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Comparative study of the effect of domain structures on piezoelectric properties in three typical Pb-free piezoceramics

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Abstract

The effect of domain structures on the piezoelectric properties of three typical lead-free piezoelectric ceramics, $(1-x)Bi_{0.5}Na_{0.5}TiO_3-xBaTiO_3$, $(Na_{0.52}K_{0.48-x})(Nb_{0.95-x}Ta_{0.05})O_3-xLiSbO_3$ and $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$–$0.5(Ba_{0.7}Ca_{0.3})TiO_3$, have been studied by transmission electron microscopy. By adding $BaTiO_3$ in single phase $Bi_{0.5}Na_{0.5}TiO_3$, domain structure changed from irregular domains into submicron lamellar domains and polar nano-regions. While in the later two system, regular submicron domains with nanodomains inside formed, which is an important feature of these two systems. It is suggested that the changes in domain structures in these systems have a dominant effect in the enhancement of the piezoelectric properties, comparing with single phase $Bi_{0.5}Na_{0.5}TiO_3$, $Na_{0.5}K_{0.5}NbO_3$ and $BaTiO_3$.

Keywords: B. Electron microscopy; C. Piezoelectric properties; D. Perovskites

1. Introduction

Environmental concerns with the toxicity of lead in lead-based piezoelectric ceramics represented by $Pb(Zr,Ti)O_3$ (PZT) and the legislative restriction of lead use in electronic devices in the European Union and part of Asia have stimulated intensive search for lead-free piezoelectric materials worldwide [1–3]. In the past decades, extensive studies have been carried out on three typical Pb-free systems, including $(Bi_{1-x}Na_x)TiO_3$-(BNT), $(Na_{1-x}K_x)NbO_3$-(NKN) and $BaTiO_3$-(BT) based systems. The piezoelectric properties of these systems have been significantly enhanced through chemical modification and different processing routes, and some of them get close to and even better than those of PZT systems [4–12]. It is well known that the macroscopic physical properties of ferroelectric materials, such as dielectric, ferroelectric and piezoelectric properties, are closely related to microscopic domain structures. Therefore, intensive studies have been focused on domain structures and the corresponding crystallographic features of PZT and other Pb-based piezoelectric systems, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN-PT). It is found that domain structures of these systems show a common feature: high-piezoelectric-response MPB composition always coincides with a “miniaturized domain structure,” which manifests itself as an “adaptive phase” consisting of nanodomains [13–18]. It should be noted that expression “nanodomains” here loosely refers to the structure of ferroelectric domain walls where separation of adjacent domain walls is on the order of tens of nanometers rather than hundreds of nanometers or more and is different from the definition “polar nanoregions (PNRs)” which are frequently found in relaxor ferroelectrics [19]. PNRs are generally considered as a result of local compositional fluctuations in relaxor ferroelectrics so that the crystal consists of nanosize polar islands which are short-range ordered and embedded into a cubic matrix in which the symmetry remains unchanged [20]. While the formation of nanodomains are due to vanishing of the anisotropy of polarization and a drastic decrease in domain wall energy in ferroelectric solid solutions with morphotropic boundaries [17]. Therefore, a better fundamental understanding of microscopic domain structure and macroscopic property interrelationship is highly important for achieving a further improvement of

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Table 1
Piezoelectric properties of three typical lead-free piezoelectric ceramics.

