J Electroceram (2010) 25:85–88
DOI 10.1007/s10832-009-9592-9

Lead-free $(K_{0.5}Na_{0.5})_{0.95}(LiSb)_{0.05}Nb_{0.95}O_3$-$BaTiO_3$ piezoceramics

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Received: 12 January 2009 / Accepted: 18 September 2009 / Published online: 3 October 2009

Abstract Lead-free (1-x)$(K_{0.5}Na_{0.5})_{0.95}(LiSb)_{0.05}Nb_{0.95}O_3$-x$BaTiO_3$ (abbreviated as (1-x)KNNLS-xBT) piezoceramics were synthesized by conventional solid state sintering and the effect of $BaTiO_3$ on the microstructure, dielectric and piezoelectric properties was investigated. It was found that both orthorhombic-tetragonal ($T_{O\text{-}T}$) and tetragonal-cubic (T_C) phase transition temperatures decreased obviously with increasing $BaTiO_3$ content. Although proper amount of $BaTiO_3$ facilitated the sintering of (1-x)KNNLS-xBT ceramics, the addition of $BaTiO_3$ affected the relaxor behavior slightly and it was not beneficial to improve piezoelectric strain coefficient d_{33}, remnant polarization P_r and piezoelectric coupling constant k_p.

Keywords Piezoceramics · Lead-free · Potassium sodium niobate · Piezoelectric properties

1 Introduction

For more than half a century, (1-x)$PbZrO_3$-x$PbTiO_3$ (PZT) ceramics are the most important and most widely used piezoelectric materials because of their excellent performance. However, PZT ceramics contain more than 60 wt% lead, the evaporation of lead caused serious environmental pollution. Thus, numerous investigators have been developing alternative lead-free materials to PZT ceramics. Potassium sodium niobate ($(K_{0.5}Na_{0.5})NbO_3$, KNN) based ceramics have become the focused materials because of their outstanding piezoelectric properties at the so-called morphotropic phase boundary (MPB) [1–6]. However, the so-called MPB of Li, Sb and Ta modified KNN ceramics is different from that of PZT and it is originated from orthorhombic-tetragonal phase transition around room temperature, which is in fact a polymorphic phase transition (PPT) [7–11]. Therefore, the outstanding piezoelectric properties of KNN are not thermally stable owing to the narrow temperature region for the existence of PPT. A new stable MPB may be obtained for (1-x)$(K_{0.5}Na_{0.5})NbO_3$-x$BaTiO_3$ (KNN-BT) system since the orthorhombic-tetragonal phase transition temperature for $BaTiO_3$ and KNN ceramics is about 0°C and 190°C, respectively. Recently, Lu and Park et al. have offered dielectric properties and improved piezoelectric properties of this system [12–14] and in this work, the effects of $BaTiO_3$ on the microstructure, dielectric and piezoelectric properties of $(K_{0.5}Na_{0.5})_{0.95}(LiSb)_{0.05}Nb_{0.95}O_3$ ceramics were investigated.

2 Experimental procedure

The ceramic samples with compositions (1-x)$(K_{0.5}Na_{0.5})_{0.95}(LiSb)_{0.05}Nb_{0.95}O_3$-x$BaTiO_3$ (x=0, 0.005, 0.01, 0.02) were prepared using analytical grades of Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Li_2CO_3 (99.0%), Sb_2O_3 (99.0%), Nb_2O_5 (99.5%), $BaCO_3$ (99.9%) and TiO_2(99.0%). The powders were mixed in a nylon bottle for 12 h using ZrO_2 milling media in anhydrous ethanol. The dried powders were pressed into 30 mm diameter disks at 70 MPa prior to reaction at 880°C for 4 h to form the desired perovskite phase. The crushed calcined pellets were again ball milled for 12 h, followed by the addition of 5 wt% PVA binder and

