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Electric-field-induced phase transition and large strain in lead-free Nb-doped BNKT-BST ceramics

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Abstract

A suite of Nb-based piezoelectric ceramics of $0.99[Bi_{0.5}(Na_{0.4}K_{0.1})(Ti_{1-x}Nb_x)]O_3$–$0.01(Ba_{0.7}Sr_{0.3})TiO_3$(BNKTN-BST), with x ranging from 0 to 0.030, was prepared by a conventional solid-state reaction method. X-ray diffraction patterns confirmed a single perovskite phase and the tetragonality was found to decrease with increasing Nb ratio. The BNKTN-BST ceramic had a high field-induced normalized strain coefficient of 634 pm/V at 2 mol% Nb content with a relatively small hysteresis compared with existing lead-free Bi-perovskite ceramics. An electric-field-dependent X-ray study was conducted to identify the main source of the high strain and ascertain the effect of electric fields on the crystal structure. The temperature-dependent $P-E$ hysteresis loops of the BNKTN-BST ceramics were measured under an electric field of 60 kV/cm at various temperatures, and the effect of temperature on the ferroelectricity is discussed.

Keywords: Lead-free; Piezoelectrics; Bismuth sodium potassium titanate ceramics; Strain; Phase transition

1. Introduction

Piezoceramics are attractive and important materials that are used for many electromechanical applications such as sensors, actuators, and transducers due to their excellent electromechanical properties. However, with respect to environmental concerns and legislation regulating hazardous materials, lead, which is considered toxic, is banned from use in many commercial applications [1]. The enforcement of these regulations and restrictions on using hazardous substances in electronic devices has resulted in efforts to discover lead-free replacements for commercial Pb-based piezoceramics. Systems that have been studied with the aim of obtaining large electric-field-induced strain include $Bi_{0.5}Na_{0.5}TiO_3$-based systems near the morphotropic phase boundary (MPB) such as $Bi_{0.5}Na_{0.5}TiO_3$–$SrTiO_3$ [2], and $Bi_{0.5}Na_{0.5}TiO_3$–$K_{0.5}N_{0.5}NbO_3$ (BNT-KNN) [3]. These systems show an MPB between a nonpolar and polar phase, and are very attractive for actuator applications over a wide temperature range. Recently, Zhang et al. [4] achieved a significant improvement in the electric-field-induced strain response of a lead-free $K_{0.5}Na_{0.5}NbO_3$-modified $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$ (BNT-BT-KNN) system, though it was accompanied by a significant reduction in its piezoelectric constant d_{33}. They further demonstrated that BNT-BT-KNN has good temperature stability and is highly attractive for actuator applications. In addition, lead-free barium strontium titanate, $(Ba_{1-x}Sr_x)TiO_3$ and doped $BaTiO_3$ are currently important dielectric materials for capacitor applications [5]. The main purpose of adding Sr^{2+} into $BaTiO_3$ is to shift the T_c (~130 °C) toward room temperature and to offer a high dielectric constant and a low dielectric loss [6]. Recently, Lee et al. [7] studied the $(1-x)(Bi_{0.5}Na_{0.5})TiO_3-x(Ba_{0.7}Sr_{0.3})TiO_3$ system. The doping

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of $(Ba_{0.7}Sr_{0.3})TiO_3$ into $(Bi_{0.5}Na_{0.5})TiO_3$ generated a phase transition from rhombohedral to tetragonal, and an improvement in both dielectric and piezoelectric performance was found at an MPB of $x = 0.08$. A binary system of BNT and BKT ceramics exhibits an MPB of $0.16 \leq x \leq 0.20$, which results in improved ferroelectric and piezoelectric properties as compared with other lead-free ceramics. In a $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}K_{0.5}TiO_3$ (BNKT) system, when Na^+ is partially substituted by K^+ on the A-site of BNT, the system shows high strain and ferroelectric properties, which has been studied by many researchers [8–12]. The high strains observed in the BNKT system under a strong electric field are due to a 90° domain reorientation [13]. To identify a new lead-free alternative material with high strain and possible application as an actuator, a system consisting of $0.99[Bi_{0.5}(Na_{0.4}K_{0.1})Ti_{1-x}Nb_x]O_3$–$0.01(Ba_{0.7}Sr_{0.3})TiO_3$ (BNKTN-BST) ceramics was examined. In this study, encouraging results are reported in terms of high field-induced strain with a relatively slim-type hysteresis loop, and the possible mechanism of the FE-NP phase transition in Bi-perovskite is discussed. Electric-field-dependent XRD was used to determine the mechanism for the high strain of the system. Current literature does not yet address how the phase structure evolves under the application of an electric field or if or how it relates to the final piezoelectric properties of BNKTN-BST ceramics, particularly in the vicinity of the tetragonal–cubic phase boundary. In the present work, X-ray diffraction of unpoled $0.99[Bi_{0.5}(Na_{0.4}K_{0.1})(Ti_{1-x}Nb_x)]O_3$–$0.01(Ba_{0.7}Sr_{0.3})TiO_3$ ceramics was conducted and experimental evidence of the electric-field-induced phase transition and phase instability was obtained. These results correlate with the dielectric and piezoelectric properties and address whether the applied electric field induces additional lattice distortion. The effect of Nb concentration on the phase, microstructure, and electrical properties of the ceramics was also investigated and is discussed.

