



Structure and electrical properties of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ -based ferroelectric ceramics with lithium and cerium modification



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ABSTRACT

Aurivillius-type ceramics, $\text{Sr}_{0.6}(\text{BiNa})_{0.2}\text{Bi}_2\text{Nb}_2\text{O}_9$ (SBNBN) with lithium and cerium modification, were synthesized by using conventional solid-state processing. X-ray diffraction analyses (XRD) and Raman spectroscopy revealed that the lithium and cerium modified SBNBN ceramics had a single phase with perovskite-type orthorhombic structure. The effect of lithium and cerium substitution for A site on structure and electric properties of the SBNBN-based ceramics was investigated. Piezoelectric properties of the SBNBN ceramics were significantly improved by the modification of lithium and cerium. Curie temperature T_c and piezoelectric coefficient d_{33} of the $\text{Sr}_{0.5}(\text{BiNa})_{0.2}(\text{LiCe})_{0.05}\text{Bi}_2\text{Nb}_2\text{O}_9$ ceramics were 583 °C and 28 pC/N, respectively. Reasons for enhancement in piezoelectric properties of the SBNBN ceramics were discussed.

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1. Introduction

Aurivillius-type bismuth layer-structured ferroelectric ceramics (BLSFs) have general formula of $(\text{Bi}_2\text{O}_7)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where A is a mono-, di-, tri-valent ion (e.g. Na^+ , K^+ , Ca^{2+} , Ba^{2+} or Bi^{3+}) or combination of them allowing dodecahedral coordination, B is a transition element (Ti^{4+} , Nb^{5+} or W^{6+}) or combination of cations well suited to octahedral coordination, and m is an integer which represents the number of BO_6 octahedral in the pseudo-perovskite $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ layers between the $(\text{Bi}_2\text{O}_7)^{2+}$ layers. This provides a good possibility for various combinations of dopings in BLSFs [1–6].

BLSFs have received significant attention for their potential applications in high temperature piezoelectric devices, owing to their high Curie temperatures [7]. In addition, they possess low temperature coefficients of dielectric, piezoelectric properties and resonant frequency, low aging rate, and strong anisotropic electromechanical coupling factors, making them suitable for pressure sensors and trapped energy filter, etc. [8]. Recently, considerable efforts have been devoted to the enhancement of piezoelectric properties of high temperature BLSFs [9–15]. However, it is difficult to achieve high piezoelectric performance in ordinary BLSFs with randomly oriented grains structure, due to its plate-like grains and spontaneous polarization restricted to lying in the a – b -plane [16]. As a consequence of the anisotropy of the microstructures and properties, the piezoelectric properties of BLSFs in

directions parallel to the a – b -plane can be significantly enhanced by texturing technologies, such as hot-forging (HF), templated grain growth (TGG) and spark plasma sintering (SPS) [17–19]. But high cost limits their applications in industrial practice. It is desirable to obtain high piezoelectric and perfect electromechanical properties BLSFs piezoelectric ceramics by using conventional sintering method.

It has been reported that A-site modification is more effective than B-site modification in enhancing ferroelectric and piezoelectric properties of BLSFs [14,17]. In addition, it is found that cerium or alkali-cerium complex oxides can significantly enhance the piezoelectric performances in four-layered $\text{M}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ ($\text{M} = \text{Na}, \text{K}$) and/or other Aurivillius-type ceramics [20–22]. In previous study [23], $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) ferroelectric ceramics with bismuth and sodium modification were prepared by using conventional sintering processing. We found that $\text{Sr}_{0.6}(\text{BiNa})_{0.2}\text{Bi}_2\text{Nb}_2\text{O}_9$ has higher Curie temperature ($T_c = 586$ °C) and piezoelectric coefficient ($d_{33} = 22$ pC/N). In the present work, lithium and cerium were used to further modify $\text{Sr}_{0.6}(\text{BiNa})_{0.2}\text{Bi}_2\text{Nb}_2\text{O}_9$ ferroelectric ceramics.