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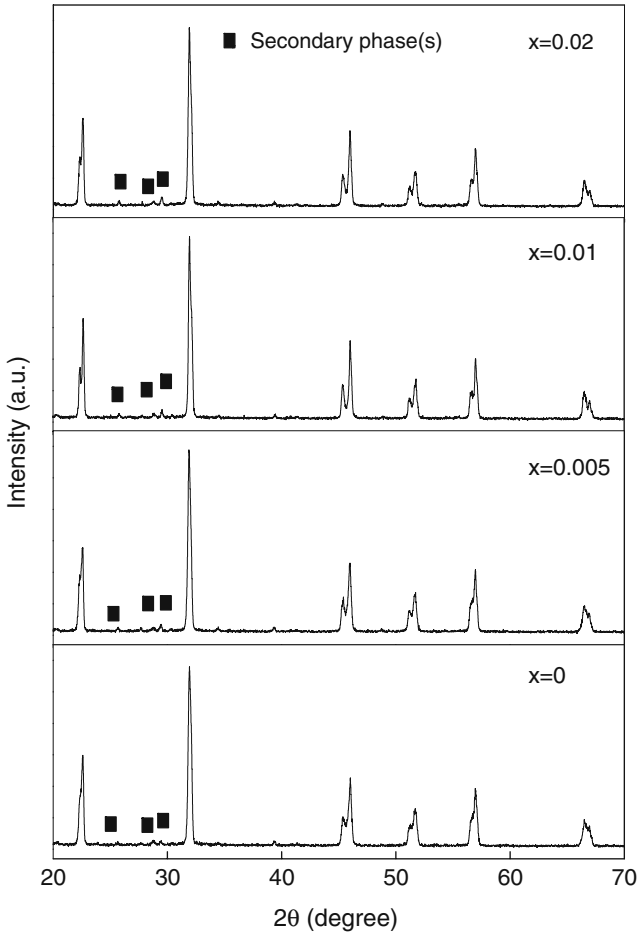

Fig. 1 XRD patterns of (1-x)KNNLS-xBT ceramic samples

pressed into 15 mm diameter disks with 1.5 mm thickness at 200 MPa. After burning out the PVA binder at 650°C for 3 h, the disks were sintered at 1080°C for 3 h. Densities of the samples were determined using the Archimedes method. To measure the electrical properties, silver electrodes were made on both surfaces of the sintered disks.

The microstructure of the sample surfaces was analyzed by scanning electron microscopy (SEM) (JSM-5900, Japan) and the phase was analyzed by X-ray diffraction (XRD) using Cu $K\alpha$ radiation (λ=1.54178 Å) in the 2θ range of 20°–70° (D8 Advance, Bruker incorporation, Germany). *P*–*E* hysteresis loops were recorded at room temperature using an aix-ACT TF2000FE-HV ferroelectric test unit (Trek 610D). Polarization was carried out in silicon oil at 30 kV/cm field for 20 min and the piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} meter (Sznocera Piezotronics INC). The dielectric properties were determined using an Agilent 4294A precision Impedance Analyzer in the temperature range from 25°C to 450°C. The electromechanical coupling factor k_p was determined

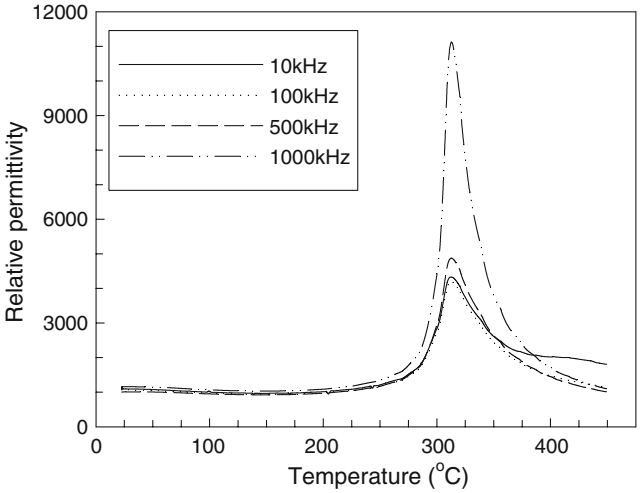

Fig. 3 Temperature dependence of relative permittivity for the sample of 0.98KNNLS-0.02BT measured at different frequency

