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Comparison of structural, ferroelectric, and strain properties between A-site donor and acceptor doped $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ ceramics

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Abstract

Effects of Li- and La-doping on the structural, ferroelectric, and strain properties of $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ (BNKT) ceramics were compared. In this study, Li^+ was selected as the A-site acceptor and La^{3+} as the A-site donor. Li doping resulted in hardening of BNKT with an improved mechanical quality factor (Q_m) of 253 and an increased coercive field (E_c), while La doping brought about a softening effect that was evidenced by an improved piezoelectric constant (d_{33}) of 172 pC/N and decreased E_c. In addition, the large normalized bipolar strain (S_{max}/E_{max}) was obtained up to 650 pm/V in 3 mol% La-doped BNKT.

Keywords: B. Defects; C. Ferroelectric properties; C. Piezoelectric properties; Solid state reaction

1. Introduction

Recently, lead-free piezoelectric ceramics have been extensively studied from both physical and technical points of view. Among various lead-free materials, binary $(Bi,Na)TiO_3$–$(Bi,K)TiO_3$ (BNKT) solid solutions are considered as potential candidates due to their excellent electromechanical properties near the morphotropic phase boundary (MPB) [1–4]. A number of previous studies have reported that electromechanical properties can be improved by modification of the MPB composition with various dopants or modifiers, such as BNKT–$BiAlO_3$ [5], BNKT–$LiSbO_3$ [6], Nb-doped BNKT [7], Ta-doped BNKT [8], Sn-doped BNKT [9,10], Li- and Ta-codoped BNKT [11], BNKT–$LaFeO_3$ [12], La-doped BNKT [13], and Ta-doped BNKT–$LiSbO_3$ [14].

It has been well known in Pb-based piezoelectric ceramics that the hardening or softening through the addition of dopants is a key technique to tailor their properties [15–17]. The best known examples are hard and soft $Pb(Zr,Ti)O_3$ (PZT) ceramics, the most widely used piezoelectric materials. Hardening can be induced by the addition of acceptor dopants [18]. A better understanding of the hardening and softening in Pb-based ceramics has been presented by Chandrasekaran et al. [19]. Oxygen vacancies in acceptor (Fe) doped $PbTiO_3$ (PT) are responsible for the formation of polar defect complexes. Both of the "bulk effects" and the "domain-wall effects" contribute similarly to the hardening phenomenon [19], while donor (Nb) doping increased domain mobilities, resulting from the lack of polar defect complexes. The effects of donor (Nb^{5+}, Ta^{5+}) doping on the electromechanical properties of lead-free $Bi_{0.5}Na_{0.5}TiO_3$ ceramics have been also reported [20]. In 2012, Han et al. [21] also compared the effects of B-site acceptor and B-site donor doping and they found that donor-doping contributed to the destabilization of ferroelectric phases. More recently, the electromechanical properties of Mn- or Fe-doped BNT–BKT–$Bi_{0.5}Li_{0.5}TiO_3$ piezoelectric ceramics were examined by Taghaddos et al. [22] in 2014. It

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was found that the acceptor dopants can slightly decrease the optimum sintering temperature and enhance the mechanical quality factor considerably.

Therefore, there is a great attraction from both scientific and technical points of view to investigate the effects of A-site acceptor as well as A-site donor on the piezoelectric properties of lead-free BNKT ceramics. In BNKT system (near MPB), due to difference between the ionic radius of doping elements and lattice ions, there are limited acceptor ions that can occupy the A-site (e.g. Li^{+}, Rb^{+}, Cs^{+}) or B-site (e.g. Fe^{3+}, Mn^{3+}, Al^{3+}) and restricted donor ions that can substitute into A-site (e.g. In^{3+}, Tl^{3+}, La^{3+}) or B-site (e.g. Ta^{5+}, Nb^{5+}, Sb^{5+}).

This work compared the crystal structure, ferroelectric, and electromechanical properties of Li- and La-doped BNKT ceramics. It is expected to see a hardening effect in Li-doped BNKT ceramics due to creation of oxygen vacancies when Li^{+} ions occupy the A^{2+}-sites. In contrast, a softening effect is presumed in La-doped BNKT ceramics due to generation of A-site vacancies when La^{3+} ions substitute doubly charged A^{2+}-site ions. The oxygen vacancies or A-site vacancies created in the lattice are compensated by the incorporated acceptor or donor ions, respectively. This can be understood by considering the Schottky defect reaction

$$Li_A \rightarrow Li_A^{'} + 1/2V_O \quad (1)$$

$$La_A \rightarrow La_A + 1/2V_A^{''} \quad (2)$$

where V_O and V_A indicate oxygen and A-site vacancies, respectively.