2. Experimental procedures

$\text{Sr}_{0.6-x}(\text{LiCe})_{x/2}(\text{BiNa})_{0.2}\text{Bi}_2\text{Nb}_2\text{O}_9$ (SLCBNBN) ceramics, with x varying from 0.0 to 0.15 (abbreviated as SBNBN, SBNBN-LC5, SBNBN-LC10 and SBNBN-LC15 respectively), were prepared by using the standard solid-state reaction method. Reagent-grade oxide and carbonate powders, Bi_2O_3 (99.9%, Sinopharm Chemical Reagent), SrCO_3 (99%, Sinopharm Chemical Reagent), Li_2CO_3 (99.9%, Sinopharm Chemical Reagent), $\text{Ce}(\text{NO}_3)_3$ (99%, Sinopharm Chemical Reagent) and Nb_2O_5 (99.4%, Sinopharm Chemical Reagent) were used as the starting materials. The powders of these raw materials were mixed and ball milled for 12 h in acetone, followed by calcining at 800 °C for 4 h. The calcined powders were milled again for 24 h. The obtained

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powders were pressed into pellets of 15 mm in diameter and ~1 mm in thickness at 250 MPa for 1 min. The pellets were sintered at 1100 °C for 1 h, covered by alumina crucible followed by furnace cooling.

Crystal structure of the samples was characterized by using an automated diffractometer (XRD; X'Pert PRO MPD, Philips, Eindhoven, Netherlands) with Cu K α_1 radiation with an applied voltage of 40 kV and current of 500 mA. Morphology of the samples was observed by using a scanning electron microscopy with an applied voltage of 20 kV (SEM, JSM-6360LV, Tokyo, Japan). The pellets were polished to the thickness of about 1 mm. Silver paste was daubed on two sides and fired as electrodes at 850 °C for 30 min. Specimens for piezoelectric measurements were poled at 120 °C in silicone oil bath 8 kV/mm for 30 min. Piezoelectric coefficient (d_{33}) was measured by using a piezoelectric d_{33} -meter (ZJ-4NA, Institute of Acoustics Academic Sinica, Beijing, China) at 100 Hz. Dielectric measurement was conducted by using an Agilent 4294A impedance analyzer (Agilent, New Mexico, USA) with an applied voltage of 500 mV over 100 Hz–1 MHz.

3. Results and discussion

XRD of the SLCBNBNO specimens are shown in Fig. 1. The main diffraction peaks are indexed on the basis of orthorhombic symmetry and no secondary phases are detected, which implies that lithium and cerium ions have diffused into the lattices to form solid solutions. The strongest diffraction peak (115) is typical (112 m + 1). The main diffraction peaks of the lithium and cerium modified SBNBN ceramics shift to the higher angles slightly (shown in inset of Fig. 1), which is attributed to the lattice distortion induced by the lithium and cerium ions co-substituting the strontium ions of SBNBN ceramic. The complex structure caused by the lattice distortion may lead to the enhanced polarizability of the specimens [24].

Room temperature Raman spectra of the SLCBNBNO are shown in Fig. 2. By fitting the spectra and deconvolution of the fitting curves into individual Gaussian components, the peak position of each component, i.e., the natural frequency (cm⁻¹) of each Raman active mode was obtained in these specimens. As shown in Fig. 2, the Raman spectrum exhibits intense phonon modes at about 176, 207, 436, 573 and 833 cm⁻¹, which are related to the orthorhombic phase and are in good agreement with those reported by Nelis et al. [25]. The modes at about 176 and 207 cm⁻¹ can be attributed to the vibrations of A site ions, which indicates that the vibrations of A site ions are changed by the introduction of lithium and cerium. The mode at about 436 cm⁻¹ is completely dominated by the Bi–O₃ force constant [26–28]. The peak at about 573 cm⁻¹ corresponds to an unbending sublattice mode and indicates that the equivalent and opposite displacements of positive and negative ions are slightly changed. The mode at about 833 cm⁻¹ can be related to a symmetric stretching of the octahedral NbO₆ [29,30]. The mode at about 833 cm⁻¹ slightly shifting to lower frequency

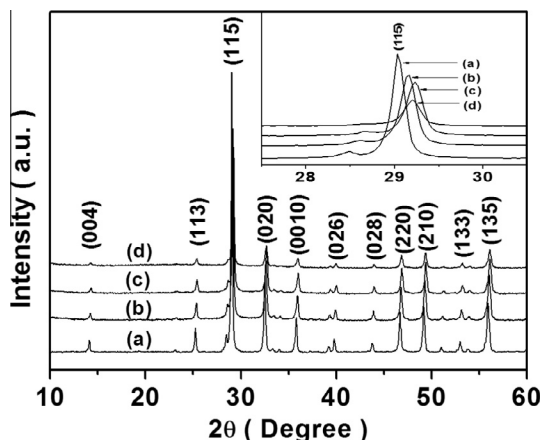


Fig. 1. XRD patterns of (a) SBNBN, (b) SBNBN-LC5, (c) SBNBN-LC10 and (d) SBNBN-LC15.

