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Effects of $SmCoO_3$ on the microstructure and piezoelectric properties of $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics

Lin Shao [a], Ruiqing Chu [a,*], Zhijun Xu [a], Yong Liu [a], Mingli Chen [a], Jianli Zhao [b], Guorong Li [c]

[a] College of Materials Science and Engineering, Liaocheng University, Liaocheng 252059, China
[b] College of Mathematical Sciences, Liaocheng University, Liaocheng 252059, China
[c] The State Key Lab of High Performance Ceramics and Superfine microstructure, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, China

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ABSTRACT

$(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (abbreviated to BNBT6) ceramics doped with 0–0.6 mol.% $SmCoO_3$ were synthesized by the conventional solid-state reaction method, and the effect of $SmCoO_3$ addition on the dielectric and piezoelectric properties was investigated. X-ray diffraction (XRD) patterns show that $SmCoO_3$ diffuses into the lattice of the BNBT6 ceramics to form a solid solution with a pure perovskite structure. SEM images indicate that the addition of $SmCoO_3$ caused a remarkably promoted grain growth. Our results reveal that both the piezoelectric and electromechanical properties of BNBT6 ceramics could be greatly improved by certain amount of $SmCoO_3$ substitutions. At room temperature, the BNBT6 ceramics doped with 0.4 mol.% $SmCoO_3$ exhibit the optimum properties with high piezoelectric constant ($d_{33}=144$ pC/N), high planar coupling factor ($k_p=29.1\%$), and high mechanical quality factor ($Q_m=219$).

1. Introduction

Nowadays, lead-free piezoelectric ceramics have received much attention, as potential alternatives to the widely used lead zirconate titanate (PZT) based piezoelectric ceramics. Among all the lead-free ceramics, Bi1/2Na1/2TiO3 (abbreviated as BNT) is considered as an excellent lead-free piezoelectric ceramic candidate because of its large remanent polarization ($P_r=38\ \mu C/cm^2$) and high Curie temperature ($T_c=320\ ^\circ C$) [1]. However, high conductivity and high coercive field ($E_c=73$ kV/cm) can cause problems in the poling process, and thus limit its practical application [1–3]. Besides, pure BNT ceramic exhibits a weak piezoelectric property ($d_{33}=73$–80 pC/N) [4,5]. In order to improve its properties, several BNT-based solid solutions such as BNT-BaTiO3 [6], BNT-(Ba,Sr)TiO_3 [7], BNT-$Bi_{0.5}K_{0.5}TiO_3$ [8–10] have been studied. Compared with pure BNT, the BNT-BT compositions near the morphotropic phase boundary (MPB) show excellent piezoelectric properties. However, for practical applications, the piezoelectric and electromechanical properties of BNT-BT ceramics need to be further enhanced.

Fu et al. [11] found that Sm_2O_3 doping could improve the piezoelectric constant d_{33} of BNBT6 ceramic significantly with the decrease of mechanical quality factor Q_m. Xu et al. [12] reported that the CoO doped 0.93BNT-0.07BT ceramics showed a high mechanical quality factor Q_m and a relatively low piezoelectric constant d_{33}. As known, high d_{33} and Q_m are in favor of the practical application of lead-free piezoelectric ceramics [13]. It motivated us to examine the effect of $SmCoO_3$ on piezoelectric properties of BNBT6 ceramics.

In this paper, the $SmCoO_3$-doped $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics were synthesized by the conventional solid-state reaction method. The effects of $SmCoO_3$ additives on the phase composition, microstructure, dielectric and piezoelectric properties were investigated.

2. Experimental

Powders with a nominal composition of $(1-x)(0.94Bi_{0.5}Na_{0.5}TiO_3\text{-}0.06BaTiO_3)+x$ mol.% $SmCoO_3$ ($x=0$–0.6) (abbreviated to BNBT6-x) were fabricated by the conventional solid-state reaction method. Reagent grade oxide or carbonate powders of Na_2CO_3 (99.8%), TiO_2 (99.5%), Bi_2O_3 (99.64%), $BaCO_3$ (99%),Sm_2O_3 (99.9%) and Co_2O_3 (99%) (All raw materials were made by Sinopharm Chemical Reagent Co., Ltd) were used as starting materials. All the starting materials were mixed by ball milling for 12 h and then were calcined at 900 °C for 2 h.

* Corresponding author. Tel.: +86 635 8230913; fax: +86 635 8230923.
E-mail address: rqchu@lcu.edu.cn (R. Chu).

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After calcination, the mixture was ball milled again and mixed thoroughly with a poly vinylbutyral (PVB) binder solution and then pressed into 12 mm diameter and 1.5 mm thickness disks. After burning off PVB, the pellets were embedded into pre-prepared powder with similar composition and sintered in air in the temperature range of 1140–1160 °C for 2 h. The bulk density of the sintered samples was determined by the Archimedes method. The phase structure was examined by X-ray diffraction (XRD) analysis using a Cu K_α radiation ($\lambda = 1.54178$ Å) (D8 Advance, Bruker Inc., Germany). The surface morphology of the ceramics was studied by scanning electron microscope (SEM) (JSM-5900, Japan).

