

## Structure and piezoelectric properties of (1-x)K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>-xLiBiO<sub>3</sub> lead-free piezoelectric ceramics

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**Abstract:** Lead-free piezoelectric ceramics (1-x)(K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>-xLiBiO<sub>3</sub> [(1-x)KNN-xLB] (x=0, 0.0005, 0.002, 0.004, 0.006, 0.008, 0.010) were prepared by an traditional solid-state reaction. The microstructure and electrical properties of the ceramics were investigated. The results show that all (1-x)KNN-xLB ceramics possess pure perovskite structure when x≤0.01, no trace of any secondary phase is detected, and the phase structure of the ceramics transits abnormally from orthorhombic to cubic. With the increase of the LB content, the size of grain gradually becomes small, the piezoelectric constant  $d_{33}$  and the planar electromechanical coupling coefficient  $k_p$  first increases and then decreases. The  $d_{33}$  and  $k_p$  of the ceramics reach their maximum values 115 pC/N at x=0.002 and 0.2701 at x=0.001, respectively. The dielectric constant  $\epsilon_r$  of the ceramics firstly increases evidently and then decreases with the increase of x, the maximum value 871.8 is obtained at x=0.006.

**Key words:** lithium bismuthate; sodium potassium niobate; lead-free piezoelectric ceramics; piezoelectric properties; dielectric properties

### 1 Introduction

Piezoelectric ceramics are widely applied in the devices such as sensors and actuators [1,2]. However, at present most of piezoelectric ceramics used are PbTiO<sub>3</sub>-PbZrO<sub>3</sub> (PZT) system. It is recently desired to use lead-free materials for environmental protection during the waste disposal of products. So, it is very urgent and important for people to develop new lead-free piezoelectric materials. To today, people have already developed many lead-free ceramic systems [3–5]. And among these systems, KNbO<sub>3</sub>-NaNbO<sub>3</sub>(KNN)-based lead-free piezoelectric ceramics is one of the leading candidates because of its strong piezoelectric properties, low density and high Curie temperature, etc [2].

According to the previous reports [6,7], there are several studies on the critical ratio of Na, K and Li elements in KNN systems and the effect of Bi additions

on its properties. LI et al [8] reported that Bi or Li elements single-doping could evidently improve piezoelectric properties of (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub> (BNT)-based ceramics. However, there is a contrary result for Bi and Li co-doping 0.94(Na<sub>0.8</sub>K<sub>0.16</sub>Li<sub>0.04</sub>)Bi<sub>0.5</sub>TiO<sub>3</sub>-0.06Ba-(Zr<sub>0.055</sub>Ti<sub>0.945</sub>)O<sub>3</sub> system. According to Ref. [9], the compound LiBiO<sub>3</sub> is perovskite structure which is similar to LiSbO<sub>3</sub>. Furthermore, it is reported that the addition of LiSbO<sub>3</sub> can well improve the piezoelectric properties of KNN. For example, the piezoelectric constant  $d_{33}$  of the LiSbO<sub>3</sub>-doping KNN ceramic is increased from 80 pC/N of the pure KNN to over 200 pC/N [10].

To today, the structure and piezoelectric properties of LiBiO<sub>3</sub> doped K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> lead-free piezoelectric ceramics are not reported. Single LiBiO<sub>3</sub> isn't very stable at high temperature and changes easily to the compound LiBiO<sub>2</sub> as one dopant. Furthermore, the physical and chemical reactions in the ceramics during the sintering

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are very complex with the additions of many elements, which will probably affect the structure and property and get some new phenomenon. In this paper,  $\text{LiBiO}_3$  is selected as the dopant, and the effect of its content on the microstructure, phase transition and piezoelectric properties is investigated.

