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Synthesis and piezoelectric properties of $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ lead-free piezoelectric ceramics

Dunmin Lin · Dingquan Xiao · Jianguo Zhu · Ping Yu

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Abstract $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ lead-free piezoelectric ceramics were fabricated by ordinary ceramic technique and the piezoelectric and ferroelectric properties of the ceramics were studied. The ceramics can be well sintered at 1,100–1,150 °C for 2 h. X-ray diffraction (XRD) analysis shows that K^+, Li^+ and Ba^{2+} diffuse into the $Bi_{0.5}Na_{0.5}TiO_3$ lattices to form a solid solution with a single-phase perovskite structure. The introduction of K^+, Li^+ and Ba^{2+} into $Bi_{0.5}Na_{0.5}TiO_3$ significantly decreases the coercive field E_c but maintains the large remanent polarization P_r of the materials. The ceramics provide piezoelectric constant d_{33} of 205 pC/N, electromechanical coupling factor k_p of 0.346, remanent polarization P_r of 31.7–38.5 μC/cm^2, and coercive field E_c of 3.18–5.16 kV/mm.

Keywords $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ · Lead-free piezoelectric ceramics · Piezoelectric properties · *P-E* hysteresis loop

1 Introduction

Pb(Ti,Zr)TiO_3-based piezoelectric ceramics are widely used for various electronic and microelectronic devices. However, the toxicity of lead oxides and the volatilization during sintering process have caused serious environmental problems. To minimize lead pollution, it is necessary to develop environmental-friendly lead-free piezoelectric ceramics.

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At present, alkali metal niobate-based, bismuth layer-structured-type, $Bi_{0.5}Na_{0.5}TiO_3$-based (abbreviated as BNT) and $BaTiO_3$-based ferroelectrics are known as lead-free piezoelectric ceramics. Among these materials, BNT is thought to be a strong candidate of lead-free piezoelectric ceramics because of its relatively large remanent polarization (P_r=38 μC/cm^2)[1]. However, because pure BNT ceramics have a high coercive field (E_c=7.3 kV/mm) and large electric conductivity[1], these ceramics are difficult to be completely polarized.

In order to improve the piezoelectric and ferroelectric properties of BNT ceramics, some solid solutions of BNT with $BaTiO_3$ [2,3], $Bi_{0.5}K_{0.5}TiO_3$ [4], $NaNbO_3$ [5], $Ba(Cu_{1/2}W_{1/2})O_3$ [6], $BiFeO_3$ [7] are extensively investigated. But, the piezoelectric constant and the electromechanical coupling factor of these solid solutions are not desirable enough, too. According to the characteristics of BNT ferroelectric, it is believed that a key point to further enhance the piezoelectric properties is to decrease the coercive field efficiently and simultaneously retain the strong ferroelectricity of BNT-based ceramics. Therefore, the research and development of new BNT-based systems with a larger P_r and lower E_c may be a promising way to obviously enhance the piezoelectric properties of BNT-based ceramics.

In this paper, new $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ (abbreviated as BNKLB-x/y/z) ceramics were prepared by the conventional ceramic processing and their microstructures and piezoelectric properties were studied.

2 Experimental

Conventional ceramic fabrication technique was used to prepare BNKLB-x/y/z ceramics. Electronic-grade metal

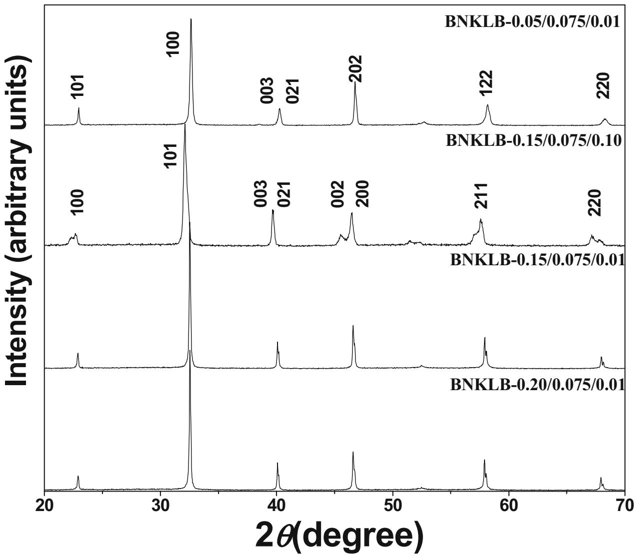

Fig. 1 XRD diffraction patterns of BNKLB-x/0.075/z ceramics in the range 2θ of 20–70 °

oxides or carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, Li_2CO_3, $BaCO_3$ and TiO_2 were used as starting raw materials. All the raw materials mixed by ball-milling were calcined at 850 °C for 2 h. After calcination, the ball-milled powders were granulated by adding PVA as a binder and pressed into discs and then sintered at 1,100–1,150°C for 2 h in air. Silver paste was coated to form electrodes on both sides of sintered samples and the samples were fired at 810 °C for 10 min. The samples were poled in a silicone oil bath with a dc field of 3–4 kV/mm at 80 °C for 20 min.

