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Structural phase stability and electric field induced relaxor–ferroelectric phase transition in $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$xBaTiO_3$ ceramics

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ABSTRACT

Structure, phase transition, and dielectric relaxor behavior have been investigated in morphotropic phase boundary compositions of $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ ceramics for $x = 0.06$, 0.07, and 0.075. In-situ structural thermal stability has been analyzed by using high-resolution synchrotron X-ray diffraction as a function of temperature. A transition sequence of rhombohedral + tetragonal – tetragonal – cubic phases is observed upon heating. The "rhombohedral + tetragonal" indicates a coexistence of rhombohedral *R3c* and tetragonal *P4bm* phases. The two-phase coexistence extends from room temperature to 200 °C. Zero-field dielectric permittivity reveals a frequency dispersion at low temperature region ($T < T_m$) and polar nanoregions below Burns temperature (T_B). The two-phase coexistence plays a vital role for frequency dispersion below T_m. Dielectric spectra of pre-poled samples reveal a field-induced ferroelectric–relaxor phase transition at depolarization temperature T_d.

1. Introduction

Piezoelectric ceramics have been widely used in energy conversion devices such as sensors, actuators, filters, and resonators. Lead-based perovskites, such as zirconate titanate (PZT), have been dominating the piezoelectric market. However, the large amount of lead content in PZT materials has drawn increasing attention due to environmental concern as well as government regulations against hazardous substances [1]. Therefore, extensive studies have been done in search of lead-free materials which could replace lead compositions. Among the studied materials, solid solutions between a rhombohedral $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT) and tetragonal $BaTiO_3$ (BT) [2] have been of particular interest, whose nature appears similar to PZT piezoceramics.

One of the interesting properties exhibited by both PZT and BNT–BT is the existence of morphotrophic phase boundary (MPB) which is responsible for high piezoelectric property. According to Jaffe et al. [3], the ferroelectric region in PZT consists mainly two different regions: the Zr-rich rhombohedral region which contains two phases with space groups *R3m* and *R3c*, and the Ti-rich tetragonal region with space group *P4mm*. The two regions are separated by a boundary, which lies at a composition close to 47 mol% of Ti. Noheda et al. reported that the piezoelectric enhancement occurs in the region of the composition–temperature phase diagram where crystal structure changes from tetragonal (T) to rhombohedral (R) via an intermediate monoclinic (M) phase for Zr/Ti > 52/48 [4].

In BNT–BT compositions, there have been many unclear issues regarding the existence of MPB. For example, Raman spectroscopy and X-ray diffraction (XRD) [5] proposed a structural transition between 5 and 6 mol% BT contents. This boundary turns out to be nearly temperature-independent from ~10 K to ~470 K and shifts to somewhere between 6 and 7 mol% BT after electrical poling [6]. In situ XRD [7] showed that two-phase boundaries exist for unpoled BNT–xBT ($0 \leqslant x \leqslant 0.15$) ceramics, one between 5 and 6 mol% BT and the other at 11 mol% BT. The tilt boundary shifts to somewhere between 6 and 7 mol% BT and a structural MPB existing initially at BNT–0.11BT extends to a broad range of compositions, i.e. 6–11 mol% BT when the materials are electrically

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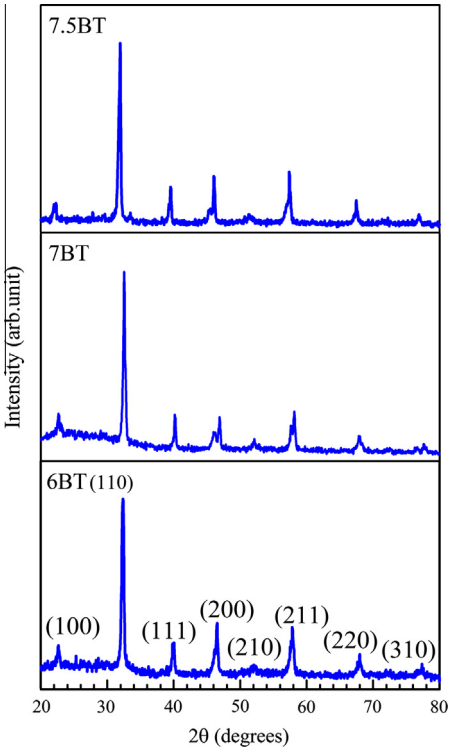

Fig. 1. XRD diffraction patterns.

poled, though the MPB-induced property enhancement takes place only for 6–7 mol% BT [1].

