Effects of (LiCe) co-substitution on the structural and electrical properties of $CaBi_2Nb_2O_9$ ceramics*

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The piezoelectric, dielectric, and ferroelectric properties of the (LiCe) co-substituted calcium bismuth niobate ($CaBi_2Nb_2O_9$, CBNO) are investigated. The piezoelectric properties of CBNO ceramics are significantly enhanced and the dielectric loss $\tan\delta$ decreased. This makes poling using (LiCe) co-substitution easier. The ceramics (where □ represents A-site Ca^{2+} vacancies, possess a pure layered structure phase and no other phases can be found. The $Ca_{0.88}(LiCe)_{0.04}\square_{0.04}Bi_2Nb_2O_9$ ceramics possess optimal piezoelectric properties, with piezoelectric coefficient (d_{33}) and Curie temperature (T_C) found to be 13.3 pC/N and 960 °C, respectively. The dielectric and piezoelectric properties of the (LiCe) co-substituted CBNO ceramics exhibit very stable temperature behaviours. This demonstrates that the CBNO ceramics are a promising candidate for ultrahigh temperature applications.

Keywords: co-substitution, structural properties, electrical properties, $CaBi_2Nb_2O_9$

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1. Introduction

Piezoelectric ceramics such as $Pb(Zr,Ti)O_3$ (PZT) have been widely used in sensors, transducers, actuators, and other important devices for decades.[1−4] PZT Curie temperature (T_C) is about 490 °C, which corresponds to the paraelectric–ferroelectric transition temperature and is associated with an anomaly in the dielectric constant. It therefore sets an upper temperature limit to the application of ferroelectric ceramics.[3−6] When an operating temperature of 400 °C or higher is required, the choice of materials for high-temperature piezoelectric transducers is limited.[3,4] When an operating temperature up to 750 °C is required, there are no suitable commercial ceramics available. The two-layer Aurivillius phase piezoelectric ceramics calcium bismuth niobate ($CaBi_2Nb_2O_9$, CBNO) is chosen herein due to its high Curie temperature ($T_C > 940$ °C),[5,6] which is made up of $(CaNb_2O_7)^{2-}$ and $(Bi_2O_2)^{2+}$ layers. The CBNO ceramic is a good lead-free candidate for high-temperature piezeoelectric applications up to 800 °C.[4−6] However, the piezoelectric performances of pure CBNO ceramics were found to be rather low because of the two-dimensional orientation restriction on the rotation of their spontaneous polarization (P_s) as well as their high coercive field (E_C).

Recently, we have successfully prepared A-site cerium co-substituted CBNO–Ce piezoelectric ceramics, which show superior piezoelectric properties and excellent thermal stability.[7−9] The optimal CBNO–0.50 wt% Ce piezoelectric ceramics possess a high piezoelectric coefficient $d_{33} = 10.2$ pC/N and a high T_C above 925 °C. It is believed that A-site modification is more obvious than B-site modification in enhancing the ferroelectric and piezoelectric properties of Aurivillius phase piezoelectric ceramics, since the cations in B-site are similar in size but do not play a major structural role in the polarization process of Aurivillius phase piezoelectric ceramics.[5−8] Yan *et al.* and Wang *et al.* have achieved distinct results in the studies of Aurivillius phase piezoelectric ceramics substitution, whereas few studies have been reported on the (LiCe) co-substituted CBNO.[3−23] Therefore, in this paper, the ordinarily fired A-site (LiCe) co-substituted $Ca_{1-3/2x}(LiCe)_{x/2}\square_{x/2}Bi_2Nb_2O_9$ (where □ represents A-site Ca^{2+} vacancies) ceramics are fab-

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ricated using conventional solid state processing methods, with $x$ranging from 0 to 0.12. The microstructure, dielectric, piezoelectric, and ferroelectric properties are investigated.

