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Effect of domains configuration on crystal structure in ferroelectric ceramics as revealed by XRD and dielectric spectrum

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Abstract. It is well known that domains and crystal structure control the physical properties of ferroelectrics. The *ex-situ* electric field-dependent structural study, carried out in unpoled/poled crushed powder and bulk samples for $(Li_{0.5}Nd_{0.5})^{2+}$ modified $0.95Bi_{0.5}Na_{0.5}TiO_3-0.05BaTiO_3$ solid solution, established a correlation between domain configuration and crystal structure variation. Under applying electric field, the smeared ferroelectric phase structure due to coherence diffraction effect of nanodomains reappeared due to obsolescent coherence effect associated with the field-induced ordered nanodomains. The macroscopic characterizing techniques of domain configuration such as dielectric constant spectroscopy and X-ray diffraction measurement can provide a basis for understanding the correlation between domains configuration and crystal structure in ferroelectric ceramics.

Keywords. Electronic ceramics; ferroelectricity; piezoelectricity.

1. Introduction

It is well known that ferroelectric domains and crystal structure control the physical properties of ferroelectrics [1–5]. Therefore, intensive studies have focused on domain structures and the corresponding crystallographic features of ferroelectrics material. It has been long understood that high piezoelectric response of ferroelectrics material can be achieved at the morphotropic phase boundary (MPB) region among two ferroelectric phases in their phase diagrams due to a low polarization anisotropy caused by the phase instability [6,7]. Nevertheless, the exact structure at MPB region is still under controversy with several assumptions like the two-phase states, the single phase and the adaptive phase [7,8].

Studies on domain structure at MPB region in the $PbZrO_3-PbTiO_3$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PMN–PT), $Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PZN–PT) ceramics and Pb-free $Ba(Zr_{0.2}Ti_{0.8})O_3-(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT–BCT) solid solution indicated a common feature of nanodomains [9–12]. It was reported that the diffraction intensity from nanoscale ferroelectric domains coherently superimposed in lattice diffraction due to the coherence effects and thus caused anisotropic broadening, asymmetries, intensity distribution variation between the peaks and even new peaks appeared in diffraction patterns [12]. Therefore, the domain configuration and size play a crucial role in the crystal structure analyses of ferroelectrics.

The traditional crystal structure analyses, domain structure and morphology observation have been conducted by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively [13,14]. However, the microstructure of the domains obtained from TEM in the very thin foil samples may be altered due to sample processing and therefore, the results may not be representative of the bulk ceramics. Furthermore, the local structure obtained from TEM is usually different from the average structure of bulk ceramics due to the heterogeneities feature in polycrystalline ferroelectric ceramics. Meanwhile, it was reported that the domain size was approximately proportional to the specimen thickness and grains size [15–17].

On the other hand, the domain state in powder particle state from XRD measurement should be completely different from that of TEM specimen due to compression and tensile stress, elastic and electric boundary condition [18]. Therefore, a comprehensive understanding of the structure factor of ferroelectric materials would require a characterization of not only structural features in the unpoled powder and bulk samples, but also the structural changes, which accompany the domain state orientation through electrical poling.

The purpose of the present work is to study the influence of domains configuration and size on crystal structure in $(Li_{0.5}Nd_{0.5})^{2+}$ modified $0.94Bi_{0.5}Na_{0.5}TiO_3-0.06BaTiO_3$ ceramics. The *ex-situ* electric field-dependent structural study, carried out in unpoled/poled crushed powder and bulk samples, unambiguously established a direct correlation between domain configuration, size and crystal structure variation. In addition, the results indicated that the macroscopic characterization techniques of domain configuration and size such as dielectric spectroscopy and XRD measurement can provide

a basis for understanding the correlation between domains configuration and crystal structure in ferroelectric ceramics.

