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Domain morphology evolution associated with the relaxor–normal ferroelectric transition in the Bi- and Zn-modified $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ system☆

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Abstract

To understand the dielectric behavior from a viewpoint of domain configuration, the domain morphology evolution in $(Pb_{0.985}Bi_{0.01})(Ni_{1/4}Zn_{1/12}Nb_{2/3})_{0.2}(Zr_{1-\sigma}Ti_{\sigma})_{0.8}O_3$ ceramics ($0.30 \leqslant \sigma \leqslant 0.60$) has been investigated by transmission electron microscopy and high resolution electron microscopy. The results indicated that the domain morphology evolved from the normal micron-sized domains to herringbone domain patterns, and finally to the polar nanodoamains approximately 3∼6 nm in size when the PT content was decreased from 60 to 30 mol%. The normal twin-related 90° macrodomains are closely correlated with the normal dielectric response of the composition with higher PT content, whereas the relaxor response of the composition with lower PT content is directly attributable to nanometer domains that contain 1:1 short-range ordering on the B-site sub-lattice. A model is proposed to describe the effect of the $PbTiO_3$ content on the ferroelectric domain morphology evolution in the system.

Keywords: Domains; Electron microscopy; Ferroelectric properties; $Pb(Ni,Nb)O_3$; $PbTiO_3$; $PbZrO_3$; Perovskites

1. Introduction

During the past 30 years, much pure and applied work has been done on the relaxor ferroelectric with the $Pb(B'_{1/3}B''_{2/3})O_3$-based perovskite structure due to their excellent dielectric and electromechanical properties.[1–3] The relaxor ferroelectrics are characterized by a diffuse and dispersive phase transition.[4] The dielectric constant of relaxor materials exhibits a broad Curie peak in the ferroelectric–paraelectric phase transition range. The Curie maximum temperature, which is frequency dependent over a wide frequency range, shifts toward higher temperature with increasing frequency. Compositional fluctuations occurring on a nanometer scale on the B-site sublattice of the $Pb(B'_{1/3}B''_{2/3})O_3$-based perovskites explain most of the diffuse phase transition (DPT) characteristics of the relaxors.[5,6]. For example, Chen et al.[7] observed that the Mg^{2+} and Nb^{5+} ions are short-range ordered on the B-site sublattice in undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN).The electrical properties of the $Pb(B'_{1/3}B''_{2/3})O_3$-based relaxor ferroelectrics are greatly influenced by the manner in which the B-site cations (B′ and B″ ones) are disordered or ordered on the B-site sublattice.[4] It has been reported that the degree of order on the B-site sublattices is decreased with increasing PT content, since Ti ions are believed to dilute the forces responsible for the ordering process.[8] Therefore, the dielectric behavior in the solid-solutions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT), $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ (PNN–PZ–PT) systems can be varied from a strong relaxor ferroelectric behavior to the normal ferroelectric behavior by suitably adjusting the PT content. Preliminary studies on the phase structure

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and dielectric behavior of the bismuth- and zinc-modified PNN–PZ–PT systems indicated that a spontaneous relaxor–normal ferroelectric transformation occurred corresponding to the structural phase transformation from rhombohedral to tetragonal phase as the PT content was increased from 30 to 60 mol%.[9] It has been suggested that domain evolution may accompany the above structural phase transformation and relaxor–normal ferroelectric transition.[10–12] To better understand the dielectric behavior transition from the relaxor to normal ferroelectrics from a viewpoint of domain configurations, it is necessary to investigate the domain morphology evolution associated with the structural phase transformation and relaxor–normal ferroelectric transition. Transmission electron microscopy (TEM) provides the most direct method to study the domain structure with much better resolution than scanning electron microscopy (SEM).[13] The high-resolution transmission electron microscopy (HRTEM) can image the domain configurations at the atomic scale and determine the specimen structure with atomic-level accuracy. To the knowledge of the authors, however, only a few TEM works on the domain configurations of PNN–PZ–PT ferroelectric ceramics have been published.[14–16] The main purpose of the present study is to investigate the effect of PT content on the domain morphology evolution by TEM and HRTEM, to give an in-depth understanding of the dielectric behavior variation at the microscopic domain level, for which there have been few reports to date.

