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A correlation between piezoelectric response and crystallographic structural parameter observed in lead-free $(1\text{-}x)(Bi_{0.5}Na_{0.5})TiO_3$–$xSrTiO_3$ piezoelectrics

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ABSTRACT

The structure of lead-free $(1\text{-}x)(Bi_{0.5}Na_{0.5})TiO_3$-$xSrTiO_3$ (BNT-STx) ceramics was analyzed by the Rietveld method, using X-ray diffraction and neutron scattering data. The structural refinement results suggest that the crystal structure successively changes with $SrTiO_3$ concentration, x, from the rhombohedral phase ($x = 0.00$) to rhombohedral and tetragonal ($x = 0.10$–0.30), tetragonal and cubic ($x = 0.40$–0.60), and finally cubic ($x = 0.80$–1.00) phases. Correlation between the charge sensor constant (d_{33}) and the weighted off-center value (d_w) was observed, which may be attributed to the increased dipole motion in the unit cell due to an increased tendency to respond to external stimulation. Furthermore, an improved charge sensor constant (d_{33}) of 140 pC/N was observed for BNT-ST0.20, and a large strain of 0.25% and a d_{33}^* value of 443 pm/V were observed from $x = 0.30$.

1. Introduction

Lead-based perovskite piezoelectric ceramics, such as $Pb(Zr,Ti)O_3$, (PZT) are widely used in actuators, sensors and microelectronic devices due to their excellent piezoelectric properties [1,2]. However, the toxicity of Pb and its high vapor pressure leads to a demand for alternative environment-friendly lead-free piezoelectric materials [3].

Potential alternatives to PZT are lead-free ABO_3 type perovskites, such as $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT). Pure BNT has a rhombohedral ($R3c$) structure at room temperature [4,5], showing a large remnant polarization ($P_r = 38\ \mu C/cm^2$) [6] and a low charge sensor constant ($d_{33} = 58$ pC/N) [7]. It is known that BNT undergoes a series of phase transitions during heating; from rhombohedral to tetragonal phase at $T_{R\text{-}T} = 300\ ^\circ C$, and from tetragonal to cubic phase at $T_{T\text{-}C} = 540\ ^\circ C$ [8,9]. Furthermore, a ferroelectric to anti-ferroelectric phase transition has been reported at $T_d = 190\ ^\circ C$ [10]. On the other hand, the morphotropic phase boundary (MPB) between the two solid solutions that comprise these materials, $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ (BNT-BT) [11–13] and $(Bi_{0.5}Na_{0.5})TiO_3$-$(Bi_{0.5}K_{0.5})TiO_3$ (BNT-BKT), exhibit a large charge sensor constant [14–17]. Similar MPB formation has also been reported in pure BNT-ST solid solution ceramics with good piezoelectric properties [18,19].

Experimentally, piezoelectric materials with compositions around the MPB clearly show a superior piezo-response, however, it is not clear yet why good piezoelectricity coincides with the MPB. Recently, improvement in understandings on the MPB related piezo-response were reported based on concepts of domain reorientation, coupling of the equivalent energy of two different structures, polarization reorientation and extension, etc. [20–22]. Nevertheless on these, further efforts on investigating details of the crystal structure and piezo-response for lead-free piezoelectrics should be conducted using the concept of the non-centrosymmetric nature of piezoelectrics.