2. Experimental

The $0.95(Bi_{0.5}Na_{0.5})_{1-x}(Li_{0.5}Nd_{0.5})_x TiO_3 - 0.05BaTiO_3$ ceramics (BNLN$_x$T–BT5 ($x = 0, 0.03, 0.05, 0.1$) were prepared by conventional solid-state reaction technique and the detailed process was characterized as described elsewhere [19]. The as-prepared ceramics were crushed to fine powders. X-ray diffraction data were collected from D8 Bruker diffractometer using Cu K$_\alpha$ ($\lambda = 1.540598$ Å) radiation from as-prepared ceramics and the crushed powders. After the electrodes were made by printing silver paste, poling was carried out at room temperature in silicone oil by applying a dc electrical field of 50 kV cm^{-1} for 10 min. The poled pellets were then nitric acid etched to remove the electrodes and then crushed to fine powders for collecting diffraction patterns.

3. Results and discussion

Figure 1 shows the typical results of the XRD pattern of BNLN$_x$T–BT5 for as-prepared (unpoled) and poled pellet samples and corresponding powder samples. The first striking difference between unpoled pellet samples and corresponding powder samples with $x \leq 0.05$ is the splitting peaks behaviour at $2\theta = 40°$. The XRD patterns of unpoled powder samples display more obvious splitting peaks than those of unpoled pellet samples, indicating evidently rhombohedral distortion. Compared with powder samples, the internal stress existence in ceramics causes only XRD peaks to broaden or shift. Thus, the influence of internal stress in ceramics on splitting of the diffraction peak can be negligible. It is well known that domains are formed in ferroelectric crystals to minimize the electrostatic energy associated with the spontaneous polarization and the elastic energy due to lattice distortion at the displacive solid–solid transition [16,20–23]. In polycrystalline ceramics, the no-180° ferroelectric domains are also ferroelastic domains [24,25]. The grains and domains are mechanically confined by their neighbouring grains and domains in bulk ceramics. On cooling through Curie temperature, the paraelectric to ferroelectric phase transition is usually associated with a displacive structural transition, accompanied by a relatively large lattice strain and thus internal stresses are caused between grains and domains due to the orientation difference of spontaneous train tensors across the domain wall and grain boundary [26,27]. Thus, the accompanied elastic long-range interactions play a major role in determining both domains morphology and domains growth law in ferroelectric perovskite [25,28,29]. Therefore, the growth or development of ferroelectric domains is clearly suppressed by the clamp effect of the internal stresses in bulk ceramics. After the pellets were crushed into fine powders, the relief internal stresses favour the growth of domains configuration and size,
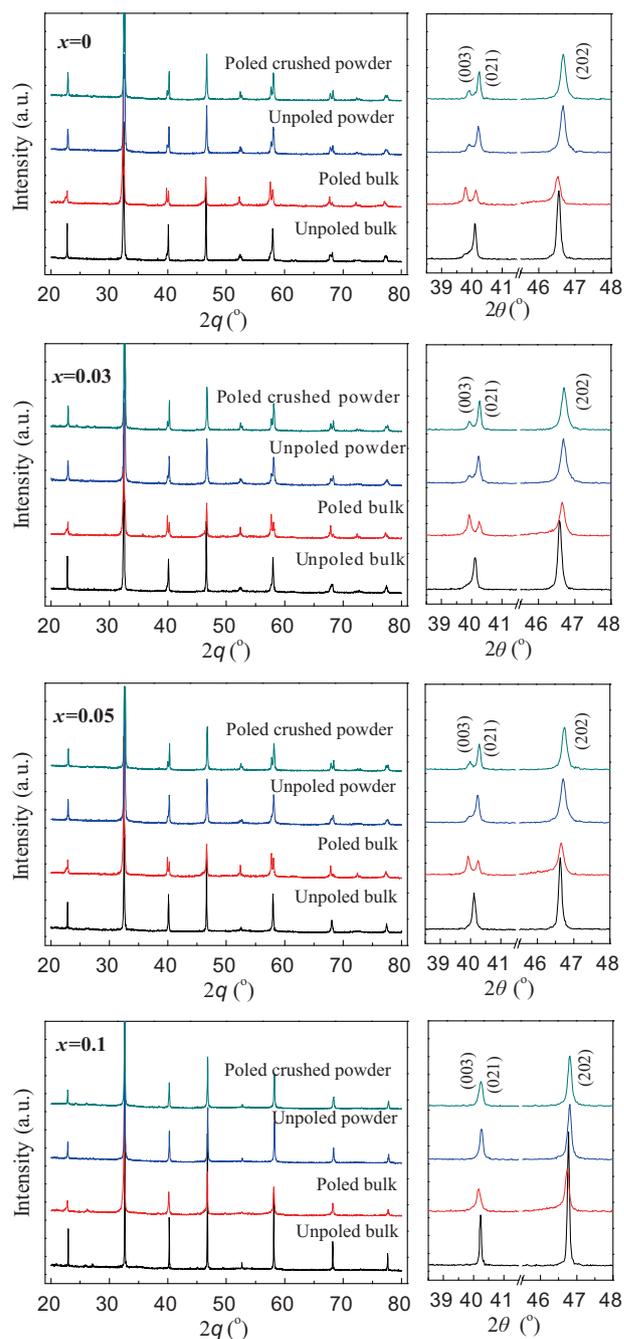