2. Experimental procedure

The compositions of the bismuth and zinc-modified $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ (PNN–PZ–PT) system used in this study were $(Pb_{0.985}Bi_{0.01})(Ni_{1/4}Zn_{1/12}Nb_{2/3})_{0.2}(Zr_{1-\sigma}Ti_{\sigma})_{0.8}O_3$ with $0.30 \leqslant \sigma \leqslant 0.60$. These ceramic samples were prepared by the method described elsewhere.[9] The final sintering of the samples was carried out at 1220–1260°C for 1–3 h inside a covered alumina crucible, and the samples were covered with powder of the same composition to minimize lead loss during sintering. After the final sintering, the samples were not processed by any thermal treatment. The phase structures of these ceramic samples were determined by X-ray diffraction patterns (D/Max-C, Rigaku, Tokyo, Japan). The specimens for TEM and HRTEM were prepared from the ceramic bulks by mechanical grinding, dimple grinding, and subsequently ion-milling. The ion-milling was done using 4 keV Ar^+ ions and 1 mA discharge current in order to minimize ion-induced damage. Specimens were coated with carbon before examination. The TEM studies were carried out on a JEOL JEM-200CX TEM operated at 200 kV. The experiments of HRTEM were performed on a JEOL JEM-4000EX HRTEM operated at 400 kV with a top entry specimen.

3. Results and discussion

XRD patterns for the samples of $(Pb_{0.985}Bi_{0.01})(Ni_{1/4}Zn_{1/12}Nb_{2/3})_{0.2}(Zr_{1-\sigma}Ti_{\sigma})_{0.8}O_3$ as a function of the PT content are shown in Fig. 1. It can be observed that the crystal structures transform from the rhombohedral to the tetragonal phase as the PT content is increased from 30 to 60 mol%, and that the composition with $\sigma = 0.50$ is close to the morphotropic phase boundary (MPB). This indicates that the MPB shifts towards a Ti-rich region when the PNN is incorporated into the PZ–PT system. Preliminary investigations on the dielectric properties of the present system have indicated that the dielectric behavior tends to vary from a strong relaxor ferroelectric behavior to normal ferroelectric behavior as the PT content increases from 30 to 60 mol%.[9] The relaxor–normal ferroelectric transformation and the structural phase transition are strongly related to the domain morphology evolution.

The domain evolution in the bismuth and zinc-modified PNN–PZ–PT system as a function of the PT content at room temperature is shown in Fig. 2 (a)–(c). The normal micron-sized tetragonal 90° ferroelectric domains showing light or dark contrast can be readily seen in the composition with $\sigma = 0.60$, which was found to be the dominant domain structure by extensive bright-field TEM examination of many grains. For the composition with $\sigma = 0.50$, a complex herringbone domain structure can be frequently observed, which is due to the coexistence of the ferroelectric tetragonal and rhombohedral phases in the composition near the

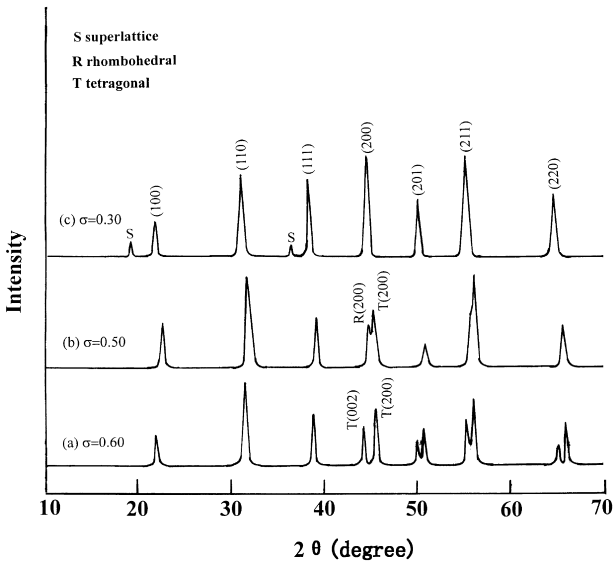

Fig. 1. X-ray diffraction patterns for the samples of $(Pb_{0.985}Bi_{0.01})(Ni_{1/4}Zn_{1/12}Nb_{2/3})_{0.2}(Zr_{1-\sigma}Ti_{\sigma})_{0.8}O_3$ as a function of the PT content.

