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Ceramics International 38 (2012) 3591–3594

CERAMICS INTERNATIONAL

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Microstructure and electrical properties of $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ceramics with a low dielectric loss and a low sintering temperature

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Received 19 December 2011; received in revised form 29 December 2011; accepted 29 December 2011
Available online 4 January 2012

Abstract

A low sintering temperature is demonstrated for $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ (BCLTZN-x) piezoelectric ceramics, where BCLTZN-x lead-free piezoelectric ceramics were prepared by the normal sintering. Effects of Li and Nb on the microstructure and electrical properties of these ceramics were investigated. The sintering temperature of BCLTZN-x ceramics was decreased greatly by introducing Li and Nb, and the grain size of these ceramics decreases with increasing x. These ceramics with a small amount of Li and Nb maintain good piezoelectric properties, together with a low sintering temperature and a lower dielectric loss. These ceramics with $x = 0.01$ demonstrate optimum electrical properties: $d_{33} \sim 353$ pC/N, $k_p \sim 41.1\%$, $T_c \sim 86\ ^\circ C$, $\varepsilon_r \sim 4236$, and $\tan\delta \sim 0.75\%$.

Keywords: C. Electrical properties; Ceramics; Low sintering temperature; Ion substitution

1. Introduction

$BaTiO_3$ as the first ferroelectric oxide is often considered as a dielectric not a piezoelectric material because of a high dielectric constant and a relatively lower piezoelectricity [1–3]. A poor piezoelectric constant of ∼190 pC/N has been demonstrated for the $BaTiO_3$ ceramic [3]. Although some attempts have been conducted to improve its piezoelectric properties, a relatively low d_{33} value has been obtained for these $BaTiO_3$-based ceramics [4–9]. In 2009, Ren et al. have found that an outstanding d_{33} value has been observed for the Ca and Zr-modified $BaTiO_3$ ceramics by constructing the phase boundary, but a high sintering temperature of >1500 °C is necessary [10].

It is well known that the $LiNbO_3$ (LN) has a highest T_c value of ∼1150 °C among all known piezoelectric materials [11]. LN belongs to be a lithium niobate structure, and is often prepared in the form of single crystals because it is very difficult to prepare the LN material in the polycrystalline form [12]. Guo et al. [13] have reported that the addition of LN improved the piezoelectric properties of $K_{0.50}Na_{0.50}NbO_3$ ceramics by forming the polymorphic phase transition, and a higher T_c value is simultaneously demonstrated. However, Chen et al. [14] found that the piezoelectric properties of $(1-x)BiScO_3$–$xPbTiO_3$ ceramics were enhanced greatly by the addition of LN, but its T_c value decreases. As a result, LN may play a different role on the T_c value of piezoelectric materials, depending on their compositions [13,14]. Moreover, the addition of LN can also improve the piezoelectric properties of these materials [13,14].

In the present work, $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ (BCLTZN-x) lead-free piezoelectric ceramics were prepared by the conventional solid-state reaction. Effects of Li and Nb content on the microstructure and piezoelectric properties of BCLTZN-x ceramics were investigated, and the underlying physical mechanism was also addressed. A low sintering temperature is obtained for the BCLTZN-x ceramics together with a low dielectric loss.

2. Experimental details

$(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ($x = 0$, 0.01, 0.02, 0.04, 0.06, 0.08, and 0.10) piezoelectric ceramics were

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doi:10.1016/j.ceramint.2011.12.075

prepared by using the conventional solid-state reaction. Raw materials were $BaCO_3$ (99%), $CaCO_3$ (99%), TiO_2 (99%), ZrO_2 (99%), Li_2CO_3 (99%), and Nb_2O_5 (99.5%). These powders were milled in alcohol with agate balls for 24 h, and then dried and subsequently calcined at 1200 °C in air for 3 h. These calcined powders were milled for 24 h again. The poly(-vinylalcohol) (PVA) binder was used to improve the green strength of compacts, and mixed with these powders. These mixed powders were pressed into the cylindrical pellets of 1.0 cm in diameter and ~1.0 mm in thickness under 10 MPa pressure. The PVA binder was removed by sintering at 550 °C for 6 h, and these pellets were finally sintered at a temperature of 1300–1400 °C for 2 h. Silver electrodes were fired on the top and bottom surfaces of these ceramics, and then these ceramics were poled under a dc field of 3 kV/mm at ~30 °C in a silicone oil bath for 30 min.