Figure 1. *Ex-situ* X-ray diffraction results from unpoled and poled ceramic/powder specimens for BNLN$_x$T–BT5 ($x = 0, 0.03, 0.05, 0.1$) ceramics.

thus inducing the obvious splitting diffraction peaks due to decreased coherence diffraction effects of nanodomains.

On the other hand, it notes that the mechanical impact due to manual crushing in poled–crushed powder may cause the structural changes. Garg *et al* [30,31] have reported that the structural change induced by mechanical impact was similar to that induced by electrical poling. However, it is clear from figure 1 that the XRD patterns of poled–crushed powder is
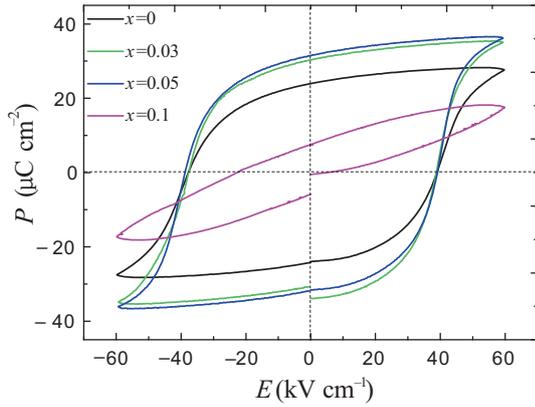
Figure 2. Ferroelectric hysteresis loops for BNLN$_x$T–BT5 ($x = 0, 0.03, 0.05, 0.1$) ceramics.

similar to that of unpoled powder, other than those of both poled ceramics and unpoled bulk when $x \leq 0.05$. The results indicate that the change of XRD splitting peaks in poled–crushed powder should not come from electrical poling. Therefore, the results clearly demonstrate that the domains configuration in ferroelectric ceramics plays a prominent role in the crystal structure.

Moreover, a careful examination reveals the second striking difference between unpoled and poled pellet samples with $x \leq 0.05$ is the splitting peaks behaviour at $2\theta = 40°$. A broadening and no obvious splitting peak is observed for unpoled bulk specimen associated with pseudocubic symmetry. However, poled pellet sample displays sharp splitting peaks similar to the feature of rhombohedral phase, which is widely considered to be field-induced phase transition from cubic phase to rhombohedral phase. However, in this case, the splitting peaks cannot be directly associated with field induced phase transition. As shown in figure 2, the normal ferroelectric phase feature with typical hysteresis loops with a relatively rectangular shape for $x \leq 0.05$ ceramics is observed. As a matter of fact, the real ferroelectric phase is smeared by the coherence diffraction effects of random orientation nanodomains, which will be further discussed in the next section. The results rather support the idea that the essential crystal structure reappears due to the decreased adaptive radiation by the ordered nanodomains induced by applying an electric field. In the same way, the diffraction data of the poled–crushed powders did not show the alignment effect for poling due to random orientation powder particles.