morphotropic phase boundary. The herringbone domain pattern contains many parallel stripes where the adjacent ones are twin-related, which form with mutual nearly 90° angles on both sides of the herringbone pattern. With further decrease of the PT content to 30 mol%, no evidence of the micron-sized domains was found, only coarse contrast relating to the existence of the nanodomains was observed. This was confirmed by the X-ray result (the weak peak at $2\theta \approx 19°$ corresponding to the (1/2, 1/2, 1/2) reflection that results from the formation of small 1:1 ordered domains). An HRTEM micrograph and a selected electron diffraction pattern are shown in Fig. 3. It is revealed that the discrete ordered nanodomains approximately 3–6 nm in size are randomly distributed in a matrix with an average rhombohedral symmetry. The superlattice reflections are readily discernible in the SAED pattern at positions of $\{h+1/2,\ k+1/2,\ l+1/2\}$ from the fundamental reflections for a pseudocubic perovskite unit cell. The existence of the superlattice spots confirms that the ordered regions have a doubled perovskite unit cell, as previous reported for PMN–PT solid solutions.[8] The present study illustrates that the domain morphologies vary from the normal micron-sized domains, to the herringbone domain structures, and finally to the polar nanodomains with size of 3 to 6 nm with decreasing the PT content. This indicates that the short-range ordering on the B-sites of the present system increases as PT content decreases. Similar phenomenon was also

