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Dielectric and piezoelectric properties of Sb^{5+} doped $(NaBi)_{0.38}(LiCe)_{0.05}[]_{0.14}Bi_2Nb_2O_9$ ceramics

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ABSTRACT

Sb^{5+}-doped $(NaBi)_{0.38}(LiCe)_{0.05}[]_{0.14}Bi_2Nb_2O_9$ (represented as NBNLCS-*x*, where [] represents A-site vacancies) ceramics were prepared by the conventional solid-state route. The ceramics well sintered to approach ~98.5% theoretical density and the tetragonality of crystal structure increased with Sb^{5+} additions. However, the Curie temperature (T_C) and the piezoelectric coefficient (d_{33}) of Sb^{5+}-modified ceramics gradually decreased. The 3 mol% Sb^{5+}-doped samples exhibited optimum properties with a d_{33} value of ~22 pC/N planar electromechanical coupling factor (k_p) of ~11.2% and relatively high T_C of ~765 °C. These results indicate that NBNLCS-*x* material is a promising candidate for high-temperature piezoelectric applications.

1. Introduction

Environmental legislation and working temperature limitations are driving research efforts into find candidates for lead zirconate titanate (PZT) piezoelectric ceramics. Thereby, some lead-free piezoelectric materials, such as well-known (K, Na)NbO_3 and (Bi, Na)TiO_3, have drawn much attention and made some breakthrough in recent years [1–5].

However, these materials can be hardly used in some hazardous environment due to the relatively low Curie-temperature. Recently, BLSFs have attracted much attention due to their high ferro-paraelectric transition temperature (T_C) [6], high anisotropic properties [7], low frequency temperature coefficients [8–10], large spontaneous polarization [11], and low ageing rate [12]. Recently, it was found that La^{3+} doped Bi_3TiNbO_9 thin films exhibited the large nonlinear absorption coefficient, making them a promising candidate for absorbing-type optical application [13]. However, it is usually difficult for these materials to obtain high piezoelectric coefficient d_{33} by using the conventional fabrication processes, because their spontaneous polarization is restricted in the *a–b* plane. New approaches to obtain textured ceramics in this material or others-hot-forging [14], reactive template grain growth [15], and tape casting [16], etc. – have been explored so as to improve the poor piezoelectric properties of BLSFs. As compared to the conventional mixed oxides route, these processes are more expensive and need a longer manufacture cycle.

Some relative high piezoelectric properties have been achieved via changing chemical compositions, such as (LiCe)- modified $(Na_{0.52}K_{0.42}Li_{0.06})_{0.5}Bi_{2.5}(Nb_{1.88}Sb_{0.06}Ta_{0.06})O_9$ [17] and W/Cr-doped $Bi_4Ti_3O_{12}$ [18], for which the optimal d_{33} values are 28 pC/N and 22 pC/N, respectively. However, the T_C values for these materials are less than 650 °C. Among the Aurivillius phase materials, $Na_{0.5}Bi_{2.5}Nb_2O_9$ (NBN) -based ceramics possess a high T_C of ~780 °C [19] and good piezoelectric coefficients by introducing $LiNbO_3$ or (Li, Ce) dopants [19,20]. Nevertheless, literature mainly focused on ionic substitution at A-sites, whereas the B sites modification is hitherto rarely reported. Quinquevalent antimony ion (Sb^{5+}) has been proved to be a desirable dopant for the improvement of piezoelectric property of Nb-based perovskite systems [21]. It was also found that Sb^{5+} and Ta^{5+} doped $Bi_4Ti_3O_{12}$ compounds possessed a high d_{33} value (~35 pC/N) recently [22]. As a result, this study aims to investigate the effects of antimony substitution for niobium on the properties of NBN based ceramics.

2. Experimental

$(NaBi)_{0.38}(LiCe)_{0.05}[]_{0.14}Bi_2Nb_{2-x}Sb_xO_9$ [abbreviated as NBNLCS-*x*] (where *x* = 0,1,3,5 mol%) ceramics were prepared by the conventional solid state route. The raw material was Bi_2O_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Sb_2O_3 (98%), Li_2CO_3 (99.99%), and CeO_2 (99.99%). All powders were weighed according to the stoichiometric compositions and then mixed for 24 h using ethanol as solvent and zirconia balls as the milling media. Calcination was carried out at ~800 °C for 4 h with a heating rate of ~3 °C min^{-1}, and then these mixtures were milled again in the same conditions. The powders were dried and then pressed into pellets using the polyvinyl alcohol (PVA) as a binder. After burning out the PVA at ~550 °C, the pellets were sintered at ~1050 °C for 2 h in a sealed crucible to prevent the volatilization. For the electrical measurements, silver electrodes were fired on both surfaces of the pellets at 700 °C for 10 min in air. Samples were poled in silicon oil at 150 °C for 10–15 min under a dc electric field of 9–11 kV/mm.