The crystalline structure of the sintered samples was examined by X-ray diffraction technique (DX-1000X, China). The bulk densities of the sintered samples were measured by the Archimedes method. The microstructures of the sintered samples were observed using scanning electron microscope (JSM-5900LV). Planar electromechanical coupling factor k_p was determined by the resonance-antiresonance method on the basis of IEEE standards using an impedance analyzer (HP4194A). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-3A, China). The dielectric properties of the ceramics were measured using a capacitance meter (HP 4287A). The *P-E* hysteresis loops were obtained using Radiant Precision Workstation.

3 Results and discussion

The XRD diffraction patterns of BNKLB-x/y/z ceramics are shown in Fig. 1. From Fig. 1, the ceramics possess a

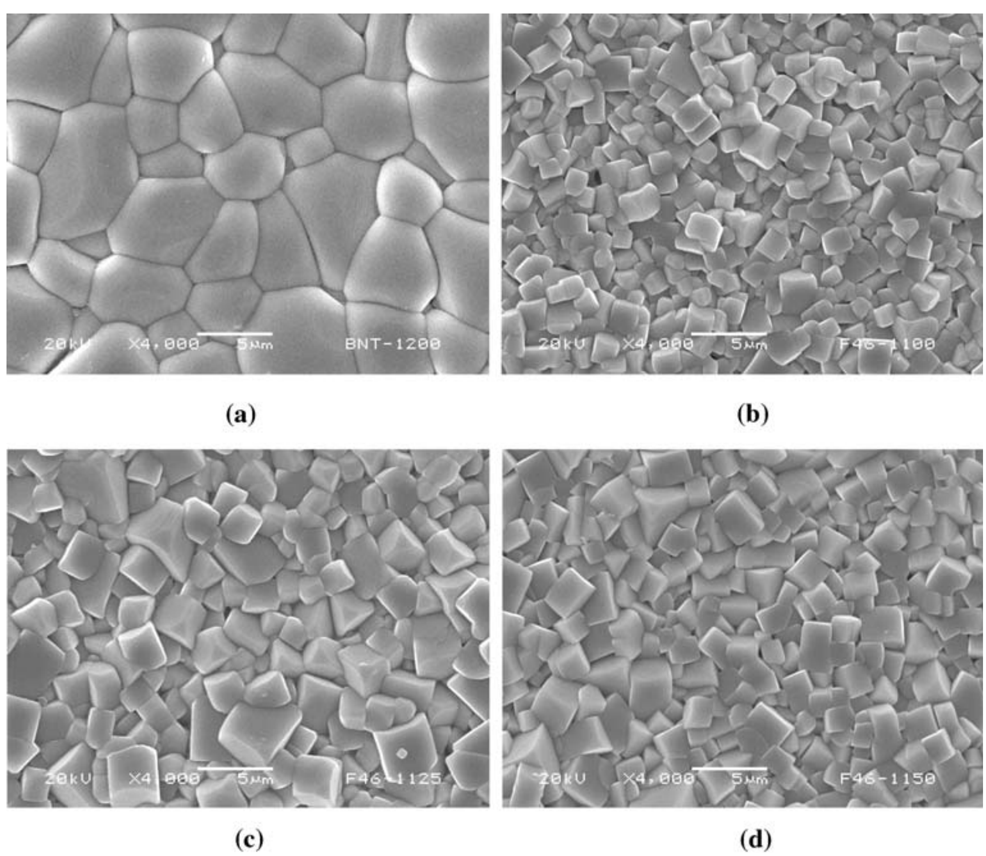

Fig. 2 SEM micrographs of the sintered samples (**a**) BNKLB-0/0/0 sintered at 1,200 °C for 2 h; (**b**) BNKLB-0.15/0.075/0.02 sintered at 1,100 °C for 2 h; (**c**) BNKLB-0.15/0.075/0.02 sintered at 1,125 °C for 2 h; and (**d**) BNKLB-0.15/0.075/0.02 sintered at 1,150 °C for 2 h