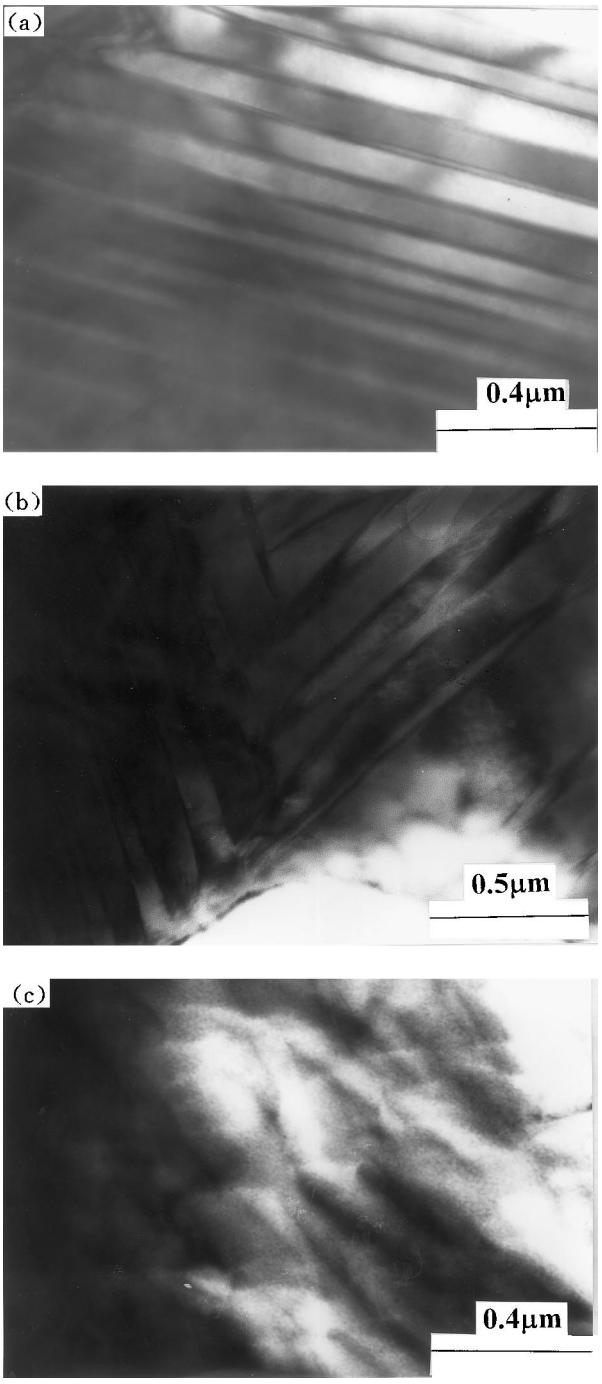

Fig. 2. Domain evolution in the bismuth and zinc-modified PNN–PZ–PT system as a function of the PT content at room temperature. (a) composition with $\sigma = 0.60$ having tetragonal symmetry, (b) composition with $\sigma = 0.50$, in which the tetragonal and rhombohedral symmetries coexist and (c) composition with $\sigma = 0.30$ having rhombohedral symmetry.

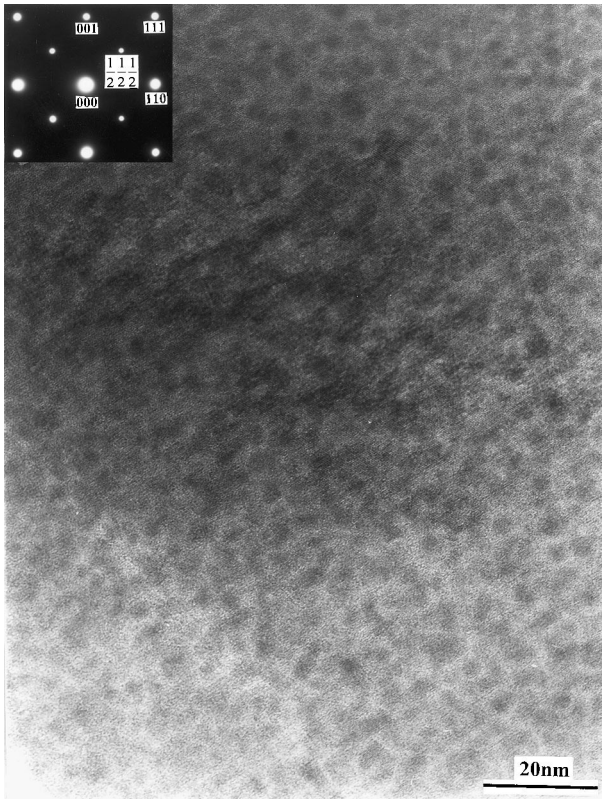

Fig. 3. Bright-field HRTEM micrograph of the composition with $\sigma = 0.30$ having rhombohedral symmetry. The discrete ordered nanodomains approximately 3–6 nm in size are randomly distributed in a matrix with rhombohedral symmety. Inset is a [110] zone axis selected electron diffraction pattern that illustrates the cell doubling.