	BNT	BNT–BT	NKN	NKTN-LSO	BT	BZT-BCT
d_{33} (pC/N)	~98	231	80–160	328	500	620
K_p (%)	48	41	23–40	50	50	56
T_c (°C)	315–337	280	400	320	120	94
Reference	[27]	[6]	[5]	[7]	[10]	[12]

BNT–BT—$0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06BaTiO_3$.
NKTN-LSO—$(Na_{0.52}K_{0.4335})(Nb_{0.9035}Ta_{0.05})O_3$–$0.0465LiSbO_3$.
BZT-BCT—$0.50Ba(Zr_{0.2}Ti_{0.8})TiO_3$–$0.50(Ba_{0.7}Ca_{0.3})TiO_3$.

piezoelectric properties of Pb-free ceramics. Unfortunately, in the past, only the domain structure of BNT-based systems has been studied in detail [4,21–24]. Currently, the outstanding piezoelectric properties of NKN-based system have been mostly attributed to the composition driven phase transitions [7]. Meanwhile, a d_{33} as high as 620 pC/N have been recently reported in one of the BT-based system, $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$–$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) [12]. Moreover, its parent system, $BaTiO_3$ ceramic, has been also reported to have a high d_{33} of >500 pC/N processed by a two-step sintering method [10,11]. Mostly recently, domain structures of the NKN-based and