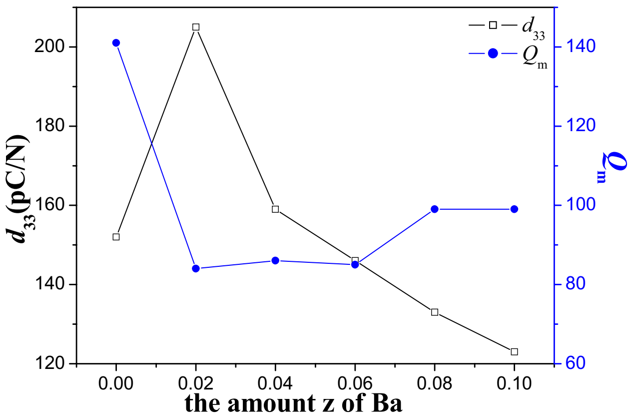

Fig. 3 Piezoelectric constant d_{33} and mechanical quality factor Q_m as a function of z for BNKLB-0.15/0.075/z ceramics

single crystalline phase with perovskite structure and no second phase can be found, which reveal that K^+, Li^+ and Ba^{2+} diffuse into $Bi_{0.5}Na_{0.5}TiO_3$ lattices to form a solid solution. The BNKLN-x/y/z ceramics sintered at 1,100–1,150°C for 2 h have the bulk densities of 5.62–5.75 g/cm^3 which are 95% higher than the theoretical densities.

The microstructures of the sintered BNKLB-x/y/z ceramics were observed using SEM, and the micrographs of these ceramics are shown in Fig. 2. Pure BNT ceramics sintered at 1,200 °C for 2 h are very dense and the shape of the grains is not regular (Fig. 2(a)). The diffusion of K^+, Li^+ and Ba^{2+} into BNT lattices greatly influences the microstructures of the materials. From Fig. 2 (b)–(d), differently from pure BNT ceramics, the grain growth of BNKLB-0.15/0.075/0.02 ceramics sintered at 1,100–1,150 °C for 2 h is suppressed, and the grains become smaller and grow into neat rectangular shapes. With sintering temperature increasing, the grains of BNKLB-0.15/0.075/0.02 ceramics slightly become larger and more rectangular. At 1,100–1,150 °C for 2 h, the ceramics are very dense and almost no holes can be found.

Figure 3 shows the piezoelectric constant d_{33} and mechanical quality factor Q_m as a function of z for BNKLB-0.15/0.075/z ceramics. The piezoelectric constant d_{33} reaches a maximum value of 205pC/N at z=0.02. The mechanical quality factor Q_m decreases sharply with z increasing from 0 to 0.02. When the amount z of Ba further increases, Q_m is almost constant.

Electromechanical coupling factors k_p and k_{31} as a function of z for BNKLB-0.15/0.075/z ceramics are shown in Fig. 4. It can be found that planar electromechanical coupling factor k_p decreases with z increasing up to 0.04, and then has no evident change with the further increasing of z. k_p reaches the maximum value of 34.6% at z=0. The variation of the electromechanical coupling factor k_{31} with x is similar to that of k_p.

Figure 5 shows dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and dielectric loss tanδ as a function of z for BNKLB-0.15/0.075/z ceramics. With the increase of x, dielectric loss tanδ decreases from 0.036 to 0.025. The dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ reaches a maximum value of 1041 at z=0.02.

The *P-E* hysteresis loops of BNKLB-x/0.075/0.01 ceramics at room temperature are shown in Fig. 6. The *P-E* hysteresis loops are almost rectangular shapes. It is believed that these *P-E* hysteresis loops are saturated. With x increasing from 0.05 to 0.20, the coercive field E_c decreases from 5.16 to 3.18 kv/mm. The maximum value of remanent polarization P_r of 38.5 μC/cm^2 appears at x= 0.20. Compared with pure BNT ceramics [8], it is concluded that the partial substitution of Na^+ by K^+ and Li^+ and partial substitution $(Bi_{0.5}Na_{0.5})^{2+}$ by Ba^{2+} greatly decrease the coercive field E_c but simultaneously keep the very high remanent polarization P_r, which leads to facilitating the poling process of the BNKLB-x/y/z ceramics and an obvious enhancement of piezoelectric properties of the materials. Therefore BNKLB-x/y/z ceramics show better piezoelectric properties.