The phase structure of these ceramics was analyzed by using X-ray diffraction (Bruker D8 Advanced XRD). Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was employed to study the surface morphologies of these ceramics. The temperature dependence of the dielectric properties of these ceramics was measured by using a programmable furnace with an *LCR* analyzer (TH2816). An impedance analyzer was employed to characterize their dielectric properties, and their ferroelectric properties were studied by using the Radiant precise workstation (Radiant Technologies, Medina, NY). The piezoelectric constant d_{33} of these ceramics was measured by using a piezo-d_{33} meter (ZJ-3A, China).

3. Experimental procedure

Fig. 1(a) shows the XRD patterns of BCLTZN-x ceramics as a function of Li and Nb content, measured at room temperature. All ceramics have a pure phase, and no secondary phases are detected. Therefore, a stable solid solution of BCLTZN-x is formed in this work. Fig. 1(b) shows the expanded XRD patterns of BCLTZN-x ceramics as a function of Li and Nb content. These BCLTZN-x ceramics endure a phase transition from the coexistence of rhombohedral and tetragonal phases, a tetragonal phase, to a cubic phase with increasing Li and Nb content. In this work, the BCLTZN-x ceramic with $x = 0$ has a coexistence of two phases [9,15–18], a tetragonal phase gradually disappears for these ceramics with $0 < x < 0.06$, and then a cubic phase forms for these ceramics with $x \geq 0.06$. Moreover, the temperature-dependent dielectric constant in Fig. 3 also confirms the existence of the phase transition of BCLTZN-x ceramics in this work.

Fig. 2(a)–(f) shows the surface morphologies of BCLTZN-x ceramics as a function of Li and Nb content. The average grain size of BCLTZN-x ceramics gradually decreases with increasing Li and Nb content, which could be attributed to that Li and Nb acting as a grain growth inhibitor. As shown in Fig. 2(b), small grain surrounds these larger ones, which helps to improve the density of BCLTZN-x ceramics. Moreover, it was found that some grains with a cubic shape begin to form for the BCLTZN-x ceramics with $x = 0.06$, and gradually increase with further increasing Li and Nb content, as shown Fig. 2(e) and (f). This result is in agreement with the temperature dependence of the dielectric constant in Fig. 3, confirming that the phase transition is involved into these BCLTZN-x ceramics in this work.

Fig. 3 plots the temperature dependence of the dielectric constant (ε_r) of BCLTZN-x ceramics with different Li and Nb content, measured at 1 kHz. The ε_r values located at T_m and the Curie temperature (T_c) simultaneously decrease with increasing Li and Nb content, which is in agreement with the result reported by Chen et al. [14]. The classical Vegard behavior has confirmed that Li^+ and Nb^{5+} ions are incorporated into the A site and B sites of the ABO_3 perovskite structure, respectively [19]. In the present work, the introduction of Li and Nb cannot induce a higher T_c value in the BCLTZN-x system as expected. Although the present work is obviously different from that of the $K_{0.5}Na_{0.5}NbO_3$–$LiNbO_3$ system [13], it is very similar to the reported result of the $BiScO_3$–$PbTiO_3$–$LiNbO_3$ system [14]. The decrease of T_c values could be attributed to the structural evolution with increasing LN content. The insert of Fig. 3 plots the ε_r value of BCLTZN-x ceramics as a function of Li and Nb content, measured at 1 kHz and room temperature. The ε_r value of BCLTZN-x ceramics increases with increasing Li and Nb

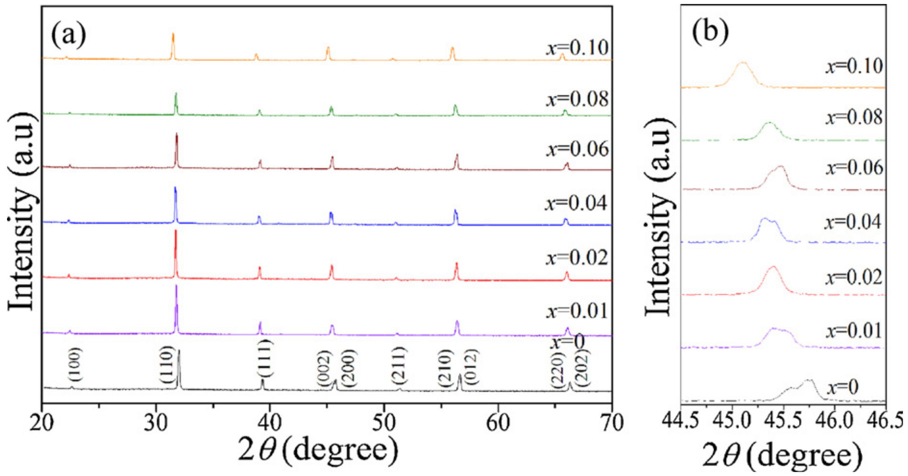

Fig. 1. (a) XRD patterns and (b) expanded XRD patterns of $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ceramics.