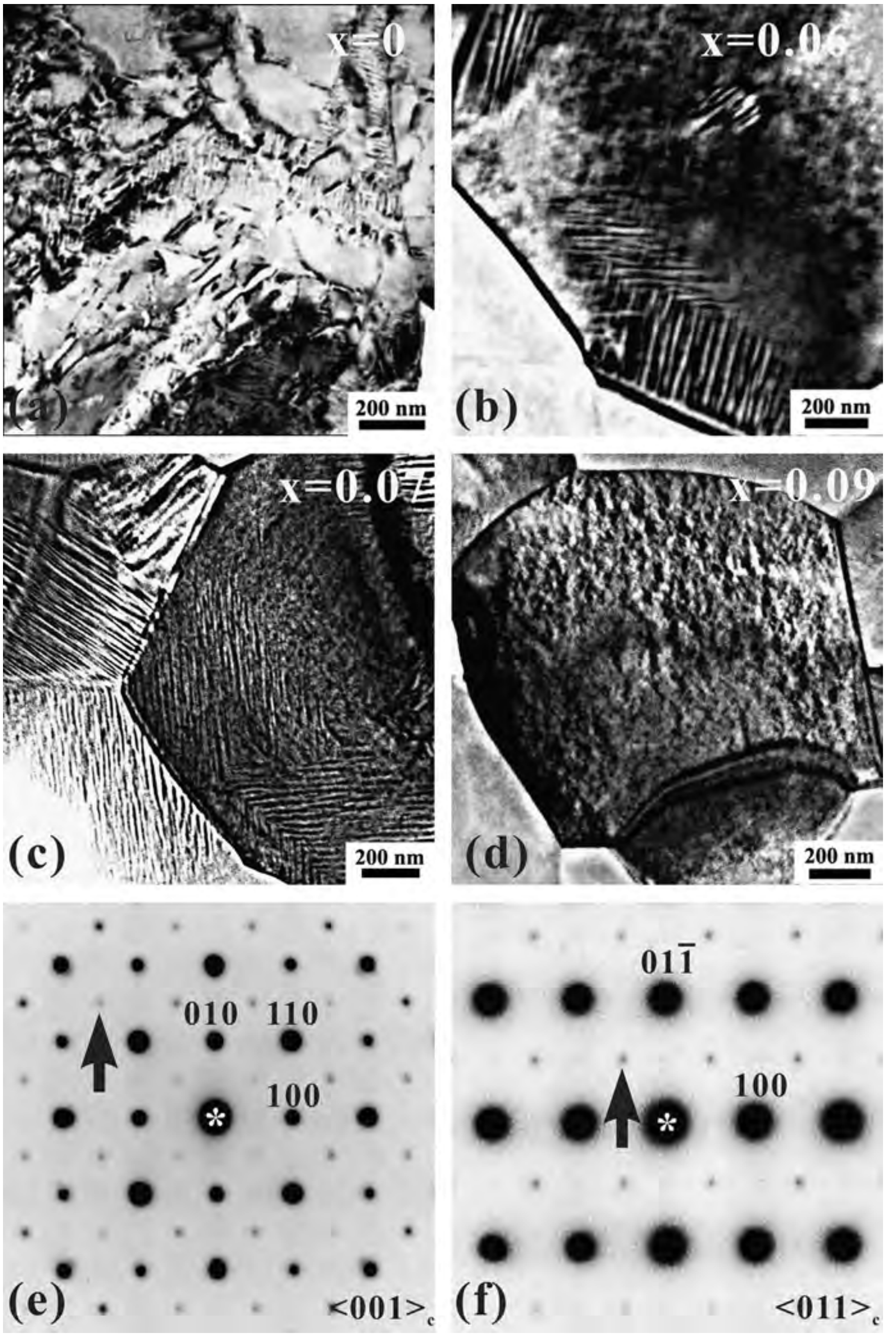

Fig. 1. Bright-field images for various $(1-x)$BNT-xBT compositions: (a) $x=0$, (b) $x=0.06$, (c) $x=0.07$, (d) $x=0.09$, and SAED of 0.94BNT-0.06BT along $\langle 0\,0\,1\rangle_c$ (e) and (f) $\langle 0\,1\,1\rangle_c$ zone axis. Arrows in (e) and (f) indicate the $1/2\langle 1\,1\,0\rangle_c$ and $1/2\langle 1\,1\,1\rangle_c$ superlattice spots, respectively. "*" indicates the transmitted beam.

BT-based system have been investigated by transmission electron microscopy [25,26]. However, comparisons of domain structures are still missing among different Pb-free piezoceramic systems. In this work, a comparative study of the domain structures of the three Pb-free piezoelectric systems was carried out by transmission electron microscopy (TEM). Differences in measured piezoelectric properties among the three systems are discussed in terms of observed different features of domains in corresponding lead-free systems.

2. Experimental procedure

$(1-x)Bi_{0.5}Na_{0.5}TiO_3-xBaTiO_3$ ((1-x)BNT–xBT), $(Na_{0.52}K_{0.48-x})(Nb_{0.95-x}Ta_{0.05})O_3-xLiSbO_3$ (NKTN-xLSO) and $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$–$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) ceramics were fabricated by a conventional solid-state reaction method. The specimens for TEM studies were prepared from bulk samples by mechanical thinning to ~10 μm, followed by ion milling to perforation. All specimens were annealed at 80 °C for at least one day to release the stress induced during preparation. TEM studies were carried out on a Philips CM20 microscope operated at an accelerating voltage of 200 kV. Convergent beam electron diffraction (CBED) patterns were recorded at 120 kV.

3. Results and discussion

Table 1 lists the best piezoelectric properties of the three lead-free piezoelectric ceramic systems, comparing with those of pure BNT, NKN and BT ceramics. Clearly, a significant improvement of piezoelectric properties can be found in the modified systems comparing with their single phase counterparts. This improvement will be related to the domain structure in different systems as analyzed blow.

Fig. 1 shows a series of TEM bright field images revealing the change in the domain structure with the addition of BT and selected area electron diffraction (SAED) patterns along $\langle 0\,0\,1\rangle_c$ and $\langle 0\,1\,1\rangle_c$ zone axis from the MPB BNT–BT with $x=0.06$. Single phase BNT with $x=0$ has an irregular or dirty domain structure (Fig. 1(a)), while the BNT–BT with $x=0.06$ and 0.07 near MPB shows a combination domain structure of PNRs and fine lamellar domains (Fig. 1(b) and (c)). With a further increase of BT concentration, $x=0.09$, PNRs become the dominant domain structure, which is a typical domain contrast of relaxor ferroelectrics (Fig. 1(d)) [28]. These results are quite consistent to the results reported by Ma et al. recently [29], and indicate that the addition of BT has a significant impact on domain structure in the BNT–BT system, which will correspondingly affect the macroscopic properties of the lead-free ceramics. In addition, crystal structure of the MPB BNT–BT ceramic with $x=0.06$ was