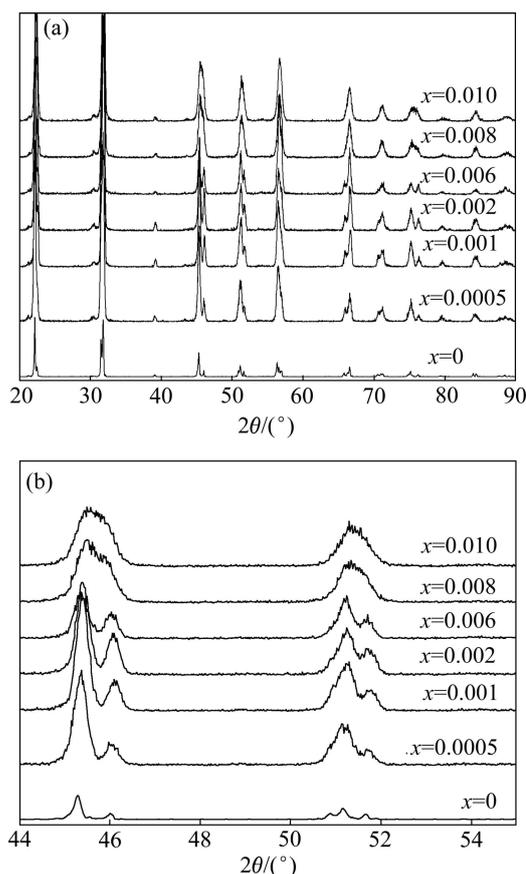
## 2 Experimental

$\text{Nb}_2\text{O}_5$  (99.5%),  $\text{K}_2\text{CO}_3$  (99%),  $\text{Na}_2\text{CO}_3$  (99.8%),  $\text{Li}_2\text{CO}_3$  (99%) and  $\text{Bi}_2\text{O}_3$  (99.97%) were used to prepare  $(1-x)\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-x\text{LiBiO}_3$  [(1-x)KNN-xLB] ( $x=0, 0.0005, 0.001, 0.002, 0.004, 0.006, 0.008, 0.010$ ) ceramics by the conventional mixed-oxide method. All powders were separately dried in an oven for 4–6 h prior to mix. The stoichiometric powders were mixed by ball-milling in ethanol for 12 h, then dried and calcined at 880 °C for 6 h. And ball milled for 6 h once again. The calcined powders were mixed with 5% (mass fraction) poly vinyl alcohol (PVA) solution, and then pressed into pellets with a diameter of 1.8 cm under 100 MPa pressure. The green disks were sintered at 1100 °C for 3 h. Silver electrodes were formed on both surfaces of each sintered disk by firing at 600 °C for 30 min. The samples were polarized in silicon oil for 15 min at 60–80 °C. The applied poling fields were 3.5 kV/mm for 15 min. After 24 h, the properties were measured.

The phase structure of sintered ceramics was measured by X-ray diffraction (XRD, D8-2-Advance) with  $\text{Cu K}\alpha$  radiation (step was 0.02°). Surface microstructure and composition analysis were carried out using a scanning electron microscope (SEM, JSM-5610LV) with the Energy Disperse Spectroscopy (EDS, Noran). The piezoelectric coefficient  $d_{33}$  was recorded from 1 d aged sample using a quasi-static piezoelectric  $d_{33}$  meter (ZJ-3AN, China). Dielectric properties were obtained using an impedance analyzer (Agilent 4294A) by measuring the capacitance and loss. The planar coupling coefficient ( $K_p$ ) and the mechanical quality factor ( $Q_m$ ) were determined by the resonance and antiresonance technique using an impedance analyzer (Agilent 4294A).

## 3 Results and discussion

Figure 1 shows that XRD patterns of (1-x)KNN-xLB ceramic samples sintered at 1150 °C for 3 h. Seen from Fig. 1, for (1-x)KNN-xLB ceramic, the XRD patterns show single perovskite structure, and no secondary phase is detected. At  $x=0.0005$ , the ceramics have orthorhombic perovskite phases, which agree with the pure KNN ceramic (at  $x=0$ ). However, with the

