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Good temperature stability of $K_{0.5}Na_{0.5}NbO_3$ based lead-free ceramics and their applications in buzzers

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Abstract

$(K_{0.5-x}Li_x)Na_{0.5}(Nb_{1-y}Sb_y)O_3$ (KLNNSx–y, x = 0–4 mol% and y = 0–8 mol%) lead-free piezoelectric ceramics were prepared by the conventional mixed oxide method. The denser microstructure and better electrical properties of the ceramics were obtained as compared to the pure $K_{0.5}Na_{0.5}NbO_3$ ceramic. The temperature stability of the electrical properties of the ceramics was also investigated. The experimental results show that the KLNNS2.5–5 ceramic exhibits good electrical properties ($k_p \sim 49\%$, $k_{31} \sim 30\%$ and $\varepsilon_{33}^T/\varepsilon_0 \sim 543$, $\tan\delta \sim 0.019$), and possesses good temperature stability in the temperature range of −40 to 85 °C. The related mechanisms for improved electrical properties and temperature stability were also discussed. Moreover, buzzers based on the KLNNS2.5–5 ceramic have been fabricated and their characterization is presented. These results show that the KLNNS2.5–5 ceramic is a promising lead-free material for practical application in buzzers.

Keywords: Lead-free ceramics; Piezoelectric properties; Niobates; Temperature stability; $(K,Na)NbO_3$

1. Introduction

It is well-known that $Pb(Zr, Ti)O_3$ (PZT) based piezoelectric ceramics play a dominant role in current piezoelectric applications such as transducers, actuators, and sensors, owing to their excellent electrical properties and very good temperature stability.[1] Recently, some environmental regulations, e.g., restriction of hazardous substances (RoHS), have been enforced in the European Union. Some piezoelectric devices including lead compounds may be prohibited in the near future. Therefore, it is urgent to develop lead-free piezoelectric materials substituting for the widely used PZT system.[2]

$BaTiO_3$ (BT) was the first lead-free ceramics applied in piezoelectric devices. The low Curie temperature ($T_c \leq 120\,°C$) and the occurrence of multiple polymorphic phase transitions (at 5 °C) limited their applications.[3] Recently, considerable attention for lead-free piezoelectric ceramics has been focused on $K_{0.5}Na_{0.5}NbO_3$ (KNN) based ceramics because of its high Curie temperature (above 400 °C) and large electromechanical coupling coefficients ($k_p \sim 36\%$).[4] Nevertheless, pure KNN ceramics are difficult to densify by ordinary sintering process. Hence, hot pressing (HP) and spark plasma sintering (SPS) have been used to obtain KNN ceramics with high densities.[5,6] However, such processing techniques are not always appropriate for industrial use. Besides, with different additions, such as $LiNbO_3$,[7] $LiTaO_3$,[8] $LiSbO_3$,[9–12] Li(Nb, Ta, Sb)O_3,[13–16] (Li, Ag)(Nb, Ta, Sb)O_3,[17] (Li, Bi)NbO_3,[18] $BaTiO_3$,[19] $Bi_{0.5}Na_{0.5}TiO_3$,[20] and $K_4CuNb_8O_{23}$,[21] KNN-based ceramics sintered in the ordinary way have been reported to exhibit improved densification and enhanced electrical properties. It is noted that the KNN–$LiSbO_3$ system seems more interesting as it reveals high piezoelectric properties and relatively low cost. Unfortunately, the obvious improvement on the piezoelectric properties of the system is always accompanied by the polymorphic phase transition (from orthorhombic to tetragonal) temperature (T_{O-T}) decreasing to around room

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temperature.[9–12] Although this kind of ceramic shows excellent electrical properties at room temperature, the temperature stability of the electrical properties is relatively poor, which may limit its practical application greatly.[22] Consequently, special attention should be paid to improve the temperature stability of the ceramics for their applications.

It has also been reported that Li^+ substitution for $(K_{0.5}Na_{0.5})^+$ in the KNN–$LiSbO_3$ system is more effective than Sb^{5+} substitution for Nb^{5+} in decreasing the T_{O-T}.[23] It can be expected to improve the sinterability and piezoelectric properties further without decreasing T_{O-T} greatly by adding a proper amount of Li and Sb into KNN. Thus good temperature stability around room temperature can be achieved. Based on this consideration, 0–4 mol% of Li and 0–8 mol% of Sb were used to substitute for K-site and Nb-site in $K_{0.5}Na_{0.5}NbO_3$, respectively. The purpose of this work is not only to synthesize $(K_{0.5-x}Li_x)Na_{0.5}(Nb_{1-y}Sb_y)O_3$ (KLNNS*x*–*y*) ceramics with good temperature stability, but also to fabricate buzzers using the ceramic membranes.

