of around 1000 within the room temperature region. Meanwhile the electrical breakdown strength (BDS) of the glass modified ceramics was nearly quadruple to the pure ceramics form. Energy storage performance of the glass modified ceramics, both  $419.4 \text{ kJ/m}^3$  calculated from the product of permittivity and square of BDS and  $192.8 \text{ kJ/m}^3$  from the integration of the hysteresis loop under the electric field of 9.6 kV/mm, showed significant superiority to that of the pure ceramic form [78]. Besides, they explored the mechanism for the enhanced energy storage property by thermal stimulated current measurements, which may reveal both polarization and charge transport process [79].

## 5. Future prospects

### 5.1. Soft or Hard Modifications on BZT-BCT Ceramics

Ferroelectrics are rarely used in a chemically pure form and doping is always employed with the goal of tailoring the properties for specific applications. Most doping effects can be categorized into “hard” and “soft” effect. “Hard” effects are obtained by acceptor doping. The defect dipoles (acceptor-oxygen vacancy) can stabilize the domain structure (no matter the volume effect or the pinning effect) [80]. As macroscopic consequences, high coercive field, low permittivity and low dielectric losses are obtained. Donor dopants result in “soft” effect, i.e. high dielectric losses, low conductivity, low coercive field and high piezoelectric coefficients [81].

Further research should focus on revealing “soft” and “hard” effects within the MPB region of the present BZT-BCT ceramics. Further, the properties of BZT-BCT ceramics can be tailored to satisfy various applications and reveal the physics behind them.

### 5.2. BZT-BCT in other Forms—Single Crystal and Thin Film

It is common sense in the piezoelectric community that the single crystal always exhibits 3–4 times higher piezoelectric effect than that of a ceramic. Besides the better properties, single crystals can also be considered as standard materials to ascertain the structure properties. However, it is difficult to grow large scale single crystals with the perovskite structures. Thus far, several methods have been employed to generate good BZT-BCT single crystal samples and have not obtained satisfactory results to date [82].

Although intensive research up to date has been inclined to bulk materials, it is certainly obvious that the films will be the focus of the future industry. Since films exhibit small volume but large geometrical flexibility, can be easy for on-chip integration, which is a prerequisite for incorporation into microelectron devices. However, the development of films still lags behind bulk counterparts. For BZT-BCT films, several techniques have been employed, such as PLD, sputtering and CSD. Hereinto, the films fabricated via PLD method exhibited  $d_{33}$  of 60–140 pm/V depending on different orations [83,84]. The study of BZT-BCT film is still deficient. Further property enhancement and functionality enrichment are still the objectives to be pursued.

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