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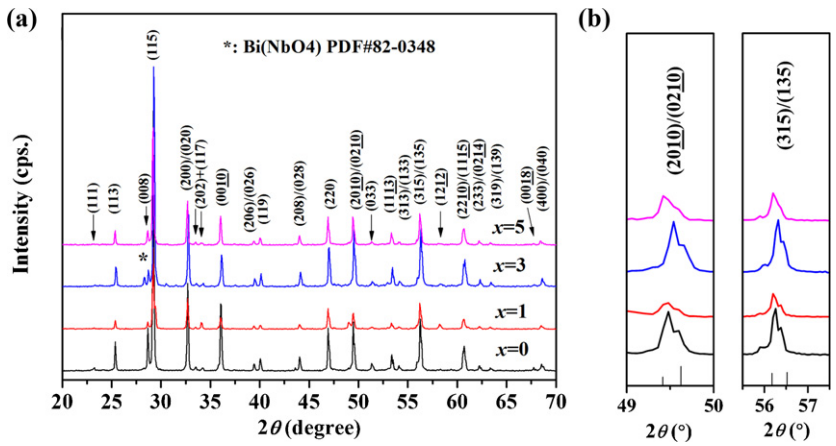

Fig. 1. XRD patterns for NBNLCS-based ceramics sintered at 1050 °C for 2 h.

The density of the ceramics was determined using the Archimedes method. The crystalline structure of the ceramics was examined using an X-ray diffractometer (DX1000, Dandong, China), employing Cu-Kα radiation (λ = 1.54178 Å). The microstructure characterization of the ceramics was conducted by scanning electron microscopy (SEM) (JSM-5900, JEOL Ltd. Tokyo, Japan). The dielectric characteristics of the ceramics were determined by an impedance analyzer (Agilent, HP4294A, US) using IEEE resonance methods. The temperature dependence of dielectric properties of the ceramics was examined using a programmable furnace with a LCR analyzer (HP 4980A, Agilent, US). Piezoelectric measurements were made using a Burlincourt-type d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China). Thermal depoling experiments were conducted by holding the poled samples for 1 h at each temperature, cooling to room temperature, measuring the d_{33} value, and repeating the procedures up to 780 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of NBNLC-based piezoelectric ceramics, and all patterns can be indexed by the PDF#54-1054 card. As shown in Fig. 1(a), secondary phase is not observed in these materials except for $x = 3$ mol%, which might be related to $BiNbO_4$ (PDF#82-0304). The presence of secondary phase was probably due to the volatilization of Na_2O during the preparation process; in fact, volatilization of alkaline element was usually found in (K, Na)NbO_3 compounds [23]. Besides this, the appearance of secondary phase confirms that the A-site vacancies reach the maximum solid state solubility limit. The diffraction peak with highest intensity is the

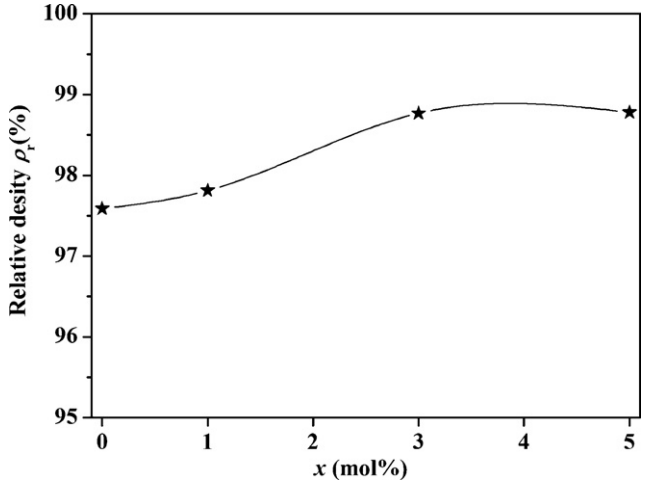

Fig. 2. Relative density for NBNLCS-based ceramics sintered at 1050 °C for 2 h.