2. Experimental

The KLNNS*x*–*y* (x = 0–4 mol% and y = 0–8 mol%) ceramics were prepared by the conventional mixed oxide method. The carbonate or oxide powders of K_2CO_3 (98%), Na_2CO_3 (99.8%), Li_2CO_3 (97%), Nb_2O_5 (99.5%), and Sb_2O_3 (98%) of the electronic grade were selected as the starting raw materials. The stoichiometric powders were mixed by ball milling for 6 h with a vibratory mill and then calcined at 850–900 °C for 4 h. The calcined powders were again ball milled, granulated, and pressed into discs by dry pressing at 10 MPa with diameters of 13–14 mm and thicknesses of 1.1–1.3 mm. The disk samples were sintered at 1050–1120 °C for 2 h in air. After the deposition of silver electrodes, the specimens were poled in silicone oil at 120 °C under 4 kV/mm for 30 min.

The X-ray diffraction (XRD) patterns of the ceramics were obtained using Cu Kα radiation (D/max-2500PC). The surface images of the ceramics were obtained by scanning emission microscope (SEM) (JSM-5900). The bulk density (ρ) was measured according to the Archimedes method. The piezoelectric constant (d_{33}) was measured using a piezo-d_{33} meter (ZJ-3A). The electromechanical coupling factors (k_p and k_{31}), planar frequency constant (N_p), and mechanical quality factor (Q_m) were measured and calculated by the resonance–antiresonance method using an impedance analyzer (HP 4294A). The temperature dependence of the dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$) of the unpoled samples was measured at 10 kHz using a programmable furnace with the impedance analyzer (HP 4278A). The polarization versus electric (*P*–*E*) hysteresis loops of the ceramics were measured using a Radiant Precision Workstation (USA). The temperature coefficient of the k_p and resonance frequency (f_r) were measured in the temperature range from −40 to 85 °C and the equations are as follows:

$$\frac{\Delta k_p}{k_{p\,25\,^\circ C}} = \frac{k_p - k_{p\,25\,^\circ C}}{k_{p\,25\,^\circ C}}$$

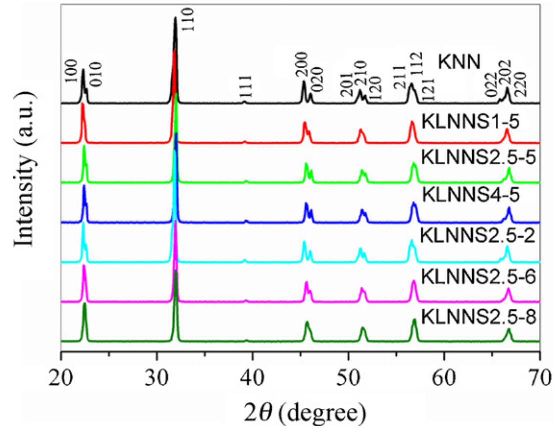

Fig. 1. XRD patterns of $(K_{0.5-x}Li_x)Na_{0.5}Nb_{1-y}Sb_yO_3$ (KLNNS*x*–*y*) ceramics.

and

$$\frac{\Delta f_r}{f_{r\,25\,^\circ C}} = \frac{f_r - f_{r\,25\,^\circ C}}{f_{r\,25\,^\circ C}}.$$

3. Results and discussion

Fig. 1 shows the XRD patterns of the KLNNS*x*–*y* ceramics in the 2θ range of 20–70°. All the ceramic samples possess a single perovskite phase with orthorhombic structure, which suggests that Li^+ and Sb^{5+} have diffused into the KNN lattice to form a solid solution. It is also found that the positions of the diffraction peak of the ceramics shift to higher angles with increasing amount of Li and Sb. It is thought that the Li^+ and Sb^{5+} substitutions induce the distortion and shrinkage of the lattice parameters, which may be attributed to the smaller ionic radii of Li^+ (0.76 Å) and Sb^{5+} (0.60 Å) than those of K^+ (1.38 Å) and Nb^{5+} (0.64 Å), respectively.