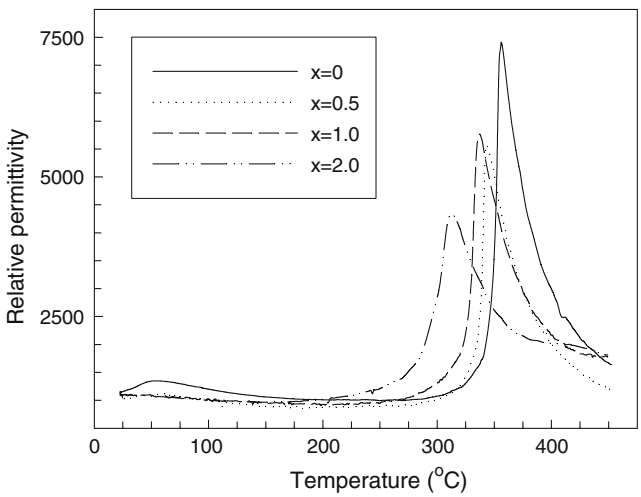

Fig. 2 Temperature dependence of relative permittivity of (1-x) KNNLS-xBT ceramics at 10 kHz

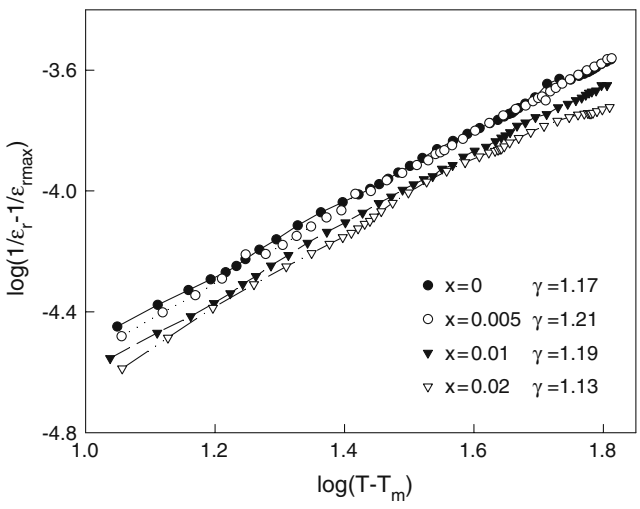

Fig. 4 $\log(1/\varepsilon_r - 1/\varepsilon_{rmax})$ as a function of $\log(T-T_m)$ at 10 kHz for (1-x)KNNLS-xBT ceramics