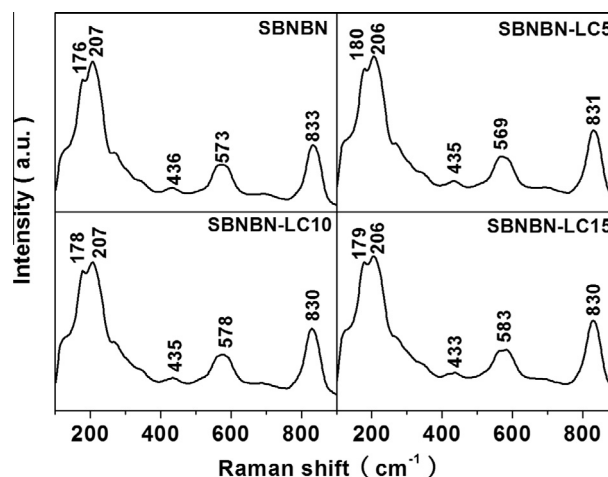


Fig. 2. Room temperature Raman spectra of the SLCBNBNO.

is attributed to the lattice distortion by the introduction of lithium and cerium introduction for A site of SBNBN.

Cross-sectional images of the SLCBNBNO samples are shown in Fig. 3. Plate-like morphologies are observed for all specimens, which is a typical characteristic of Aurivillius ceramics due to the anisotropic nature of the crystal structure. No second phases are detected, which is consistent with the XRD results. Grain micrographs of all the specimens are ruptured. Meanwhile, average grain size of the SLCBNBNO increases obviously and the grain boundaries decrease due to the introduction of lithium and cerium, which indicates that the sintering temperature is decreased.

Temperature dependence of dielectric permittivity and loss at 100 kHz are shown in Fig. 4. The dielectric permittivity maximums of all the specimens are gradually decreased with increasing content of lithium and cerium. Curie temperature (T_c) of the SBNBN specimen is found to be about 586 °C and T_c of the SLCBNBNO specimens is decreased slightly with increasing concentration of lithium and cerium ($T_c = 582$ °C, SBNBN-LC15). The changes in T_c of the SLCBNBNO could be explained by considering the dopant concentration and tolerance factor (t) of perovskite-layer units. The tolerance factor for the perovskite-layer units (AB_2O_7)²⁻ is given by:

$$t = (r_A + r_O) / \sqrt{2}(r_B + r_O) \quad (1)$$

where r_A , r_B and r_O are the ionic radius of an A-site cation, a B-site cation and an oxygen ion, respectively [31]. Clearly, t decreases as the lithium and cerium concentration is increased, because Li⁺ (0.68 Å) and Ce³⁺ (1.03 Å) have smaller radius than Sr²⁺ (1.12 Å). It has been shown that a decrease in T_c is closely related to a decrease in t . This trend is consistent with those of other (LiCe) modified Aurivillius oxides (NaBi)_{0.480.04}Bi₂Nb₂O₉ and (Na_{0.84}K_{0.16})_{0.5}Bi_{4.5}Ti₄O₁₅ [9,11,14]. Moreover, lower dielectric loss is observed in SLCBNBNO, which starts to increase gradually above 450 °C. This could be attributed to the high temperature conductivity induced by defects.

Fig. 5 shows temperature dependence of resistivity ρ for the SLCBNBNO materials. SBNBN has the highest resistivity. However, the resistivity of the modified samples is still above 10⁶ Ω cm at 550 °C, which is important for their use in high temperature piezoelectric devices [9]. The activation energy E_a was calculated according to Arrhenius law:

$$\rho = \rho_0 \exp \left(\frac{-E_a}{kT} \right) \quad (2)$$

where k is Boltzmann constant, ρ_0 is the pre-exponential factor and E_a is the activation energy. The activation energies E_a were calcu-

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