Fig. 2 presents the surface images of the (a) pure KNN ceramic sintered at 1100 °C and (b) KLNNS2.5–5 ceramic sintered at 1095 °C. It can be observed from Fig. 2(a) that many distinct pores exist in the pure KNN ceramic and the average grain size is about 10 μm. For the KLNNS2.5–5 ceramic, almost no pores are observed and the average grain size is about 2–4 μm, as shown in Fig. 2(b). In addition, the grains of the KLNNS2.5–5 ceramic become more uniform as compared to the pure KNN ceramic. For the KLNNS*x*–5 ceramics, it was found that the sintering temperature decreased and the average grain size increased with increasing amount of Li. At x = 4 mol%, a few distinct grains with diameters of about 10 μm were observed in the sample. In contrast, the sintering temperature of the KLNNS2.5–*y* ceramics increased slightly with increasing amount of Sb, and the average grain size decreased slightly and the grains became more uniform. Fig. 3 shows the bulk density and relative density ratio as a function of (a) the x of Li for the KLNNS*x*–5 ceramics and (b) the y of Sb for the KLNNS2.5–*y* ceramics. In this study, a density of 4.25 g/cm^3 was obtained for the pure KNN ceramic, which reached 94% of the theoretical value. It can be observed in Fig. 3 that all the KLNNS*x*–*y* ceramics possess high densities of about 4.40–4.57 g/cm^3, which are more than 96% of the theoretical values. From the above results,

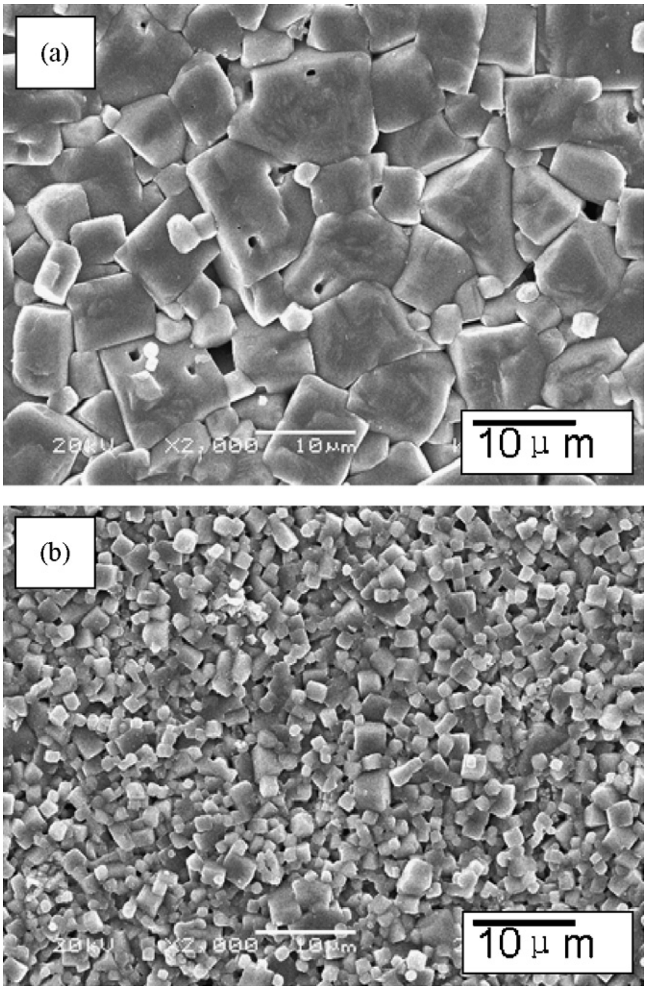

Fig. 2. SEM photographs of (a) pure KNN and (b) KLNNS2.5–5 ceramics.

it is evident that the addition of Li and Sb can assist the densification of the KNN ceramics and improve the sinterability of the ceramics. This may be related to the low melting point of Li compounds which promote the formation of a transitory liquid phase during sintering.[9,11,24]

Fig. 4 shows the temperature dependence of $\varepsilon_{33}^T/\varepsilon_0$ for the (a) pure KNN and KLNNS*x*–5 ceramics with $x = 1$, 2.5, and 4 mol% and (b) KLNNS2.5–*y* ceramics with $y = 2, 4, 6, 8$ mol% at 10 kHz. The insets in Fig. 4(a) and (b) summarize the variations of their $T_{\mathrm{O-T}}$ and T_{C} values with *x* and *y*, respectively. For the pure KNN ceramic, two phase transition peaks are observed at 215 and 430 °C, corresponding to the phase transitions of orthorhombic–tetragonal (at $T_{\mathrm{O-T}}$) and tetragonal–cubic (at T_{C}), respectively. Similar to KNN, all the KLNNS*x*–*y* ceramics undergo the same two phase transitions. This result further confirms that the KLNNS*x*–*y* ceramics is in orthorhombic phase at room temperature. However, the $T_{\mathrm{O-T}}$ of the KLNNS*x*–5 ceramics decreases almost linearly from 176 to 100 °C as *x* increases from 1 to 4 mol%, while the T_{C} increases from 317 to 360 °C, as shown in Fig. 4(a). On the other hand, it can be observed in Fig. 4(b) that the $T_{\mathrm{O-T}}$ of the KLNNS2.5–*y* ceramics decreases with increasing amount of Sb (i.e., *y*) up to 4 mol%, and then remains about 140 °C when $y \geq 5$ mol%. These results