2. Model and method

The starting raw materials included high-purity $CaCO_3$ (99.9%), Bi_2O_3 (99.975%), Nb_2O_5 (99.99%), Li_2CO_3 (99.9%), and CeO_2 (99.9%). The weighed chemicals were wetmilled in polyethylene bottles of ethanol using ZrO_2 balls for 12 h. The milled powder was dried and calcined at 950 °C for 2 h at a heating rate of 4 °C/min. After the calcination, the mixture was milled again under the same condition. The milled powder was dried, ground, and then granulated with a polyvinyl alcohol (PVA) binder. The granulated powder was pressed into discs with a diameter of 10 mm and a thickness if 0.9 mm at a pressure of 150 MPa. After burning out the PVA at 650 °C, the green compacts were placed in sealed Al_2O_3 crucibles and fully surrounded by powder of matching compositions. By ordinary firing, the CBN samples were sintered at 1150 °C for 2 h at a heating rate of 2°/min, and then cooled down to room temperature. It is found that (LiCe) co-substitution can significantly lower the sintering temperature (and/or sintering time) and can density the CBNO ceramics. Therefore, the (LiCe) co-substituted CBNO ceramics could be sintered at 1080 °C for 1 h. The final samples were about 9 mm in diameter and 0.8 mm in thickness. The density of the sintered samples was determined by the Archimedes method. Based on the theoretical density ($\rho_{\rm td} = 7.045$ g/cm^3, JCPDF No. 49–608), the relative density $\rho_{\rm rd}$ was also given for comparison.

The X-ray diffraction (XRD) patterns for the ceramics and powders were obtained with an X-ray diffractometer (D8 Advance, Bruker AXS GMBH, Karlsruhe, Germany) using Cu$K\alpha_1$ radiation. Microstructure characterization of the sintered ceramics was conducted by scanning electron microscopy (SEM, JEOL JSM 6700). To measure the room temperature electrical and dielectric properties, platinum paste electrodes were fixed on both surfaces of the sintered pellets and were fired at 850 °C for 30 min in air. The dielectric spectra measurements were performed using a 4294A impedance analyser at a frequency of 1 MHz as a function of temperature. Samples were poled in silicone oil at 140 °C for 10–20 min under a direct-current (DC) electric field of 10–15 kV/mm. The piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} meter (ZJ-2, Institute of Acoustics, Academic Sinica, Beijing, China).

3. Results and discussion

Figure 1 shows the XRD patterns of CBNO-x (x = 0.00, 0.04, 0.08, 0.12) ceramics scanned in the range 2θ of 15°–70°. By comparision, all the diffraction patterns $x = 0.00$ and CBNO-x ($x = 0.04$, 0.08, 0.012) ceramics are in agreement with that of pure CBNO (Joint Committee on Powder Diffraction Standards No. 49–608). The highest intensity of the diffraction peak is (115) in all the XRD patterns, which is consistent with the fact that the most intense reflection of the Aurivillius phase is all of the type of $(11(2m+1))$.[5–10] It can be seen from Fig. 1 that the ceramics possess a pure phase of a layered structure and no other phases are found, which is due to the diffusion of Li^+ and Ce^{3+} into the lattices to form solid solutions. With the increase of x, the diffraction peak