In this work, BNT-ST ceramics were fabricated by using a solid state reaction. In order to understand the relation between the structural and electrical properties, the structure of BNT-ST

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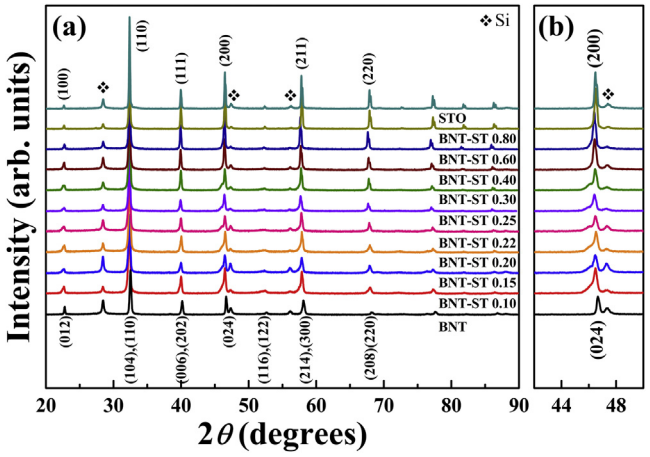

Fig. 1. XRD patterns of BNT-ST*x* bulk ceramics with selected angles of (a) 20–90° and (b) 43–49°. (Note: Si powder was used as a standard for X-ray diffraction and the XRD peaks are indexed with rhombohedral (bottom) and cubic (top) structure.).

ceramics was investigated by X-ray diffraction (XRD) and neutron scatterings, and was further refined using a Rietveld method. The piezoelectric properties of BNT-ST were characterized on the basis of the charge sensor constant (d_{33}) and the electric field-induced strain. Furthermore, changes in the piezoelectric properties along with the compositional changes were correlated with a parameter derived from the refined structures.

2. Materials and methods

Lead-free (1-*x*)($Bi_{0.5}Na_{0.5}$)TiO_3-*x*$SrTiO_3$ (BNT-ST*x*; *x* = 0.00, 0.10, 0.15, 0.20, 0.22, 0.25, 0.30, 0.40, 0.60, 0.80, and 1.00) ceramics were fabricated by a traditional solid state reaction method. High purity Bi_2O_3 (99.9%, Aldrich), Na_2CO_3 (99.5%, Aldrich), $SrCO_3$ (99.9%, Aldrich) and TiO_3 (99.9%, Aldrich) were used as starting materials. The powders were exsiccated in a drying oven due to the highly hygroscopic nature of the powders. Next, they were mixed using a ball milling method with anhydroethanol for 24 h, and were subsequently dried at 120 °C. The dried powders were calcined at 800 °C for 2 h. Then, they were ball milled again for 24 h and calcined again at 850 °C for 2 h. The samples were pressed into disks of 10 mm diameter and 1 mm thickness, and sintered at different temperatures between 1150 and 1350 °C, depending on the specific composition. The sintered ceramics were polished, and both surfaces were coated by silver paste as electrodes. Finally, the samples were poled at 2.4 kV for 30 min in silicone oil.

The sintered samples were investigated by using an X-ray diffractometer (RIGAKU, Miniflex II) with CuKα radiation ($\lambda_{K\alpha1}$ = 1.540562 Å, $\lambda_{K\alpha2}$ = 1.544398 Å). The ratio of $K\alpha_1$ and $K\alpha_2$ was 2:1. Neutron diffraction was investigated by a high resolution powder diffractometer (HRPD) (HANARO, Korea Atomic Energy Research Institute (KAERI)) using a Ge (331) monochromator with a wavelength of 1.83432(1) Å. The crystal structures were analyzed by a Rietveld refinement method using a Fullprof program [23]. The charge sensor constant was measured using a d_{33} meter (Institute of Acoustics, ZJ-6B). The electric field induced strain was measured by a linear variable differential transformer (LVDT).

3. Results and discussion

The XRD patterns of the sintered BNT-ST*x* samples are shown in Fig. 1(a). The positions and intensities of the reflection peaks are very similar in all samples. It is easy to identify the rhombohedral and cubic structures of pure BNT (*x* = 0.00) and STO (*x* = 1.00), respectively, since there are no impurity related reflections other than those of perovskites. The reflection peaks were indexed as rhombohedral (*R*3*c*) for *x* = 0.00 and cubic (*Pm*-3*m*) for *x* = 1.00 in Fig. 1. The samples with compositions ranging from BNT-ST0.10 to BNT-ST0.60 were found to be a phase mixture, as the existence of low intensity shoulders indicate on the low angle side of the rhombohedral (024) peaks shown in Fig. 1(b). These suggest that details of the structure of BNT-ST may need to be investigated by means of structural refinements.