(1 1 5) reflection, which is the typical characteristic of Aurivillius phase materials [24]. The crystalline structure is orthorhombic at room temperature when $x \leq 3$ mol%. The (2 0 $\underline{10}$)/(0 2 $\underline{10}$) and (1 3 5)/(3 1 5) peaks tended to merge into one peak with further increasing Sb^{5+} contents, respectively, indicating the structure

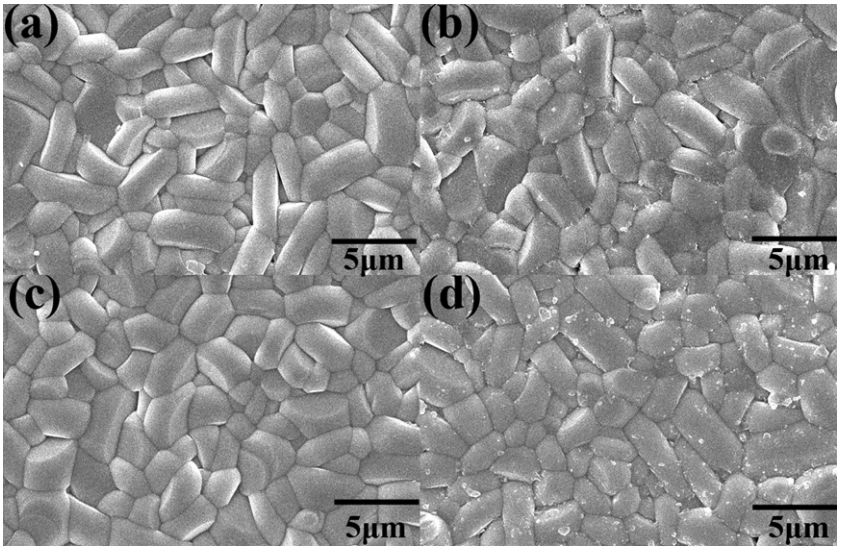

Fig. 3. Surface morphologies of the ceramics with (a) $x = 0$, (b) $x = 1$, (c) $x = 3$, and (d) $x = 5$.

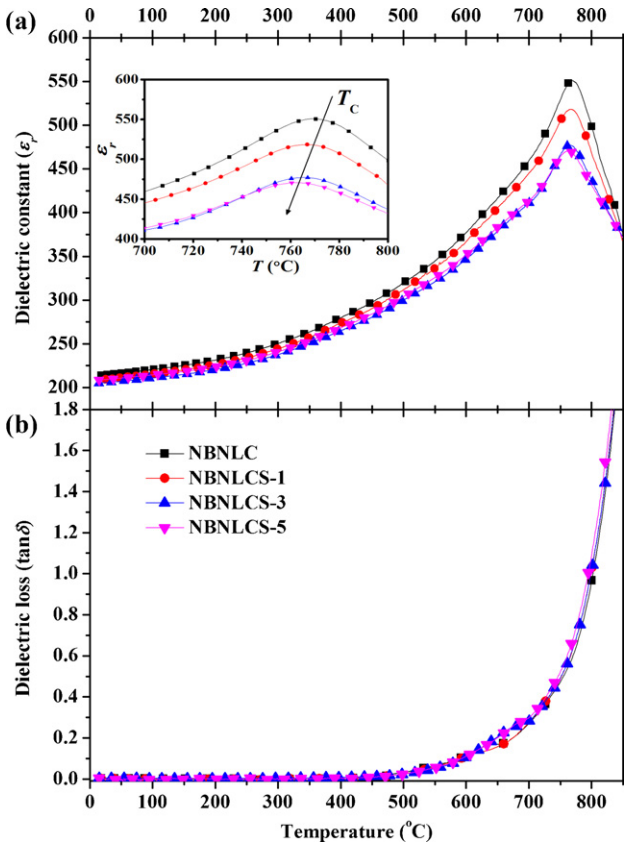

Fig. 4. Temperature dependence of (a) dielectric constant (ε_r) and (b) dielectric losses (tan δ) for NBNLCS-*x* ceramics, measured at 1 MHz.

changed from orthorhombic to pseudo-tetragonal symmetry, as shown in Fig. 1(b). This result suggests that the addition of Sb^{5+} into B sites of NBN pseudo-perovskite unit cells increases the tetragonality of the crystal structure; similar effect was found in Sb^{5+}-modified (K, Na)NbO_3 systems [21].