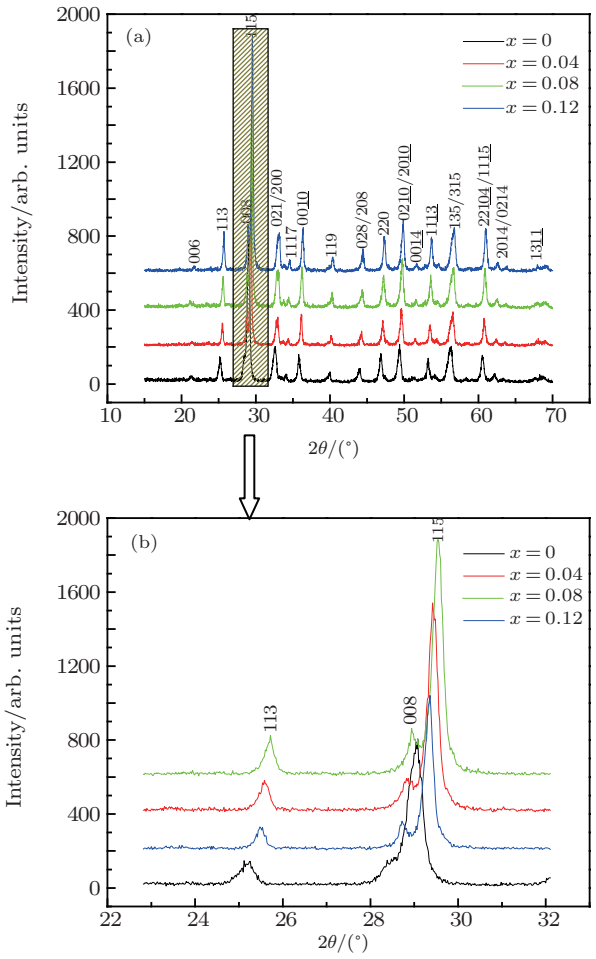


Fig. 1. (colour online) XRD patterns of pure and (LiCe)-substituted CBNO piezoelectric ceramics as a function of x. (a) $2\theta = 15°$–$70°$ and (b) $2\theta = 22.6°$–$32°$.

position moves to the higher angles side because of a decrease in the cell size. The complex structure resulting from lattice distortions may lead to enhanced polarizability of the ceramics.[9−23]

Figure 2 presents the SEM micrographs of the fractured CBNO-based ceramics. As shown in Fig. 2, the grain growth is highly structurally anisotropic, due to the high grain growth rate in the direction perpendicular to the c-axis of the Aurivillius phase crystal. The plate-like grain structure is also a characteristic of Aurivillius phase ceramics.[8−23] The CBNO ceramic exhibits the smallest grain size compared with its (LiCe) co-substituted counterparts, indicating that the addition of (LiCe) enhances the grain growth of the ceramics. It can be also seen that the length l and the thickness t of the plate-like grains increase with the contents of lithium and cerium, though the change of the length is not so obvious as that of the thickness.