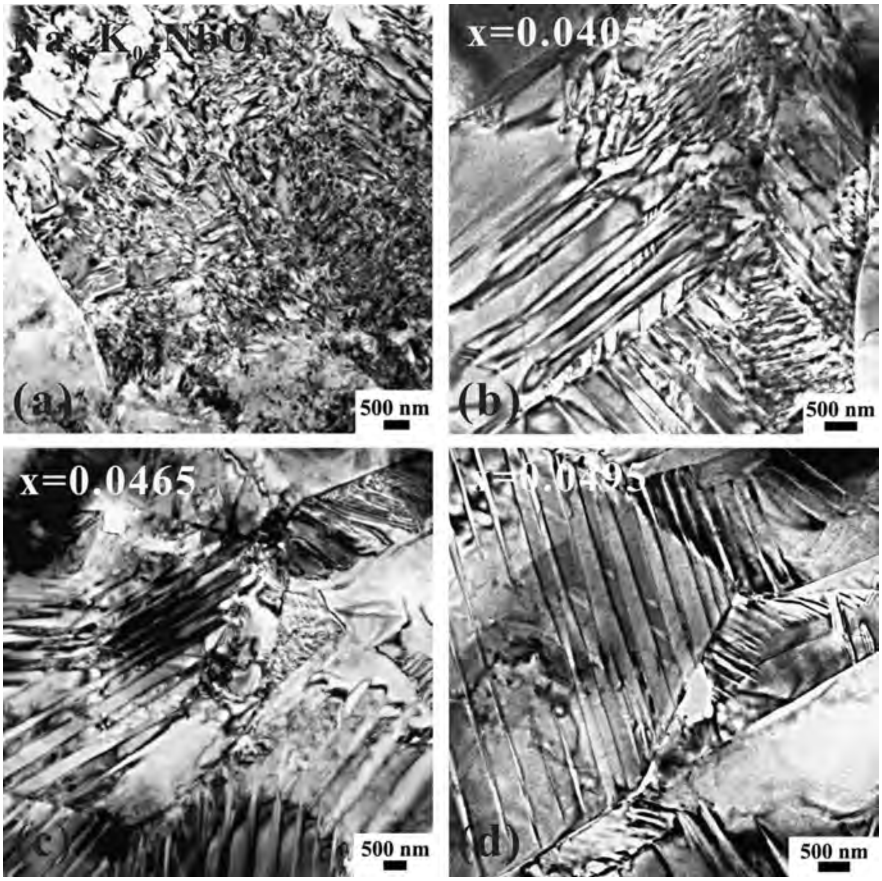

Fig. 2. Bright-field images for various NKTN-xLSO compositions: (a) $Na_{0.5}K_{0.5}NbO_3$, (b) $x=0.0405$, (c) $x=0.0465$, (d) $x=0.0495$.

further studied by SAED patterns along $\langle 0\,0\,1\rangle_c$ and $\langle 0\,1\,1\rangle_c$ zone axis, as shown in Fig. 1(e) and (f). It has been well founded and accepted that two types of oxygen octahedral tilting exist in polar ferroelectric phases, low temperature $R3c$ phase and high temperature $P4bm$ phase, of pure BNT [30], which can be described as $a^-a^-a^-$ and $a^0a^0c^+$ tilt systems after the notation of Glazer [31]. The octahedral tilting results in superlattice reflections of the type 1/2{*ooo*} for rhombohedral $R3c$ and 1/2{*ooe*} for tetragonal $P4bm$ [13], where *o* and *e* denote the odd and even Miller indices, respectively. In this case, both superlattice reflections were observed, indicating the coexistence of rhombohedral and tetragonal phases in the BNT–BT ceramics with $x=0.06$.