Contrary to XRD patterns of the composition with $x \leq 0.05$, the XRD peaks for $x = 0.1$ unpoled/poled and bulk/powder samples show a single peak at $2\theta = 40°$ associated with cubic symmetry. Similar to the substitution or doping effect in Ba(Ti$_{1-x}$Zr$_x$)O$_3$ and (Pb$_{1-x}$Ba$_x$)(Ti$_{0.65}$Zr$_{0.35}$)O$_3$ and La^{3+}/Nb^{5+} doped BaTiO$_3$ system [32–34], the increase of (Li$_{0.5}$Nd$_{0.5}$)$^{2+}$ ions content in the compound BNLN$_x$T–BT5 leads to a decrease of nanodomains size and their correlation length due to increasing quenched random electric fields. As a result, the applied field never reaches a sufficient

degree to induce a strong correlation between neighbouring domains. Namely, the applied fields cannot align the small nanodomains, transforming the relaxor (ergodic phase) to a long-range ordered state.

On the basis of these results, further investigations of the domain structure by the dielectric constant spectra were carried out. Figure 3 shows the temperature dependence of the permittivity under 1, 10 and 100 kHz frequencies for unpoled and poled pellet samples of the BNLN$_x$T–BT5. The room temperature permittivity frequency dispersion denote as $\Delta\varepsilon_r = \varepsilon_{r1kHz} - \varepsilon_{r100kHz}$ as a function of composition x for unpoled and poled ceramics is shown in figure 4. In all cases, the relatively strong permittivity frequency dispersion at low temperature range for unpoled ceramics is observed in figure 3, which increases with increasing x (figure 4). On the other hand, the permittivity and its frequency dispersion at low temperature range clearly decreases for $x \leq 0.05$ poled ceramics. However, the poling field does not change significantly the permittivity and its frequency dispersion for poled and unpoled $x = 0.1$ ceramics.

It was reported by Ma *et al* [35] in BNT–BT ceramics for composition in the MPB that regular ferroelectric domains correspond to minimum room temperature frequency dispersion in dielectric constant while nanodomains lead to strong frequency dispersion. In addition, it was reported that with increasing the ion-doping content a transformation from ferroelectric micro-sized domain structure into nanometre domains is verified, which occurs simultaneously with the induction of relaxor state [36–38]. A comparatively small nanodomain can lead to a huge relaxor.

From these results, it is clear that with increasing (Li$_{0.5}$Nd$_{0.5}$)$^{2+}$ ions concentration, the dielectric frequency dispersion usually linked to nanodomains size/content becomes more pronounced; whereas the nanodomains content increases and their size decreases. Meanwhile, the domains size, which increased abruptly on applying poling fields, can no longer be reoriented by the weak external trigger field. Thus, the large domains do not contribute to the dielectric and dielectric relaxation, which leads to the deceased dielectric constant and dielectric frequency dispersion. However, the nanodomains size should be much smaller for $x = 0.1$ ceramics and the growth is hindered by local random fields. As a consequence, the large poling fields cannot force nanodomains transform into a strong correlation ferroelectric state. Thus, the dielectric constant and dielectric frequency dispersion change little for unpoled and poled specimens.