2. Experimental

Piezoceramics $0.99[Bi_{0.5}(Na_{0.4}K_{0.1})(Ti_{1-x}Nb_x)O_3]$–$0.01(Ba_{0.7}Sr_{0.3})TiO_3$ ($x = 0$–0.030) were prepared using a conventional solid-state reaction method. Powders of Bi_2O_3, Na_2CO_3, TiO_2, K_2CO_3 (99.9% High Purity Chemicals, Japan), $SrCO_3$, and Nb_2O_5 (99.9% Cerac Speciality In-organics, USA) were used as the raw starting materials. Before weighing, the powders were dried in an oven at 80 °C for 24 h to remove moisture. Starting materials were weighed according to stoichiometric ratio and then ball milled for 24 h in ethanol with zirconia balls. The material was dried at 80 °C, and the powders were then ground and calcined at 850 °C for 2 h in a closed crucible. The powders were again ground and ball milled for 24 h. The compound was pulverized, mixed with an aqueous polyvinyl alcohol (PVA) solution, and formed into green disks of 10 mm in diameter at a pressure of 100 MPa. After binder burnout at 500 °C, the disks were sintered at a temperature 1150–1165 °C for 2 h in closed alumina crucibles. To prevent the vaporization of Bi, Na, and K, the disks were embedded in powders of their identical compositions. The crystal structure and lattice parameters of the highly polished disks were determined using an X-ray diffractometer (XRD, X'Pert-PRO MRD, Philips, KBSI). Electric-field-induced XRD was also measured by an X-ray diffractometer (M-P X-Ray, X'Pert-PRO KERI, South Korea). For microstructural analysis, the surface of the as-sintered samples was removed by lapping. The lapped samples were then thoroughly polished and thermally etched at 1050 °C for 30 min. Finally, field-emission scanning electron microscopy (FE-SEM, Hitachi.S-4200 & Japan) was employed to examine the microstructure of the polished and thermally etched samples. Silver paste was applied through a screen to both surfaces of the disks as electrodes. After applying the silver paste, the disks were fired at 700 °C for 30 min. The ferroelectric hysteresis loops were measured in silicon oil with the aid of a Sawyer–Tower circuit to apply an electric field with a sinusoidal waveform. The electric-field-induced strain was measured by a linear variable differential transducer (LVDT, Mitutoyo MCH-331 & M401).

3. Results and discussion

X-ray diffraction patterns of the BNKTN-BST system in the 2θ range of 30–50° are shown in Fig. 1a. In the studied composition range, all samples show a single perovskite phase. No noticeable unwanted secondary phase was observed. Even though, Lee and Hussain et al. have traced unwanted secondary phases in Nb-doped BNKT-based ceramics beyond 3 mol% of Nb concentration [14,15]. The possible reasons for the absence of secondary phases in this study are as follows. First, due to its precise limitations, the X-ray diffractometer may be unable to detect the small amount of Nb concentration (3 mol%). Second, the Nb-doping amount is very small and therefore may be uniformly diffused into the BNKT-BST lattice. Based on our findings and in connection with the reported works [14,15], it is suggested that the solubility limit of Nb in BNKT-based ceramics is approximately 3 mol%. Moreover, the addition of Nb has a significant effect on the phase structure of BNKT-BST ceramics. Ceramic with $x = 0$ has the feature of tetragonal symmetry, as evidenced by the splitting of the (0 0 2)/(2 0 0) peak at a 2θ of around 46.5°. However, with increasing Nb concentration, the (0 0 2)/(2 0 0) split peak of the tetragonal symmetry gradually demolished and finally merged into a single (2 0 0) peak at $x = 0.020$ suggesting that the crystal structure of the BNKTN-BST ceramics evolved from the tetragonal to a more symmetric pseudocubic phase. Structural transformations of this sort are also observed with partial Nb substitution of the Ti-site in BNKT-based ceramics [14]. In addition, with increasing Nb concentration, the peaks around 2θ of 46.5° were slightly shifted to a lower angle suggesting lattice expansion. The observed shift in peak position toward lower angles may be ascribed to the substitution of higher ionic radius ($Nb^{5+} \sim 0.64$ Å) instead of a lower ionic radius ($Ti^{4+} \sim 0.60$ Å) similar to that reported in Nb-substituted BNKT-$LiSbO_3$ ceramics [15].

In order to investigate the phase structure change in more details, the lattice parameters a and c, calculated from the (0 0 2)/(2 0 0) peaks at 2θ around 46.5°, and the tetragonality (c/a) of the BNKTN-BST ceramics are presented in Fig. 1b. It can be seen in Fig. 1b that the lattice constant c and tetragonality