For the electrical measurements, silver paste was coated on both sides of the sintered samples and fired at 740 °C for 20 min to form electrodes. Dielectric properties were measured using an Agilent 4294 A precision impedance analyzer (Agilent Inc., America) in the temperature range from room temperature to 500 °C. *P–E* hysteresis loops were recorded using an aix-ACCT TF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany). For the measurement of piezoelectric properties, samples were poled in silicon oil at room temperature under 70–100 kV/cm for 15 min. The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (YE2730 SINOCERA, China). The planar electromechanical coupling factor k_p and mechanical quality factor Q_m were calculated from the following equations:

$$\frac{1}{kp} = \sqrt{0.395\frac{f_r}{fa-fr} + 0.574} \quad (1)$$

$$\frac{1}{Qm} = 2frRC\left(\frac{fa^2 - {f_r}^2}{{f_a}^2}\right) \quad (2)$$

where f_r and f_a are the resonance frequency and the anti-resonance frequency respectively, R is the resonance impedance, and C is the capacitance at 1 kHz. All factors of f_r, f_a, R, C in the formulas were measured through an impedance analyzer (HP 4294 A) on the basis of IEEE standards.

3. Results and discussion

3.1. Structural and microstructural studies

The X-ray diffraction (XRD) patterns of 0.94BNT-0.06BT ceramics with different addition of $SmCoO_3$ have been shown in Fig. 1. All ceramics exhibit a pure perovskite structure and no second phases can be detected. Further XRD analysis is performed in the 2θ ranges from 45° to 48° as shown in Fig. 1(b). Obvious splitting of XRD peaks is detected for all specimens. The splitting peaks can be assigned to a (0 0 2)/(2 0 0) peak splitting according to a rhombohedral symmetry and a tetragonal symmetry, respectively [14], suggesting that the tetragonal–rhombohedral phase structure exists in all the ceramics. Moreover, it can be seen that the specimens displayed a progressive peak shift towards higher diffraction angle directions with increasing amounts of $SmCoO_3$, indicating the shrinkage of cell volumes. It is considered that the incorporation of Sm^{3+} and Co^{3+} into the BNBT6 ceramics changed the crystal structure. According to Shannon's effective ionic radius [15], Sm^{3+} (0.98 Å) can occupy the A-site of Bi^{3+} (1.17 Å) or Na^{+} (1.18 Å), while Co^{3+} (0.63 Å) can substitute the B-site of Ti^{4+} (0.68 Å). Both of the substitutions can cause a distortion in the crystal lattice. It is suggested to be the main reason for the peak shift.

Fig. 2 shows the SEM micrographs of the BNBT6 ceramics as a function of the $SmCoO_3$ contents sintered at 1150 °C for 2 h. All the obtained samples were well sintered and got relatively high densities in the range of 5.69–5.80 g/cm^3, which are more than 95% of the theoretical values. Moreover, the grain size is strongly dependent on the $SmCoO_3$ contents. As can be seen in Fig. 2, for the pure BNBT6 ceramics, the average grain size is about 2 μm and the ceramics are inhomogeneous. The specimens display an evidently promoted grain growth with the addition of $SmCoO_3$. The change tendency of grain size can be qualitatively explained with the generation of A-site vacancies and oxygen vacancies. Na^{+} substituted by Sm^{3+} can lead to some A-site vacancies in the lattice, which facilitate the

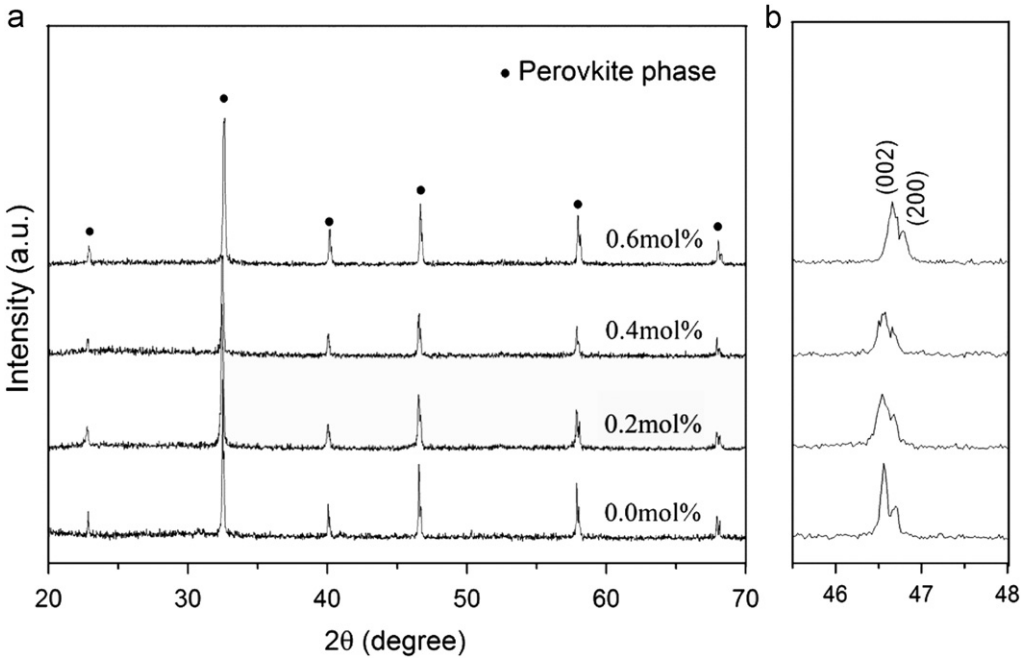

Fig. 1. XRD patterns of the $(1-x)$BNBT6-x mol.% $SmCoO_3$ ceramics.