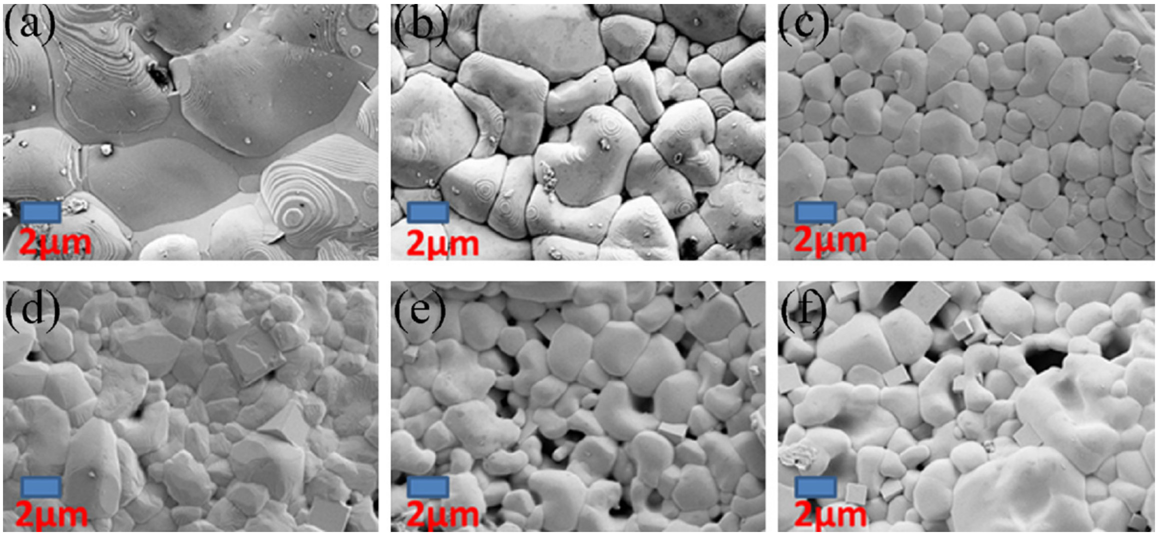

Fig. 2. Surface morphologies of $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ceramics: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.04$, (e) $x = 0.06$, and (f) $x = 0.10$.

content, reaches a maximum at $x = 0.02$, and then decreases with further increasing Li and Nb content. The actual reason for such a phenomenon is clearly demonstrated in Fig. 3. In this work, a relatively high T_c value of ~86 °C is observed for the BCLTZN-x ceramic with $x = 0.01$.

Fig. 4 shows the temperature dependence of the dielectric loss (tan δ) of BCLTZN-x ceramics with different Li and Nb content, measured at 1 kHz. The tan δ value of BCLTZN-x ceramics gradually decreases with increasing Li and Nb content, confirming that the addition of Li and Nb helps to decrease the tan δ value of BCTZ ceramics. The insert of Fig. 4 plots the tan δ value of BCLTZN-x ceramics as a function of Li and Nb content, measured at 1 kHz and room temperature. The tan δ value of BCLTZN-x ceramics decreases from 5.22% to 0.75% with increasing Li and Nb content with $x = 0.01$, and almost keeps unchanged for $x \geq 0.01$. The actual reason for such a phenomenon is also shown in Fig. 4. Therefore, the addition of Li and Nb greatly decreases the tan δ value of BCLTZN-x ceramics, which is also much lower than the reported result [20].

Fig. 5(a) shows the P–E loops of BCLTZN-x ceramics with different Li and Nb content, measured at 1 kHz and room temperature. Ferroelectric properties of BCLTZN-x ceramics gradually degrade with increasing x content, and a slim P–E loop is observed for the ceramics with $x > 0.04$, as shown in Fig. 5(a). These slim P–E loops also confirm the involvement of a cubic phase in these ceramics with $x > 0.04$, which is in agreement with the temperature dependence of dielectric properties in Fig. 3. Fig. 5(b) plots the piezoelectric properties of BCLTZN-x ceramics as a function of Li and Nb content, measured at room temperature. The d_{33} value of BCLTZN-x ceramics slightly decreases at $x \leq 0.01$, and quickly decreases with further increasing Li and Nb content. Similarity to the change of d_{33} values, the k_p value of BCLTZN-x ceramics also decreases with increasing Li and Nb content because of the increase of a cubic phase. In this work, the BCLTZN-x ceramic has optimum piezoelectric properties: $d_{33} \sim 353$ pC/N and $k_p \sim 41.1\%$.