Fig. 2 shows the relative density of NBNLCS-*x* ceramics sintered at 1050 °C for 2 h. The density of the samples increases slightly with the contents of antimony increasing. All ceramics with small amounts of Sb^{5+} have a high relative density (~98.5%).

Fig. 3 presents the surface micrographs of NBNLC-based ceramics. Because of the high grain growth rate in the direction perpendicular to the *c*-axis, the grain growth of all ceramics is structurally anisotropic [16,17]. In addition, few pores on the surfaces can be observed from Fig. 3, demonstrating the samples have high density.

Fig. 4 shows the temperature dependence of dielectric constant and loss tangent of NBNLC-based ceramics measured at 1 MHz. The Curie temperature T_C decreases from ~770 °C to ~761 °C with the addition of Sb^{5+}. Shimakawa et al. [25] suggested that the T_C of Aurivillius phase materials depended strongly on the crystal structure distortion. Since the ionic radius of $^{VI}Sb^{5+}$ (0.60 Å) is smaller than that of the $^{VI}Nb^{5+}$ ion (0.64 Å) [26], the Curie temperature should increase by the introduction of Sb^{5+} dopants [27]. Compared to the sizes of A-site cations and oxygen ions, however, the change arising from the substitution of Sb^{5+} for Nb^{5+} is so small that can be neglected, and thus the substitution does not make a significant effect on the crystalline structure. On the other hand, from the point of view of ideal ionic model, there are two 4d electrons in the Sb^{5+} ion, but none in the Nb^{5+} ion. Since the electron in the 4*d* orbital is more extensive than that in the *s* or *p* orbital, the Sb^{5+} dopants increase the length of (Nb, Sb)–O bonds, reducing the lattice distortion and increasing the tetragonality of the composition. Consequently, the T_C value decreased with the increasing Sb^{5+} dopants. In addition of this, it was found from Fig. 4(b) that the dielectric loss was very low for all samples when the measurement temperature is below 500 °C.

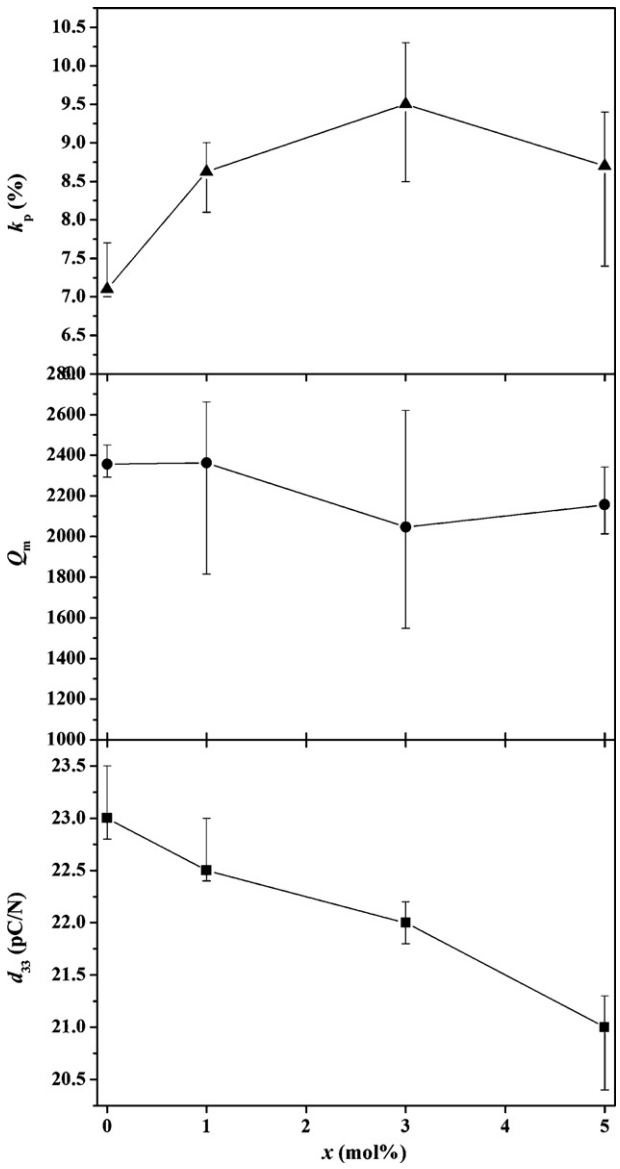

Fig. 5. Variations of average d_{33}, k_p, Q_m values for NBNLCS-*x* ceramics as a function of *x*.