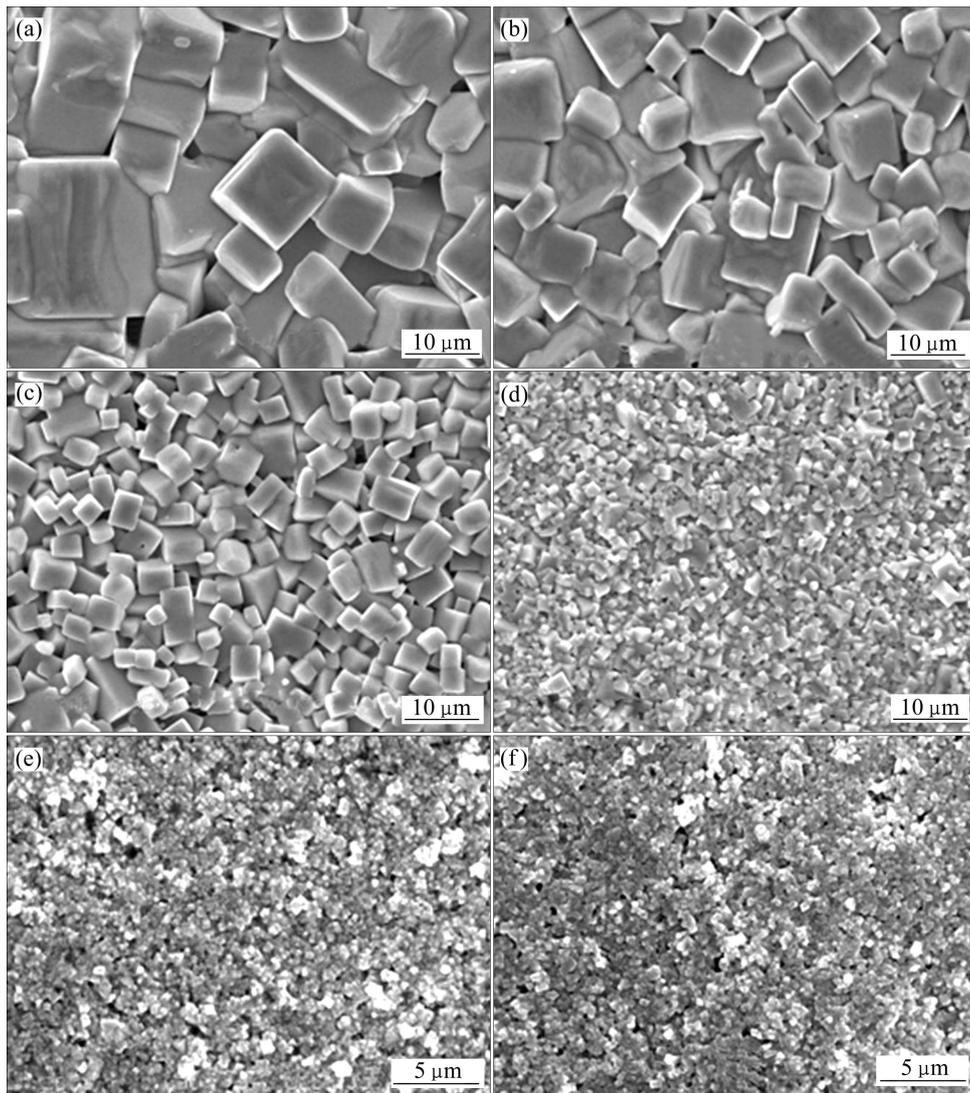


**Fig. 1** XRD patterns of (1-x)KNN-xLB ceramic samples sintered at 1150 °C for 3 h: (a)  $2\theta=20^\circ-90^\circ$ ; (b)  $2\theta=44^\circ-55^\circ$

increase of the LB content, the crystalline system of the ceramics changes abnormally. When  $x<0.002$ , the ceramic has orthorhombic phase, and mixed phases between orthorhombic and cubic phase at  $x=0.002-0.006$ , and then single cubic phase at  $x\geq 0.008$ .