Prior to investigate the structure further, piezoelectric properties were investigated since BNT-ST*x* were studied for lead-free piezoelectrics. Regarding the piezoelectric properties of these materials, the field-induced bipolar strains of the different BNT-ST*x* ceramics were analyzed (Fig. 2(a)). In addition, the charge sensor constant (d_{33}) and the normalized strain ($d_{33}^* = S_{max}/E_{max}$) were studied, as shown in Fig. 2(b). Pure BNT exhibits a butterfly shaped curve with positive and negative strains, typical for ferroelectrics. The shape of the bipolar strain changed with increasing STO content. Between *x* = 0.00 and 0.20, ferroelectric bipolar strains were observed, and small negative strains were observed in BNT-ST0.25 and BNT-ST0.30, which is closely related to domain switching [24]. On the other hand, between *x* = 0.40 and 0.80, only positive strains were observed. Thus, the negative strain reduction in BNT-ST0.25 and BNT-ST0.30 may be caused by the conversion of ferroelectric domains into dynamically active nano-domains in the ergodic relaxor state [25]. Furthermore, a large deviation of S_{max} [0.24% (BNT-ST0.25), 0.26% (BNT-ST0.30)] and negative strain [0.01% (BNT-ST0.25), 0.09% (BNT-ST0.30)] were observed in this concentration range, which can be related to the ergodicity and electric-field induced phase transformation at the boundary from an ergodic relaxor state to a polar ferroelectric state [26].

The charge sensor constant d_{33} increased with increasing STO content up to BNT-ST0.20, and then it decreased, reaching zero for BNT-ST0.80. The highest charge sensor constant (d_{33}), achieved by the BNT-ST0.20 sample, had a value of 139 pC/N. It is known that the piezoelectric response is related to the ceramic density and grain size [27–30]. Thus, the relative density and microstructure of the BNT-ST*x* studied in here are shown in Figs. 3 and 4, respectively. The measured densities are gradually decreased with the increased STO contents, and the calculated relative densities are maintained over 93% of the ideal ones in the composition range of *x* = 0.00–0.60 as shown in Fig. 3. Furthermore, grain sizes of BNT-ST*x* are gradually decreased with the increased STO contents as shown in the surface images observed by SEM (Fig. 4).

In general, the charge sensor constant (d_{33}) increases with increasing grain size and saturates with the grain size of 1–10 μm as observed in PZT, $BaTiO_3$ and BNT-ST systems [27,28,31]. Recently, it was reported that the piezoelectric properties are increased with decreasing core density in the composition fixed BNT-ST0.25 ceramics [31]. However, for the BNT-ST ceramics with a wide range of compositional variation as studied in here, it is difficult to directly correlate the measured densities and/or grain sizes to the observed maximum piezo-responses near the expected MPB (*x* = 0.15–0.30).

Therefore, it is worth to investigate the intrinsic piezoelectricity, such as that originated from the crystal structures, to explain the observed piezoelectric properties of the BNT-ST*x*. Neutron scattering data were collected to further investigate the crystal structure, and the results are shown in Fig. 5(a). The reflections have been indexed as rhombohedral and cubic phases for convenience. Since no other peaks were identified, it can be stated that there were no detectable impurity phases other than perovskites. The 2D contour plot of the selected angle range from 45.2° to 46.8° shows the peak evolution (Fig. 5(b)), where the intensity of the rhombohedral (113) peak gradually decreases with increasing STO contents, until it finally disappears for BNT-ST0.40. This suggest that there is a phase change when the STO content is modified, which cor-

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