Fig. 5 shows the variations of the average d_{33}, k_p, and Q_m values vs. *x*. The average d_{33} values decreased slightly with the increase in the concentration of antimony, but still maintained a high level of ~21.0 pC/N. In the case of Nb-based materials, the introduction of Sb^{5+} ions increases the tetragonality, thereby increasing the spontaneous polarization; whereas it is different with respect to the BLSFs. Since the high temperature paraelectric phase of BLSFs corresponds to tetragonal symmetry, the higher degree of tetragonality of crystal structure means the lower level of spontaneous polarization. It is, therefore, reasonable to understand that the d_{33} values decreased with the increasing Sb^{5+} dopants. Moreover, the average k_p values increased with Sb^{5+} content up to $x = 3$ mol%, and then decreased with the further increase of *x*. However, the trend of average Q_m values is opposite to that of k_p values. A-site vacancies, which were induced by the evaporation of alkaline metal oxides, facilitated the movement of domain walls, which directly led to the increase of inner friction, and thus decreased Q_m.

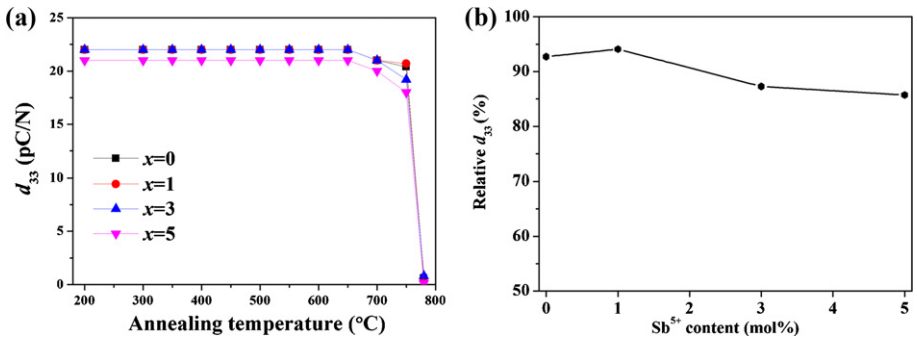

Fig. 6. Effects of thermal behavior on piezoelectric properties for NBNLCS-based ceramics: (a) the change of d_{33} values after annealing for 1 h; (b) the relative d_{33} values annealed at 750 °C for 1 h as a function of Sb^{5+} contents.

The thermal annealing behavior of NBNLCS-*x* ceramics is shown in Fig. 6. There is a slight decrease in d_{33} values when the annealing temperature is below 650 °C (see Fig. 6(a)). The d_{33} values of all samples maintain over 85% of their initial values even if the temperature reached up to 750 °C, as shown in Fig. 6(b), indicating that the NBNLCS-*x* ceramics have a good thermal stability. For all compositions, the d_{33} values decreased rapidly, and tended to be zero when the temperature was above the T_C. These results suggest that NBNLCS-*x* ceramics might be an appropriate candidate for high temperature applications. However, to evaluate the performance of BLSFs, it is necessary to measure the real-time piezoelectric properties at high temperature, as reported by Villegas [28].

4. Conclusions

Sb^{5+} doped $(NaBi)_{0.38}(LiCe)_{0.05}[]_{0.14}Bi_2Nb_2O_9$ piezoelectric ceramics were prepared by the conventional solid state method. The NBNLCS-*x* ceramics have typical Aurivillius phase structure, and the secondary phase was found in the NBNLCS-3 sample owing to the volatilization of the alkaline metal oxides. The Curie temperature T_C and the piezoelectric constant d_{33} value decreased slightly with the increase of antimony. All samples possess a good thermal stability. These results confirm that NBNLCS-based ceramics can be potential materials for high-temperature piezoelectric applications.

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