Fig. 2 shows a series of TEM bright field images revealing the changes in domain structure of NKTN-LSO lead-free piezoelectric ceramics with LSO content (Fig. 2(a)). Similar to pure BNT, very irregular domains are observed in pure NKN. This type of domain becomes less pronounced with the addition of 5 at% Ta and with increased LSO concentration (Fig. 2(b)–(d)). With small amount of LSO adding into NKTN, $x=0.0405$, it can be seen that some submicron lamellar domains with nanodomains inside begin to appear although irregular domains still exist (Fig. 2(b)). When the LSO concentration is increased to $x=0.0465$, submicron lamellar domains with nanodomains inside become the dominant domain structure in the lead-free ceramics (Fig. 2(c)). With further increase of LSO concentration to $x=0.0495$, a typical tetragonal domain

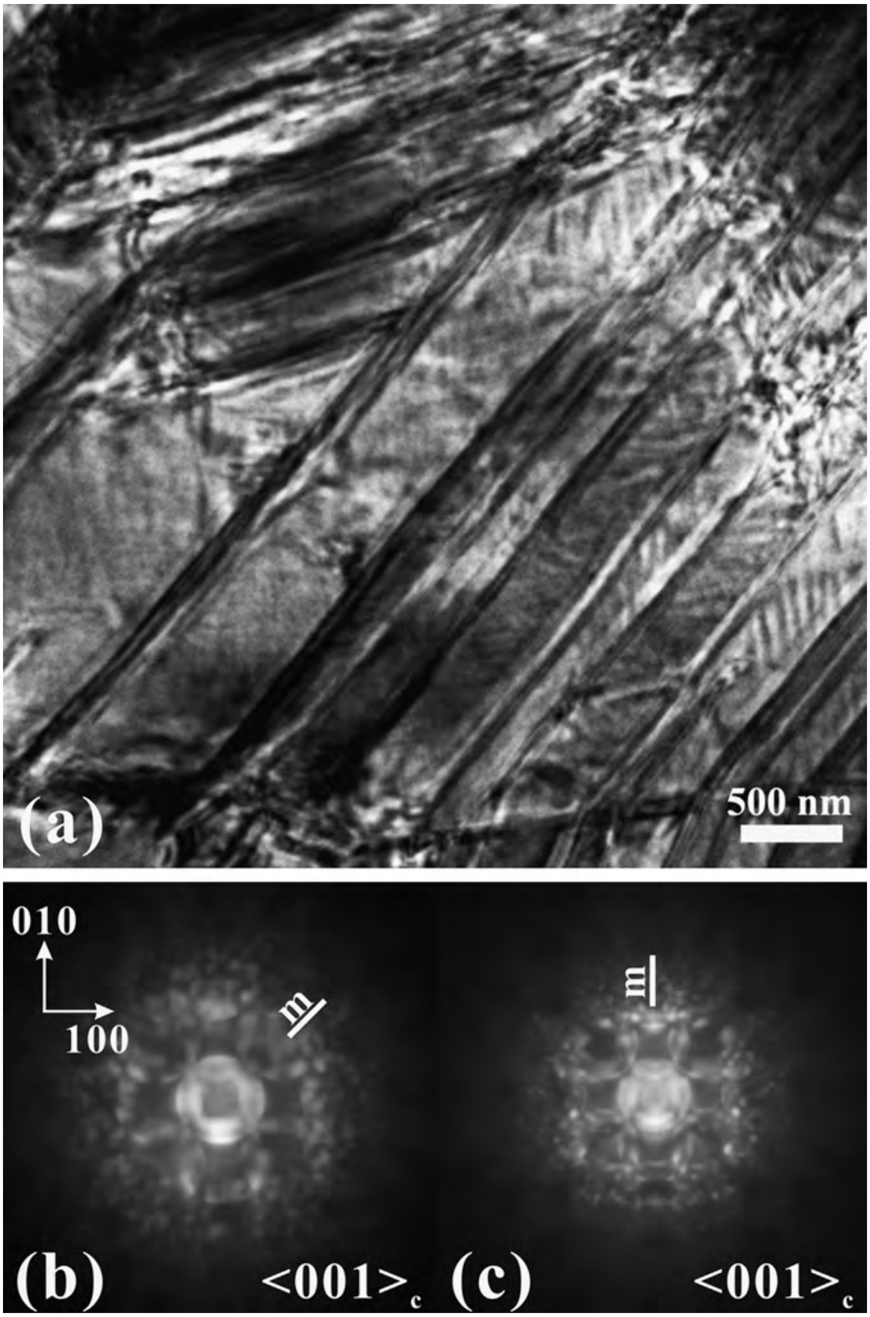

Fig. 3. Bright-field image (a) and $\langle 0\,0\,1\rangle_c$ CBED patterns ((b) and (c)) of NKTN-LSO with $x=0.0465$, which has the largest d_{33} in the NKTN-LSO system.

structure with both 90° and 180° domains can be observed. The results are quite consistent with the x-ray diffraction results in our previous report in which it was revealed that two phase coexistence, orthorhombic and tetragonal phase, was found in NKTN-LSO with $0.0405 \leq x < 0.0495$, while only a single tetragonal phase was found in the NKTN-LSO with $x = 0.0495$ [7]. In this system, NKTN-LSO with $x = 0.0465$ has the best piezoelectric property as shown in Table 1. To investigate the origin of high piezoelectric response, further domain structure of NKTN-LSO with $x = 0.0465$ was studied by bright field image and CBED patterns, as shown in Fig. 3. Micro-domains with nano-domains of ~50 nm in width inside were observed, as shown in Fig. 3(a). This important feature was found in lead-based piezoelectric materials as well, such as PZT ceramics, PMN-PT, and PZN-PT single crystals [13–18], and was attributed to their high piezoelectric coefficient. As mentioned above, NKTN-LSO with x=0.0465 has a coexistence of orthorhombic and tetragonal phase. These phases could be distinguished with CBED within a single