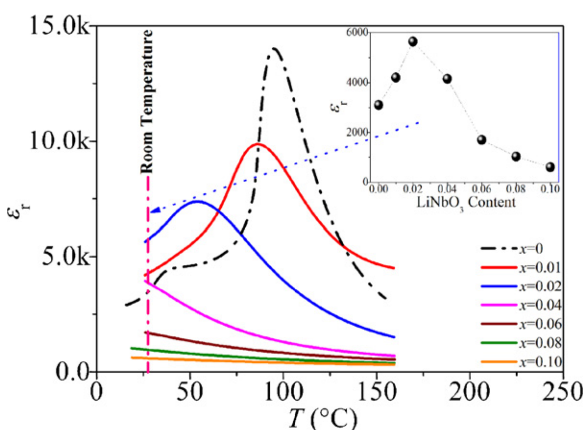

Fig. 3. Temperature dependence of the dielectric constant of $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ceramics, where the insert is ε_r values as a function of x.

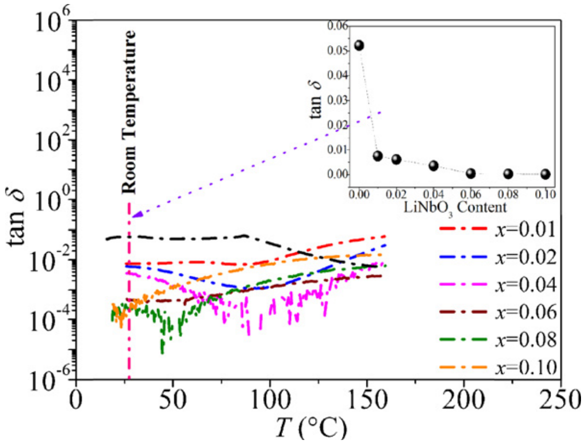

Fig. 4. Temperature dependence of the dielectric loss of $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ceramics, where the insert is tan δ values as a function of x.

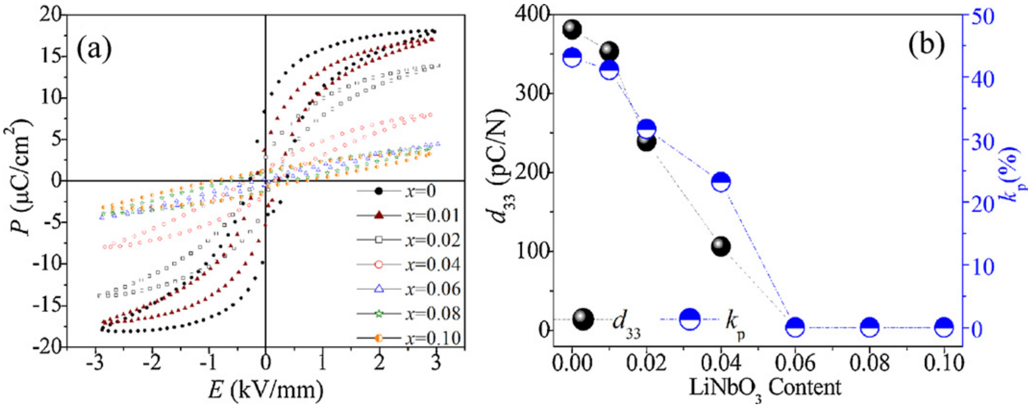

Fig. 5. (a) *P–E* loops and (b) piezoelectric properties of $(Ba_{0.85}Ca_{0.15})_{1-x}Li_x(Ti_{0.90}Zr_{0.10})_{1-x}Nb_xO_3$ ceramics as a function of *x*.

4. Conclusions

Effects of Li and Nb substitution on the electrical properties of BCTZ ceramics were investigated, and BCLTZN-*x* piezoelectric ceramics have been prepared by the normal sintering in air. The addition of Li and Nb greatly decreases the sintering temperature of BCLTZN-*x* ceramics. The dielectric loss of BCLTZN-*x* ceramics gradually decreases with increasing Li and Nb content. These BCLTZN-*x* ceramics with $x = 0.01$ exhibit optimum electrical properties: $d_{33} \sim 353$ pC/N, $k_p \sim 41.1\%$, $T_c \sim 86$ °C, $\varepsilon_r \sim 4236$, and $\tan\delta \sim 0.75\%$. As a result, an optimum LN content is an effective way to enhance the electrical properties of BCTZ ceramics, which is promising as a lead-free piezoelectric candidate.

Acknowledgement

Authors gratefully acknowledge the supports of the Chengdu Medical College.

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