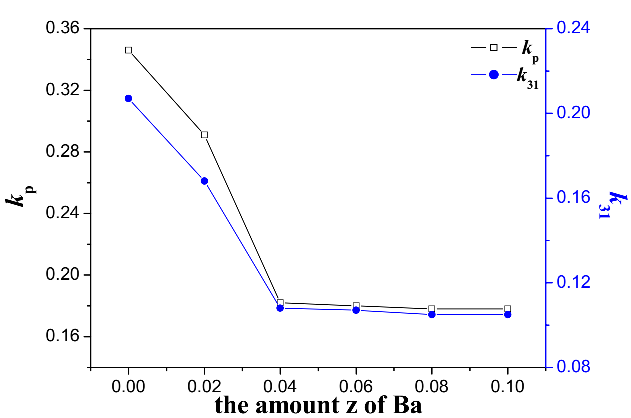

Fig. 4 Electromechanical coupling factors k_p and k_{31} as a function of z for BNKLB-0.15/0.075/z ceramics

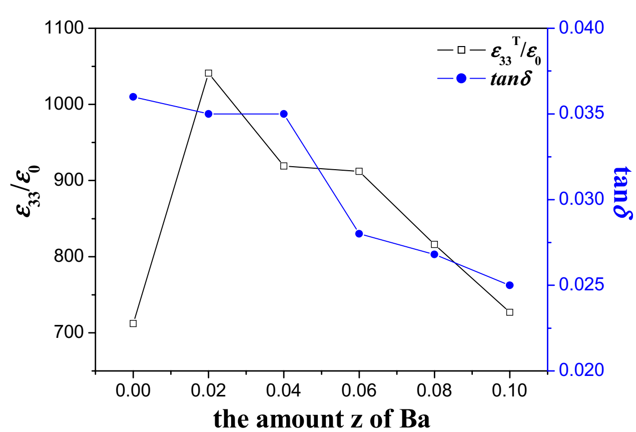

Fig. 5 Dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and dielectric loss tanδ as a function of z for BNKLB-0.15/0.075/z ceramics

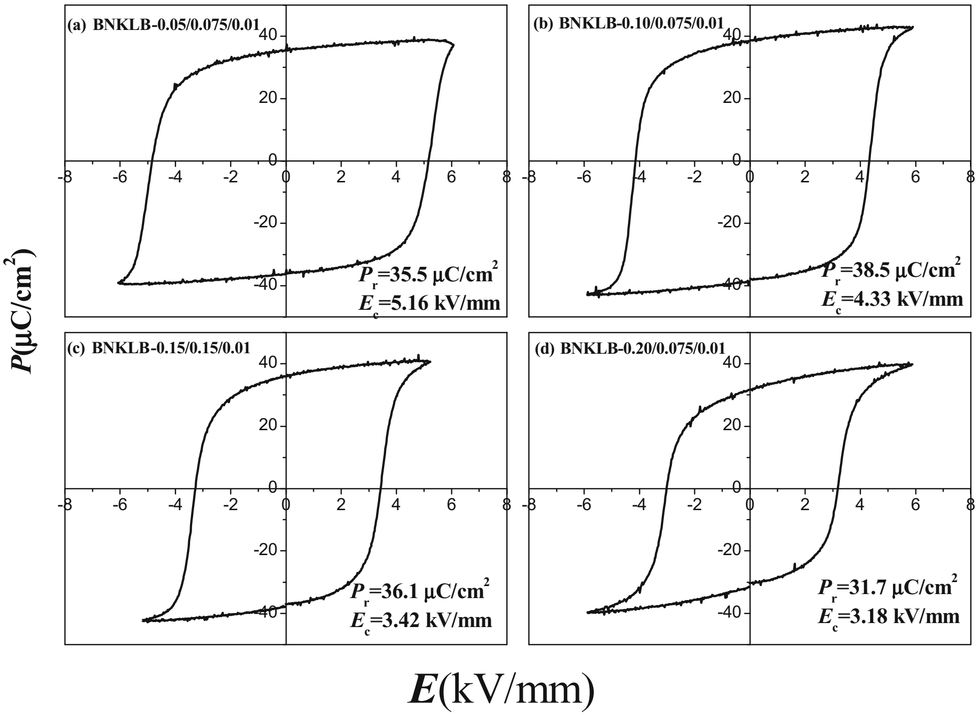

Fig. 6 *P-E* hysteresis loops of BNKLB-x/0.075/0.01 ceramics at room temperature

4 Conclusion

New $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ ceramics were prepared by the conventional ceramic sintering processing and their microstructures and piezoelectric properties were studied. The ceramics possess a single phase with perovskite structure. The introduction of K^+, Li^+ and Ba^{2+} to the BNT lattice causes an evident change in the microstructure of the BNT ceramics and decreases coercive field greatly but large remanent polarization is simultaneously maintained. The ceramics exhibit piezoelectric constant d_{33} of 205 pC/N, electromechanical coupling factor k_p of 0.346, remanent polarization P_r of 31.7–38.5 μC/cm^2, and coercive field E_c of 3.18–5.16 kV/mm.

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