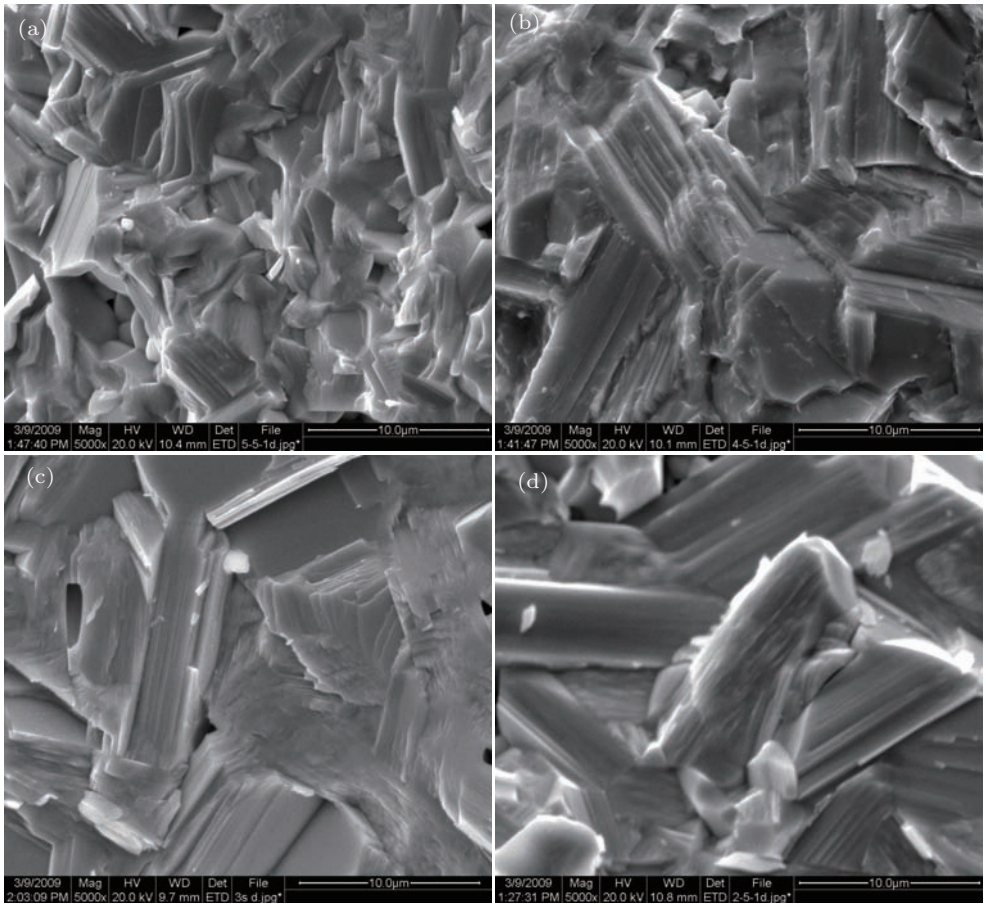


Fig. 2. Micrographs of the fracture surfaces of the CBNO-x materials for (a) $x = 0.00$, (b) $x = 0.04$, (c) $x = 0.08$, and (d) $x = 0.12$.

Figure 3 presents the relative permittivity $\varepsilon_{\rm r}$ and dielectric loss tan δ measured at 1 MHz as a function of temperature for pure CBNO and CBNO-x (x = 0.04, 0.08, 0.12) ceramics. The Curie temperatures are found to be 943 °C and 967 °C for pure CBNO and CBNO-0.04 ceramics, respectively, indicating that (LiCe) Co-substitution in CBNO materials increases the Curie temperature. The effective ionic radius[11] of octahedral coordination $^{\rm XII}(Li_{0.5}Ce_{0.5})^{2+}$ (125 pm), which was estimated according to the effective ionic radius of $^{\rm XII}Li^{+}$ (115 pm) and $^{\rm XII}Ce^{3+}$ (134 pm), is lower than that of $^{\rm XII}Ca^{2+}$ (134 pm). Subbarao[12] reported that the Curie temperature increases with decreasing size of A-site cations in Aurivillius phase. Gai *et al.*[17] reported that the Curie temperature of the ceramics gradually increases from 668 to 684 °C with increasing (LiCe) co-substitution in $[(Na_{0.5}K_{0.5})Bi]_{0.5-x}(LiCe)_{x/2}\square_{x/2}Bi_2Nb_2O_9$-based ceramics ($x \geq 0.04$). Therefore, the small-sized A-site cation substitution results in high Curie temperature,

and the (LiCe)-substitution increases the Curie temperature of CNBO ceramics. From Fig. 3, it is also found that the dielectric loss tan δ is very low, especially when the temperature is lower than 600 °C.

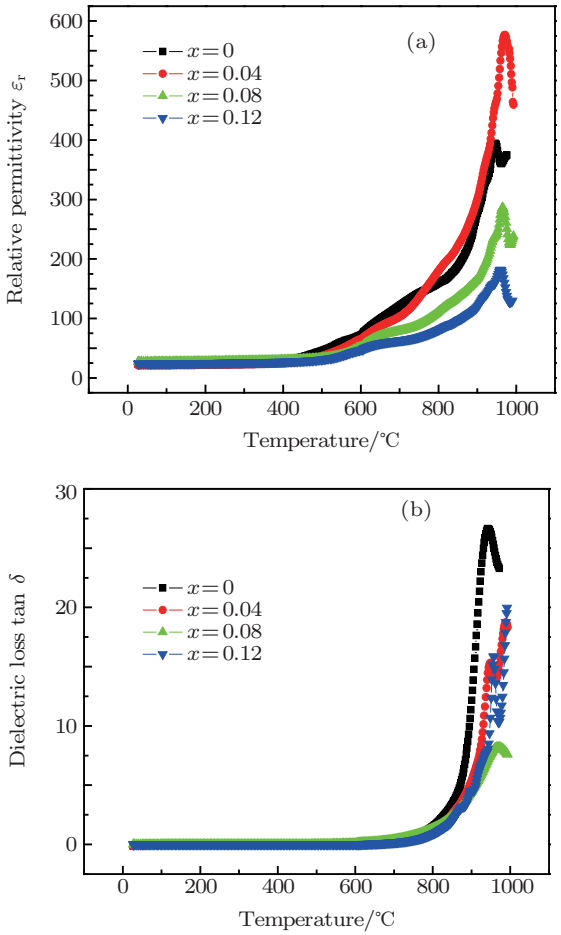


Fig. 3. (colour online) Temperature dependence of relative permittivity (a) and dielectric loss tan δ (b) for the pure and doped CBNO piezoceramics.