According to the previous reports [11,12], usually for  $\text{LiNbO}_3$ ,  $\text{LiTaO}_3$  or  $\text{LiSbO}_3$  single doping KNN ceramics, a transition between orthorhombic and tetragonal phase will appear with the increase of the dopant content, and excellent piezoelectric properties are gained near the morphotropic phase boundary (MPB) between orthorhombic and tetragonal phase. However, in this paper a transition between orthorhombic and cubic phase appears with increase of the BL content, and excellent piezoelectric properties are gained near the morphotropic phase boundary (MPB) between orthorhombic and cubic phase. Especially at  $x=0.002-0.005$ , some big single crystals (the average size of 3–5 mm) appear in the ceramics, which is probably related with the above abnormal phase transition. The reasons will be studied in-depth in the future.

Figure 2 shows the surface SEM pictures of (1-x)KNN-xLB ceramics. Seen from Fig. 2, with the increase of the LB content, the grain size of the ceramics refines and becomes more homogeneous. This indicates



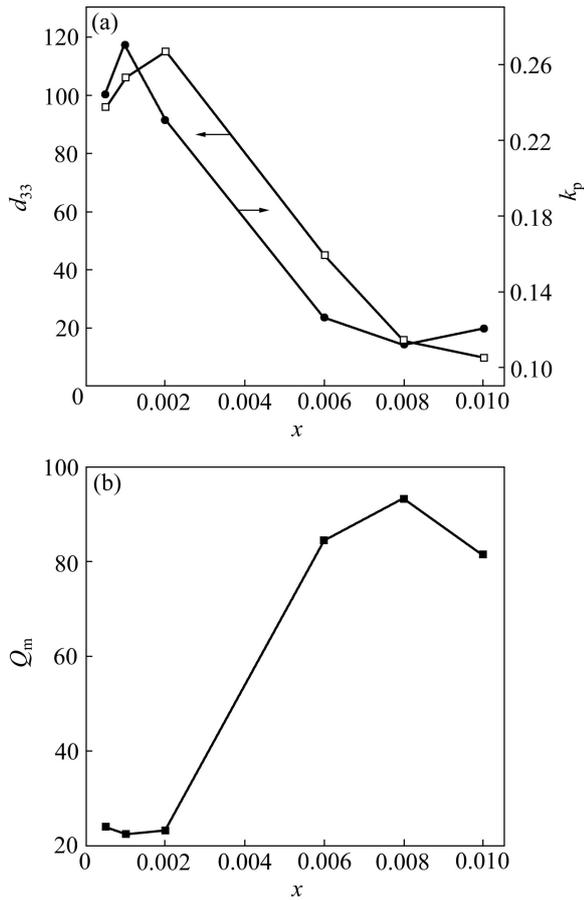
**Fig. 2** Surface SEM photographs of  $(1-x)\text{KNN}-x\text{LB}$  ceramics sintered at  $1150\text{ }^{\circ}\text{C}$  for 3 h: (a)  $x=0.0005$ ; (b)  $x=0.001$ ; (c)  $x=0.002$ ; (d)  $x=0.006$ ; (e)  $x=0.008$ ; (f)  $x=0.010$

that the addition of LB promotes the nucleation but inhibits the growth of grains in the ceramics. This is because after adding LB into KNN,  $\text{Li}^+$  and  $\text{Bi}^{5+}$  ions distribute evenly in the KNN ceramics and form nucleation points.

Figure 3 shows the dependence of  $d_{33}$ ,  $k_p$  and  $Q_m$  of the  $(1-x)\text{KNN}-x\text{LB}$  ceramics on  $x$ . Seen from Fig. 3,  $d_{33}$  of the ceramics first increases when  $x \leq 0.002$  and then decreases when  $x > 0.002$  with the increase of the LB content. When the LB content is small, the ceramics have orthorhombic phase structure with ferroelectric property which is the origin of good piezoelectric properties for the ceramics. What's more, the uniform and compact morphology of the ceramic at  $x=0.002$  is also one of the reasons. The ceramic has almost no piezoelectric properties when the LB content  $x$  is over 0.006. It can be supported by the above XRD results. Seen from Fig. 1, when the LB content  $x$  is over 0.006, the crystal structure

of the ceramic already changes from orthorhombic and cubic phase. Of course, the decrease of the ceramic density also affects its property. Table 1 shows the property parameters of LB doped KNN ceramics. Seen from Table 1, the profile of  $k_p-x$  relationship agrees with that of  $d_{33}-x$ . Although the structure of the ceramic at  $x=0.006$  is among the MPB, it is close to the cubic phase side. So, its piezoelectric properties are low. Also seen from Fig. 3, with the increase of the LB content, the  $Q_m$  of the ceramics increases accordingly. This is because that some vacancies appear in the KNN ceramics accompanied with the addition of LB. These vacancies reduce the resistance force of the ferroelectric domain rotation in the ceramics, which makes the domain rotation easy.