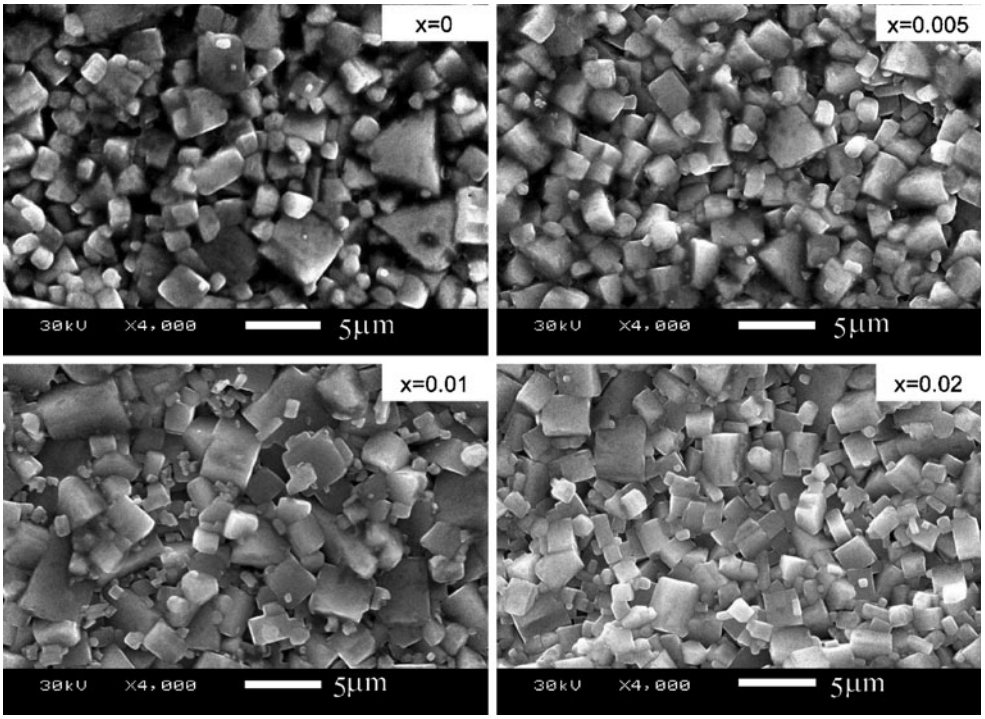

Fig. 5 SEM micrographs of all the samples

by the resonance and antiresonance method according to IEEE standards using an impedance analyzer (Agilent 4294A) [15].

3 Results and discussions

Figure 1 shows the XRD patterns of the sintered ceramics. All the samples present tetragonal perovskite structure and no MPB was found for all the compositions. Besides, a secondary phase $K_3Li_2Nb_5O_{15}$ with a tetragonal tungsten bronze structure was detected for all the samples as Guo et al. has reported [2]. This means that the appearance of secondary phase should not be resulted in by $BaTiO_3$ and 2 mol% $BaTiO_3$ can dissolve into the perovskite structure of $(K_{0.5}Na_{0.5})_{0.95}(LiSb)_{0.05}Nb_{0.95}O_3$ ceramics completely.

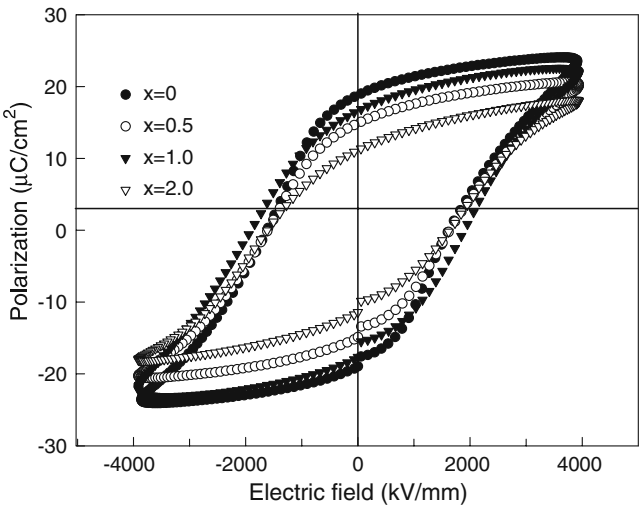

Fig. 6 Hysteresis loops of (1-x)KNNLS-xBT ceramics

It is generally known that $BaTiO_3$ ceramics exhibits tetragonal structure between 0°C and 130°C and cubic structure above 130°C. Thus, lower phase transition temperatures of $T_{O\text{-}T}$ and T_C may be obtained for (1-x) KNNLS-xBT (x=0.005, 0.01, 0.02) system considering that $T_{O\text{-}T}$ and T_C for $(K_{0.5}Na_{0.5})_{0.95}(LiSb)_{0.05}Nb_{0.95}O_3$ is 53°C and 356°C (Fig. 2), respectively. As expected, the orthorhombic-tetragonal phase transition was not observed above room temperature for the samples of x=0.005, 0.01 and 0.02 from dielectric temperature curves as shown in Fig. 2. In addition, the tetragonal-cubic phase transition temperature decreased from 356°C to 313°C and the dielectric peaks become much broader and lower with increasing $BaTiO_3$ content as Chang has observed for KNN-BT system [14]. That is, for (1-x)KNNLS-xBT system, $BaTiO_3$ leads to a diffuse phase transition which is typical for relaxor ferroelectrics. Usually, the maximum

Table 1 Some piezoelectric parameters of all the samples.