For the (LiCe) Co-substituted CBNO-x ceramics, due to the lower limits of the attainable sample thickness (0.10–0.15 mm) resulted from polishing damage as well as high conductivities at high temperature and high coercive field (E_C), it was usually impossible to obtain saturated ferroelectric hysteresis loops. Similar problems have been noted previously for Aurivillius phase materials.[14–23] Figure 4 shows the polarization versus electric field (P–E) hysteresis loops measured at 10 Hz and 180 °C for all of the compositions studied. As shown in Fig. 4, unlike the quasi oval-shaped saturated hysteresis loop of CBNO, CBNO-x ceramics show rugby-like loops. Although none of the P–E hysteresis loops are fully saturated, the E_C of CBNO-x ceramics is lower than that of CBNO, because the (LiCe) modification makes the movement of domain walls easier and also makes the poling easier.[14–25]

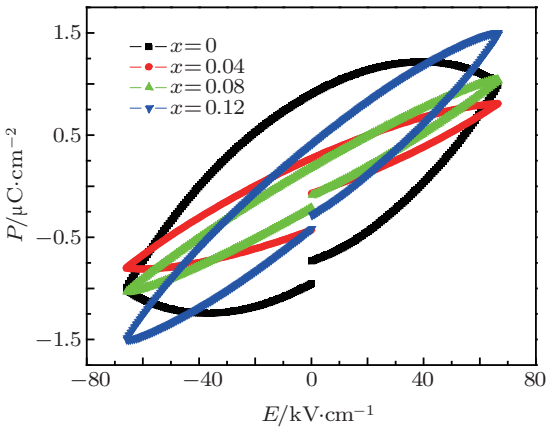


Fig. 4. (colour online) The P–E hysteresis loops of CBNO-x measured at 10 Hz and at 180 °C.

Figure 5 shows the dependence of piezoelectric coefficient d_{33} for samples poled at 140 °C and the relative densities $\rho_{rd}(\%)$ of the CBNO-x ceramics. The d_{33} value reaches its maximum (13.3 pC/N) at $x = 0.08$. The d_{33} value for $x = 0.04$ or 0.12 is also higher than that of pure CBNO ($x = 0.00$). The relative density ρ_{rd} for the doped CBNO ceramics, on the order of 98% in theory, is found to be higher than that of pure CBNO ceramics (95% in theory), although the pure CBNO ceramics were sintered at higher temperature and for a longer time. The combination of high d_{33} values and high T_C ($>$ 900 °C) suggests that the above composition can be a good candidate for ultrahigh temperature piezoelectric applications.

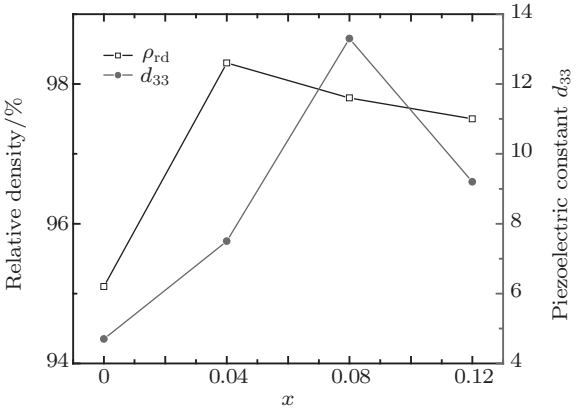


Fig. 5. The piezoelectric constant d_{33} and relative density $\rho_{rd}(\%)$ of the CBNO-x ceramics versus x.

4. Conclusion

1) The (LiCe) Co-substituted ultrahigh-temperature $CaBi_2Nb_2O_9$ piezoelectric ceramics with a bismuth layered structure are synthesized using conventional solid state processing. The substitution of

(LiCe) significantly improves the piezoelectric properties, dielectric permittivity and also makes the poling easier.

2) For $x = 0.08$, the piezoelectric coefficient d_{33}, Curie temperature $T_{\rm C}$ for the CBNO-x ceramics are found to be 13.3 pC/N and 960 °C, respectively.

3) The dielectric and piezoelectric properties of (LiCe) Co-substituted CBNO ceramics exhibit very stable temperature behaviours. This demonstrates that the CBNO ceramics are promising candidates for high temperature applications.

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