nanodomain because they belong to different space group *Bmm*2 and *P*4*mm* thus mirror planes parallel to different directions will be obtains along a given zone axis [15]. Based on this method, the coexistence of orthorhombic and tetragonal phase in individual domains was then confirmed by CBED patterns along pseudocubic $\langle 0\,0\,1\rangle_c$ zone axis, in which a mirror plane parallel to $\langle 1\,1\,0\rangle$ direction in the orthorhombic phase and to $\langle 0\,1\,0\rangle$ direction in the tetragonal phase can be seen in Fig. 3(b) and (c). As a consequence, a high piezoelectric constant can be expected in this composition due to the existence of nanodomains which response to an external electric field more noticeably than microdomains [14] and the coexistence of orthorhombic and tetragonal phase in individual domains.

Fig. 4 shows typical domain structures of BT (a) and BZT-BCT (b)–(d). Pure BT exhibits typical submicron lamellar domains (Fig. 4(a)). Domain structures changes from significantly with addition of Zr and Ca, as shown in Fig. 4(b)–(d). Not only both rhombohedral domains (Fig. 4(b) and (c)) and tetragonal domains (Fig. 4(d)) were observed but also nanodomains with several tens of nanometers inside of submicron lamellar domains, which is very similar to that observed in PZT, PMN-PT, and PZN-PT piezoelectric systems [13–18]. Accordingly, this is believed to be the reason why BZT-BCT shows the best piezoelectric response at room temperature among the three systems compared in this work.

According to the classical theory of ferroelectric domains, the domain size is proportional to the square root of domain wall energy, since domain size is determined by a balance between the energy of domain wall and the energies of electric and elastic fields caused by the spontaneous polarization and strain [32]. Accordingly, the corresponding domains have been miniaturized in MPB regime, as has been observed in the three systems studied in this work. With lowered energy of nano-sized domain walls, the miniaturized domains can be more easily reoriented under external applied electrical field, which leads to strong piezoelectricity.