Compositions	x=0	x=0.005	x=0.01	x=0.02
Q_m	44	50	51	79
d_{33}(pC/N)	241	209	204	150
k_p	0.48	0.42	0.32	0.30
tanδ	0.029	0.026	0.034	0.028
ρ(g/cm^3)	4.22	4.29	4.27	4.29

of dielectric constant ($\varepsilon_{r\ max}$) decreases and their corresponding temperature (T_m) increases with increasing measurement frequency for relaxor ferroelectrics [16, 17]. Figure 3 shows the temperature dependence of the dielectric responses for the sample of x=0.02 in the frequency range from 10 k to 1 MHz. As can be seen, $\varepsilon_{r\ max}$ changes obviously but rulelessly whereas T_m, unchanged with increasing measurement frequency. This indicates that (1-x) KNNLS-xBT system may exhibit slight ferroelectric-relaxor behavior. In order to describe the diffuseness of the ferroelectric phase transition, Uchino et al. proposed an empirical expression as Eq. 1 [16]:

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{r\max}} = \frac{(T - T_m)^\gamma}{C}, \quad (1)$$

where γ and C are constant, the γ value is between 1 and 2. The limiting values γ=1 and γ=2 reduce the equation for normal ferroelectrics and ideal relaxor ferroelectrics, respectively. The γ values can be obtained from the slopes of log ($1/\varepsilon_r - 1/\varepsilon_{rmax}$) versus log($T - T_m$) lines which are plotted in Fig. 4. Results obtained from the fitting curves are almost a constant value about 1.2 with increasing $BaTiO_3$ content. That is, all the samples are nearly normal ferroelectrics and 2 mol% $BaTiO_3$ can hardly affect the relaxor behavior of (1-x)KNNLS-xBT system.

Figure 5 shows the SEM pictures of all the samples. As can be seen, the sample without $BaTiO_3$ has a microstructure with blur grain boundary and unconspicuous liquid phase whereas the samples show clearer grain boundaries with increasing $BaTiO_3$ content. From the SEM pictures it also can be found that the sample with 0.5 and 1 mol% $BaTiO_3$ exhibits more homogeneous and lager grains, respectively. For KNN-based ceramics, the evaporation of alkaline metal elements which can lead to niobium excess is the most important reason for poor sintering [18]. Proper amount of melting phase originated from the niobium excess can facilitate the grain growth during sintering whereas superfluous will suppress the growth. Figure 5 indicates that 2 mol% $BaTiO_3$ may suppress the volatilization of alkaline metal elements efficiently and 1 mol% $BaTiO_3$ is beneficial to the growth of (1-x)KNNLS-xBT ceramics.

In order to investigate the ferroelectric properties of (1-x) KNNLS-xBT system, the *P-E* hysteresis loops were measured at room temperature as shown in Fig. 6. The remnant polarization P_r of x=0 is about 20 μC/cm^2 and with increasing x, the spontaneous polarization becomes lower. The coercive field E_c for the sample of x=0.01 is relatively high while for the other samples is almost equal to the same value about 1,700 V/mm. These results strongly suggest that the addition of $BaTiO_3$ is not beneficial to improve the ferroelectric properties for (1-x)KNNLS-xBT ceramics.

Some piezoelectric parameters of all the samples are listed in Table 1. The results show that $BaTiO_3$ has a great influence on the piezoelectric properties of (1-x)KNNLS-xBT system. With increasing x, the piezoelectric strain coefficient d_{33} and piezoelectric coupling constant k_p decrease greatly whereas the mechanical quality factor Q_m increases from 44 to 79. The change of k_p, d_{33} and Q_m in opposite directions indicates that $BaTiO_3$ may play a "hard" role for (1-x)KNNLS-xBT system.

4 Conclusions

Tetragonal perovskite structure (1-x)KNNLS-xBT ceramics were prepared by conventional ceramic processing. $BaTiO_3$ has great effect on the microstructure, piezoelectric and ferroelectric properties. Both $T_{O\text{-}T}$ and T_C decreased significantly with increasing x and 0.5%mol $BaTiO_3$ led to a downward shift of $T_{O\text{-}T}$ from 53°C to below room temperature. 2%mol $BaTiO_3$ can suppress the volatilization of sodium efficiently and promote Q_m from 44 to 79.

Acknowledgements Supported by National Natural Science Foundation of China (No. 50802038), the Doctor Foundation of Shandong province (Grant No. 2007BS04047) and National High Technology Research and Development Program of China (No. 2006AA03Z437).

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