Figure 4 shows the dependence of  $\epsilon_r$  and  $\tan \delta$  of the  $(1-x)\text{KNN}-x\text{LB}$  ceramics on  $x$ . Seen from Fig. 4, with the increase of  $x$ , the dielectric constant  $\epsilon_r$  of the ceramics



**Fig. 3** Dependence of  $d_{33}$ ,  $k_p$  and  $Q_m$  of (1-x)KNN-xLB ceramics on  $x$

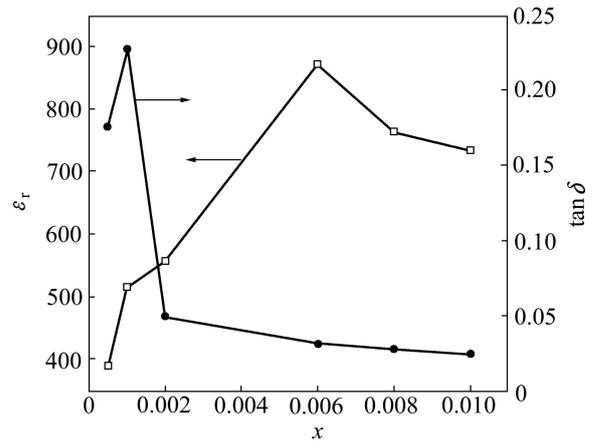
**Table 1** Piezoelectric properties of (1-x)KNN-xLB ceramics sintered at 1150 °C for 3 h at 1 kHz

$x$	$d_{33}/$ (pC·N <sup>-1</sup> )	$V_p/$ V	$\epsilon_r$	$\tan \delta/$ %	$k_p$	$Q_m$
0.0005	96	1000	486.7	17.50	0.2445	24.07
0.001	106	1600	568.7	22.70	0.2701	22.52
0.002	115	1800	557.2	4.95	0.2304	23.25
0.006	45	7000	871.8	3.14	0.1263	84.4
0.008	16	7500	764.2	2.78	0.1123	93.1
0.010	10	8100	733.8	2.46	0.1206	81.4

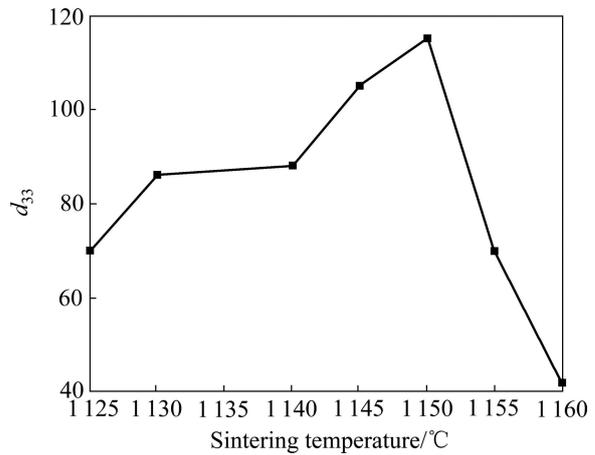
$V_p$ —polarization Voltages.

first increases evidently and then decreases slightly, and at  $x=0.006$ ,  $\epsilon_r$  reaches its maximum value (871.8). In a whole, the dielectric loss  $\tan \delta$  of the ceramic decreases gradually. These agree with the above microstructure analysis results.