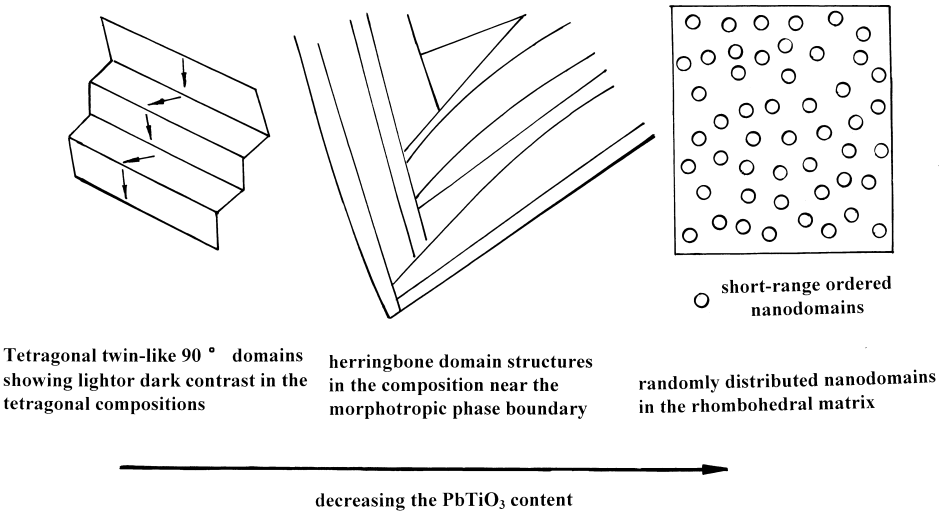

Fig. 4. A schematic drawing showing the effect of $PbTiO_3$ content on the ferroelectric domain evolution in the present system at room temperature.

observed in the PMN–PT system with the perovskite structure. With decreasing PT content the tetragonal 90° macro-domains, observed in the composition with $\sigma = 0.60$ having tetragonal symmetry, became unstable and disappeared in the composition with $\sigma = 0.30$ and the symmetry became rhombohedral. The normal 90° twin-related macrodomains observed in the composition with $\sigma = 0.60$ are formed by a mechanism of stress relief. The increase of the intergranular stresses associated with the structural transformation from the cubic phase to the tetragonal ferroelectric phase, on cooling in the ceramic sample with $\sigma = 0.60$, can be effectively released by the formation of macrodomains. The intergranular stresses are most effectively relieved by the formation of twin-related 90° macrodomains with tetragonal symmetry. Therefore, the 90° twin-related macrodomains are the dominant domain structures and stable in a matrix having tetragonal symmetry because of the higher PT content in the composition with $\sigma = 0.60$, the dielectric behavior of which is mainly dominated by PT. The normal ferroelectric PT has tetragonal symmetry at room temperature and exhibits a normal dielectric behavior. With lower PT content in the composition with $\sigma = 0.30$, the relaxor dielectric response is directly attributable to the nanometer-sized ordered domains containing the 1:1 distribution of two different cation sites that give a doubled perovskite unit cell.[17] The 1:1 short-range ordering on the B-site sub-lattice can be explained by a "random-site" model,[18] in which the B′ sites in the 1:1 ordered Pb $(B'_{1/2}\ B''_{1/2})O_3$ phase contain a random distribution of B^{2+} and B^{5+} ions in a 2:1 ratio, the B″ sites are occupied exclusively by B^{5+} ions. Therefore, the 1:1 ordered domains are charge balanced and the overall 1:2 stoichiometry of the B-site cations is maintained in all regions of the sample. In the composition with $\sigma = 0.30$ having rhombohedral symmetry, the zinc, nickel, zirconium, titanium and niobium cations on the B′ sites of the 1:1 ordered structure are randomly distributed, the B″ sites are occupied exclusively by niobium ions. Since such an atomic-level disorder is an inherent property of the random-site structure, the relaxor behavior can be readily expected. Based on the above analyses, the domain evolution associated with the normal to relaxor ferroelectric transformation as a function of the PT content can be depicted and schematically shown in Fig. 4.

4. Conclusions

The domain evolution in the $(Pb_{0.985}Bi_{0.01})(Ni_{1/4}Zn_{1/12}Nb_{2/3})_{0.2}(Zr_{1-\sigma}Ti_{\sigma})_{0.8}O_3$ system $(0.30 \leqslant \sigma \leqslant 0.60)$ has been investigated by using TEM and HRTEM techniques. The domain morphology evolved from the normal micron-sized domains to herringbone domain pattern, and finally to the polar nanodoamains with approximate 3–6 nm in size as $PbTiO_3$ content was decreased from 60 to 30 mol%. The dielectric behavior variety from relaxor to normal ferroelectrics is discussed from a viewpoint of domain configuration. A model is proposed to describe the effect of PT content on the domain morphology evolution in the present system.

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