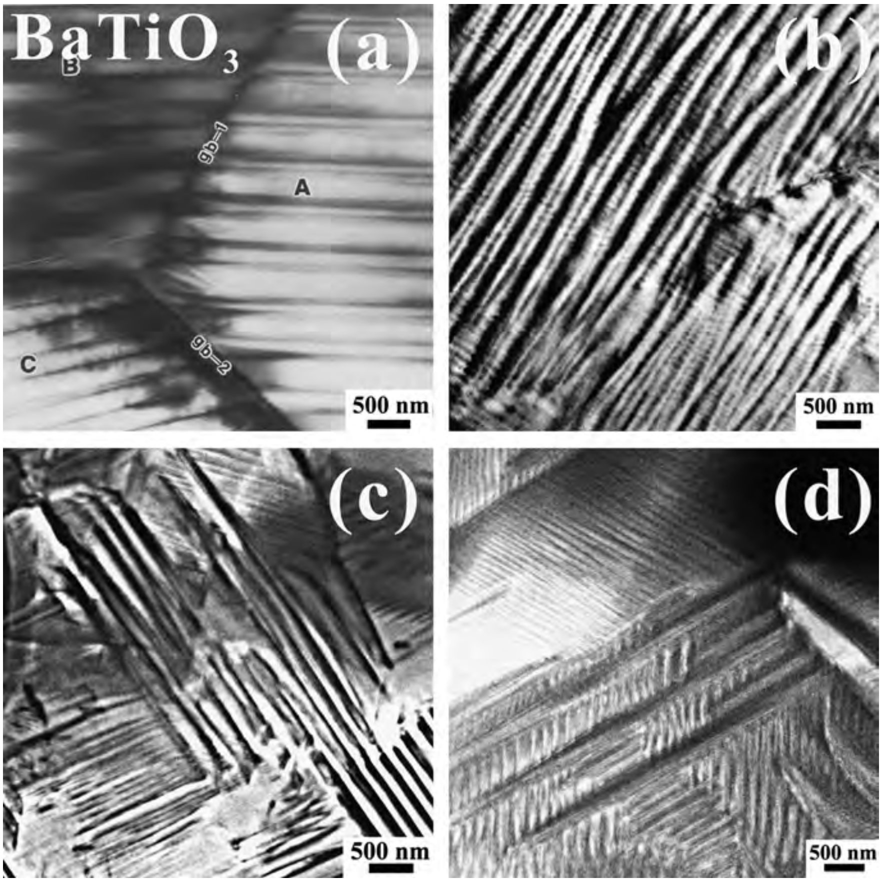

Fig. 4. Bright-field images of BaTiO$_3$ ceramics (a) and of BZT-BCT ((b)–(d)). “gb” in (a) indicates grain boundaries that separate three adjacent grains, A–C.

4. Conclusions

In summary, a systematic study of the effect of domain structure on the piezoelectric properties in three typical lead-free piezoelectric ceramics, BNT–BT, NKTN-LSO, and BZT-BCT, was performed by transmission electron microscopy. For single phase BNT, NKN and BT, irregular or dirty domains exist in the first two and submicron straight lamellar domains in the third. These two kinds of domain features as well as single phase crystal structure make polarization switching process difficult in three pure ceramics. Domain structures in NKTN-LSO and BZT-BCT ceramics were compared as well. A domain miniaturization was found in these two systems when their compositions reach the MPB regime, which contributes to the high piezoelectric response. Regular submicron lamellar domains with nanodomains inside are an important feature of domain configurations in these two Pb-free systems. On the other hand, fine tweed-like and nanodomains were observed in BNT–BT. In addition, at least two phases coexistence were found in all three MPB compositions. Both observed domain features and two phase coexistence facilitate polarization switching process, which result in much strong piezoelectric effect. Among three studied Pb-free systems, observed domain structure in BZT-BCT is very close to that reported in the excellent PZT ceramics, PMN-PT and PZN-PT piezoelectric crystals, which is believed to be the reason why BZT-BCT exhibits the highest piezoelectric response among the three systems studied in this work.

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