Figure 5 shows the dependence of  $d_{33}$  of the (1-x)KNN-xLB ceramics on the sintering temperature. Seen from Fig. 5, with the increase of the sintering temperature from 1125 to 1160 °C,  $d_{33}$  of 0.2%LB (atom fraction) doped KNN ceramics first increases and then



**Fig. 4** Dependence of  $\epsilon_r$  and  $\tan \delta$  of (1-x)KNN-xLB ceramics on  $x$



**Fig. 5** Dependence of  $d_{33}$  of the (1-x)KNN-xLB ceramics on different sintering temperatures

**Table 2** Piezoelectric properties of 0.998KNN-0.002LB ceramics sintered at different temperatures

Sintering temperature/ °C	$d_{33}/$ (pC·N <sup>-1</sup> )	$\epsilon_r$	$\tan \delta/$ %	$k_p$	$Q_m$
1125	70	322	23.10	0.1847	41.00
1130	86	315	13.90	0.1899	45.00
1140	88	465	22.20	0.2000	43.00
1145	105	486	18.40	0.2423	48.00
1150	115	557	4.95	0.2304	23.25
1160	87	511	24.00	—	—

reduces, and when the sintering temperature is 1150 °C,  $d_{33}$  reaches its maximum value (115 pC/N). At the same time,  $k_p$  and  $Q_m$  of the ceramics first increases and then decreases. Table 2 lists the piezoelectric properties of 0.998KNN-0.002LB ceramics. Also seen from Table 2,  $\epsilon_r$  of the ceramics increases in a whole with the addition of the sintered temperature, and reaches its best value

(557). The dielectric loss  $\tan \delta$  of the ceramics first decreases and then increases quickly. When sintering at 1150 °C,  $\tan \delta$  of the ceramics reduces 4.93%.

## 4 Conclusions

1) Lead-free piezoelectric ceramics  $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{-NbO}_3\text{-}x\text{LiBiO}_3$  are prepared by the traditional solid-state reaction. The ceramics at  $x \leq 0.01$  possess pure perovskite structure, and no trace of any secondary phase is detected. The phase structure of the ceramics changes abnormally from orthorhombic to cubic phase.

2) With the increase of  $\text{LiBiO}_3$  content, the piezoelectric constant  $d_{33}$  and planar electromechanical coupling coefficient  $k_p$  at first increases and then decreases, and achieved their maximum value, i.e., 115 pC/N and 0.2701 at  $x=0.001$  and 0.002, respectively. The dielectric constant  $\epsilon_r$  of the ceramics firstly increases evidently and then decreases slightly with the increase of  $x$ .

3) With the increase of the sintering temperature from 1125 °C to 1160 °C,  $d_{33}$  of 0.2% (atom fraction)  $\text{LiBiO}_3$  doped  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  ceramics first increases and then reduces, and at 1150 °C  $d_{33}$  reaches its maximum value (115 pC/N). At the same time,  $k_p$  and  $Q_m$  of the ceramics first increase and then decrease.

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# $(1-x)\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{-}x\text{LiBiO}_3$ 无铅压电陶瓷的结构与压电性能

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**摘要:** 采用传统固相反应制备了  $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}x\text{LiBiO}_3$  [(1-x)KNN-xLB] ( $x=0, 0.0005, 0.001, 0.002, 0.004, 0.006, 0.008, 0.010$ ) 压电陶瓷, 并分析研究了其微结构及电性能。结果表明, LB 掺杂的 KNN 陶瓷主要形成了钙钛矿结构, 没有检测到第二相的存在, 并且陶瓷的相结构出现直接由正交相过渡到立方相的“反常”转变; 随着 LB 掺杂量的增加, 晶粒尺寸逐渐细化, 陶瓷的压电常数  $d_{33}$ 、平面机电耦合系数  $k_p$  先略有增加后显著下降, 且分别在  $x=0.002$  和  $x=0.001$  时达到最大值, 分别为 115 pC/N 和 0.2701; 陶瓷的介电常数  $\epsilon_r$  随  $x$  增大先增加后略有降低, 当  $x=0.006$  时获得最大值, 为 871.8。

**关键词:** 铋酸锂; 铌酸钾钠; 无铅压电陶瓷; 压电性能; 介电性能