2. Experiments

Ceramic specimens with composition of $[Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}]_{1-x}A_xTiO_3$ (A=Li or La; x=0.00–0.05), abbreviated as A100x, were synthesized using a conventional solid state reaction route. Reagent grade Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2, Li_2CO_3, and La_2O_3 (99.9%, High Purity Chemicals, Japan) powders were used as raw materials. These reagents were dried in an oven at 100 °C for 24 h and then weighed according to the formula. The powders were mixed in ethanol with zirconia balls by ball milling for 24 h, dried at 80 °C for 24 h, and calcined at 850 °C for 2 h in an alumina crucible. After calcination, the powder was mixed with polyvinyl alcohol as a binder and then pressed into green discs with a diameter of 12 mm under a uniaxial pressure of 98 MPa. Green pellets of Li100x and La100x were sintered at 1100 °C and 1175 °C, respectively, in covered alumina crucibles for 2 h in air with a heating rate of 5 °C/min.

For electrical measurements, a silver paste was screen-printed on both sides of each specimen, fired at 700 °C for 30 min, and then poled in silicone oil bath at 80 °C under a direct electric field of 50 kV/cm for 15 min. The crystal structures of the poled and unpoled samples were analyzed with an X-ray diffractometer (XRD, RAD III, Rigaku, Japan) using Cu Kα radiation. The relative density of the fired specimen was determined by the Archimedes method. A field-emission scanning electron microscope (FE-SEM, JEOL, JSM-65OFF, Japan) was used to examine the surface morphology of samples. The electrical polarization (P) and electromechanical strain (S) as a function of external electric field (E) were recorded at 0.3 Hz with a 15 μF measurement capacitance using a Sawyer-Tower circuit equipped with an optical sensor (Philtec, Inc., Annapolis, MD, USA). The piezoelectric constant d_{33} was measured using a Berlincourt d_{33}-meter after poling samples under a direct electric field of 50 kV/cm for 15 min in silicone oil kept at 80 °C. The planar piezoelectric coupling coefficient (k_p) and electromechanical quality factor (Q_m) were characterized by the resonance-antiresonance method.

3. Results and discussion

Field-emission scanning electron microscopic investigations were carried out to study grain size and grain morphology of Li100x and La100x, and the results are shown in Fig. 1. All

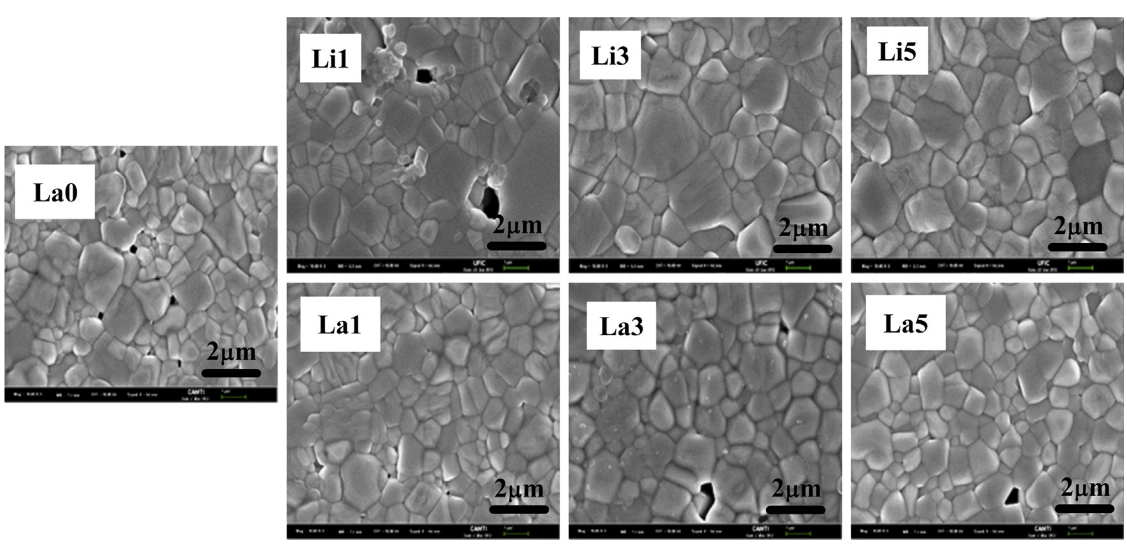

Fig. 1. Comparison of scanning electron micrographs between Li- and La-modified BNKT ceramics with different dopant levels.