From figure 3, it is found that the dielectric constant ε_r and ε_r dispersion for $x \leq 0.05$ poled ceramics are decreased obviously in the low temperature region ($T < 140°$C). However, the ε_r(T) curves of poled and unpoled ceramics are almost overlapped when temperature is above 140°C. The results display that field-stabilized ordered state t is destroyed and the ordered nanodomains is restored on heating the poled specimen above the critical temperature. The XRD patterns and ε_r(T) curves of the poled ceramics after annealing at 150°C are the same when compared with that of unpoled ceramics
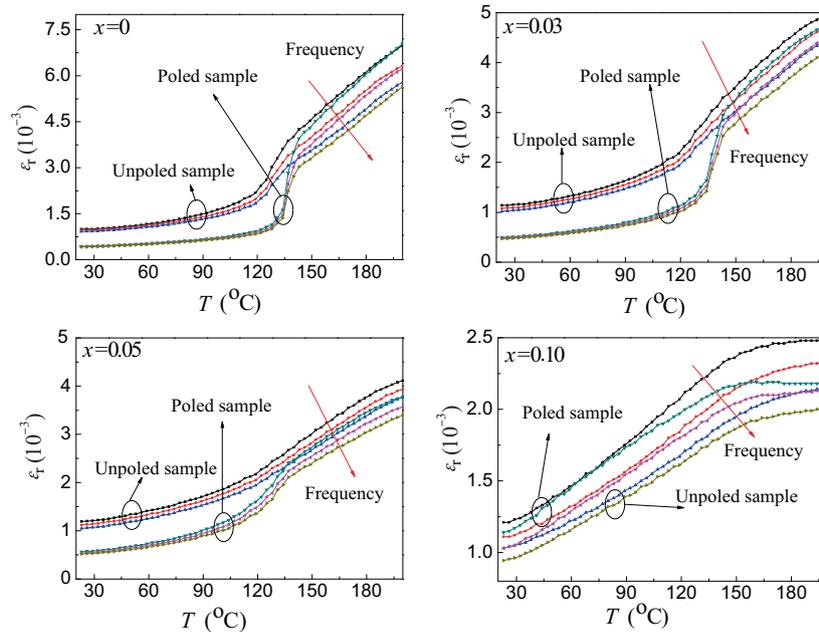
Figure 3. Temperature dependence of the dielectric constant ε_r under 1, 10 and 100 kHz frequencies for unpoled/poled BNLN$_x$T–BT5 ($x = 0, 0.03, 0.05, 0.1$) ceramics measured heating.
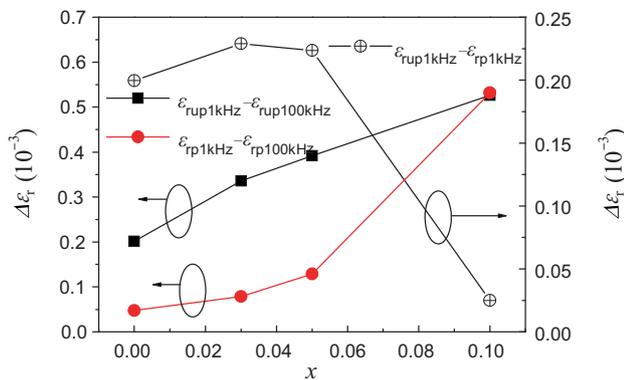

Figure 4. Room temperature dielectric constant frequency dispersion $\Delta\varepsilon_r = \varepsilon_{r1kHz} - \varepsilon_{r100kHz}$ of BNLN$_x$T–BT5 ($x = 0, 0.03, 0.05, 0.1$) ceramics. $\varepsilon_{rup1kHz}$ and $\varepsilon_{rup100kHz}$ are the ε_r for unpoled sample at 1 and 100 kHz, respectively; ε_{rp1kHz} and $\varepsilon_{rup100kHz}$ are the ε_r for poled sample at 1 and 100 kHz, respectively.

due to random nanodomains. The results are merely a manifestation that the ceramics undergo the electric field-induced domains alignment other than phase transition.

It is well known that the ferroelectric and piezoelectric properties measurement is applied to a high electric field using bulk samples. Therefore, a comprehensive understanding of the structural origin of electrical properties in ferroelectrics would require a characterization of not only the structural feature in XRD powder samples, but also the structural changes of bulk, which accompany the application of a high electric field. We believe that our results will stimulate further work on researching the structure–properties correlation in ferroelectrics.

4. Conclusions

The different XRD patterns for bulk and powders in unpoled and poled ferroelectric materials originate from different domain configuration and size. The ferroelectric phase structure is smeared by the coherence diffraction effect of the nanodomains with random distribution. In addition, the observed electric fields induce phase transformation behaviour, which is a consequence of the obsolescent nanodomains coherence effect brought about by the field-induced ordered nanodomains. It suggests that the permittivity spectroscopy and XRD measurement are simple indirect ways to characterize the ferroelectric domains structure.

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