BNT–BT compositions in the range of MPB exhibit relaxor behavior characterized by a broad frequency dispersion in the complex dielectric spectra [1,8], which are similar to lead-based compositions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). Viehland et al. proposed that the deviation from the Curie–Weiss law in the dielectric spectra of PMN is associated with the correlation between polar regions [9]. Yan et al. explained the anomaly in the dielectric loss around 340 K in $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ceramics ($0 < x < 0.23$) by the dynamic relaxation of ferroelectric nanodomains [10]. The origin of nanoregions is attributed to disorder in octahedral tilting and cation ordering [11]. For relaxor $Pb(Mg_{1/2}Nb_{2/3})O_3$, the dielectric relaxation was attributed to disorder in the occupation of Mg^{2+} and Nb^{5+} ions in the B site of ABO_3 perovskite unit cell. For $Pb_{1-x}La_x(Zr_yTi_{1-y})O_3$ relaxors, it is the contribution of disorder in A site (Pb^{2+} and La^{3+} ions) that yield the relaxor behavior [12]. However, it is more complex in BNT–BT system as A-site is occupied by three different ions with different charges and ionic radii (Bi^{3+} = 1.03 Å, Ba^{2+} = 1.35 Å, Na^{1+} = 1.24 Å) [13]. The random occupations of Bi^{3+}, Na^{1+}, and Ba^{2+} ions at the A-site sublattices of perovskite unit cell can cause the formation of polar nanoregions (or nanoclusters) with distinctive compositions of the A-site cations. These nanoregions possess various dielectric responses leading to the diffuse phase transition [14]. Therefore, inconsistent results of structure, phase transitions, piezoelectric, and dielectric properties of $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$xBaTiO_3$ ceramics call for attention even today.

In this work we have studied the structural phase stability and relaxor behavior of $(1-x)$BNT–xBT compositions with x = 0.06. 0.07, and 0.075 as a function of temperature using high energy synchrotron XRD and dielectric measurement. The above compositions show the coexistence of rhombohedral and tetragonal phases from room temperature up to ~200 °C. Dielectric measurements of pre-poled samples reveal transition from ferroelectric phase to a relaxor phase at depolarizing temperature T_d.

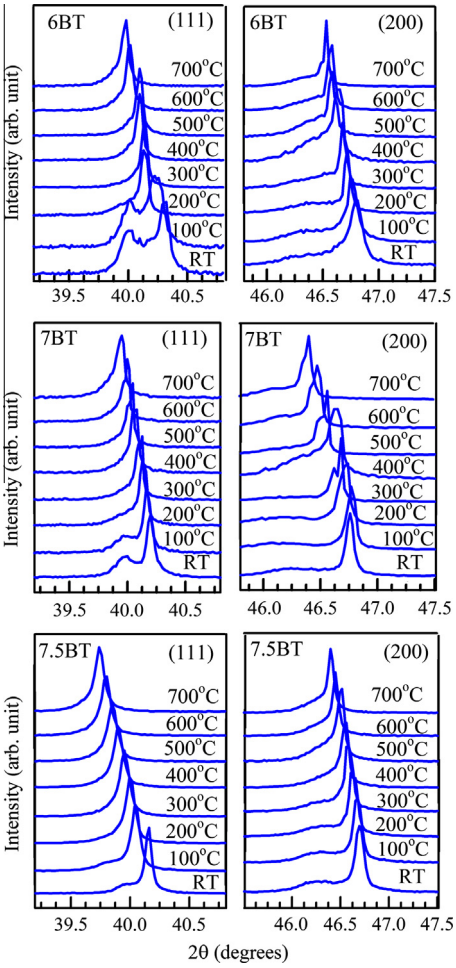

Fig. 2. High-resolution (111) and (200) synchrotron diffraction patterns upon heating.

2. Experimental procedure

Polycrystalline $(1-x)$BNT–xBT (x = 0.06, 0.07, and 0.075) ceramics were prepared by solid state reaction method. High-purity (>99%) powders of Bi_2O_3, Na_2CO_3, $BaCO_3$, and TiO_2 were used as starting materials. Stoichiometric amounts of powders were mixed with zirconia balls in an agate mortar for more than 24 h using ethanol as a medium. The mixture was calcined at 900 °C for 2 h and a high-energy ball milling by using the Retsch PM100 planetary mill was used to reduce particle size. The powder mixture was then pressed into a 1.0 cm-diameter disk for sintering at 1150 °C for 1 h. As-sintered samples were polished to 0.5 mm thickness and annealed at 650 °C for 30 min in order to remove residual stress. The diffraction peaks were analyzed using high-resolution synchrotron XRD (BL17B1 at NSRRC, Taiwan with a photon energy of 8 keV (λ = 1.555 Å)). XRD spectra were fitted by using PeakFit software with the Gaussian profile. Two processes were used in the dielectric measurements by using a Wayne–Kerr Analyzer PMA3260A. The first is called the zero-field-heated (ZFH), in which the dielectric permittivity was taken upon zero-field heating without a prior E-field poling. The second process is called the prior-poled before zero-field heating (PP-ZFH), in which the sample was poled at room temperature with a dc field of E = 40 kV/cm, then ZFH dielectric measurement was carried out without a dc field. High-resolution TEM (JEOL JEM-2100 LaB6) observations were performed to study polar nanoregions and structures.

3. Results and discussion

The XRD spectra in Fig. 1 show perovskite structures without second phase. The mild peak splitting reveals a coexistence of two different phases. The (111) and (200) reflections in Fig. 2 show the temperature evolution of phases from the coexistence of rhombohedral (R) and tetragonal (T) phases, then tetragonal phase at intermediate temperatures, and end in cubic phase above