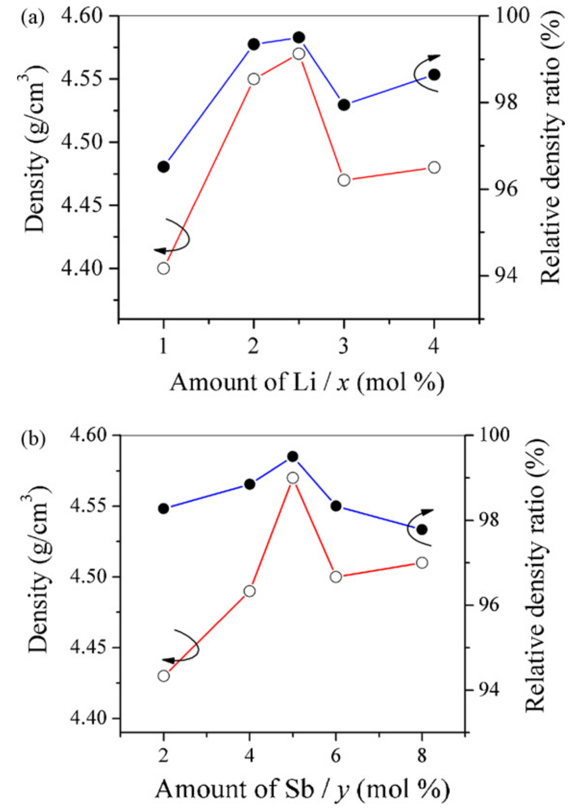

Fig. 3. Density and relative density ratio of KLNNS*x*–*y* ceramics as function of (a) *x* for KLNNS*x*–5 ceramics and (b) *y* for KLNNS2.5–*y* ceramics.

suggest that the KLNNS*x*–*y* ceramics can possess relatively good temperature stability of the electrical properties around room temperature.

Table 1 summarizes the piezoelectric and dielectric properties for pure KNN and some typical compositions of the KLNNS*x*–*y* ceramics. As shown in Table 1, all the KLNNS*x*–*y* ceramics exhibit higher piezoelectric and dielectric properties as compared to the pure KNN ceramic. It is known that piezoelectric properties of KNN ceramics are sensitive to densification. This phenomenon has been observed in the air-sintered ($\rho = 4.25$ g/cm^3, $d_{33} = 80$ pC/N, and $k_{\mathrm{p}} = 36\%$) and hot-pressed ($\rho = 4.46$ g/cm^3, $d_{33} = 160$ pC/N, and $k_{\mathrm{p}} = 45\%$) KNN ceramics.[4,5] Thus the main reason for the improved piezoelectric properties of the KLNNS*x*–*y* ceramics can be ascribed to the dense microstructure. Another possible reason may partly be attributed to the substitution of Li^+ for K^+ and the substitution of Sb^{5+} for Nb^{5+} in the KNN cause lattice deformation, which facilitates domain movement leading to higher piezoelectric properties. In particular, a high k_{p} of 49% and a low $\tan\delta$ of 0.019 were obtained for the KLNNS2.5–5 ceramic, while the other electrical properties remains reasonably good: $k_{31} = 30\%$, $d_{33} = 155$ pC/N, $Q_{\mathrm{m}} = 193$, $N_{\mathrm{p}} = 3390$, and $\varepsilon_{33}^T/\varepsilon_0 = 543$. Subsequently, the temperature stability of the KLNNS2.5–5 ceramic was mainly studied.

Fig. 5 shows the temperature dependence of k_{p} and N_{p} in the temperature range of −40 to 85 °C for the KLNNS2.5–5 ceramic. The k_{p} was found to be 48.5% at −40 °C and 50% at 85 °C. In addition, the N_{p} decreased slightly from 3430 to

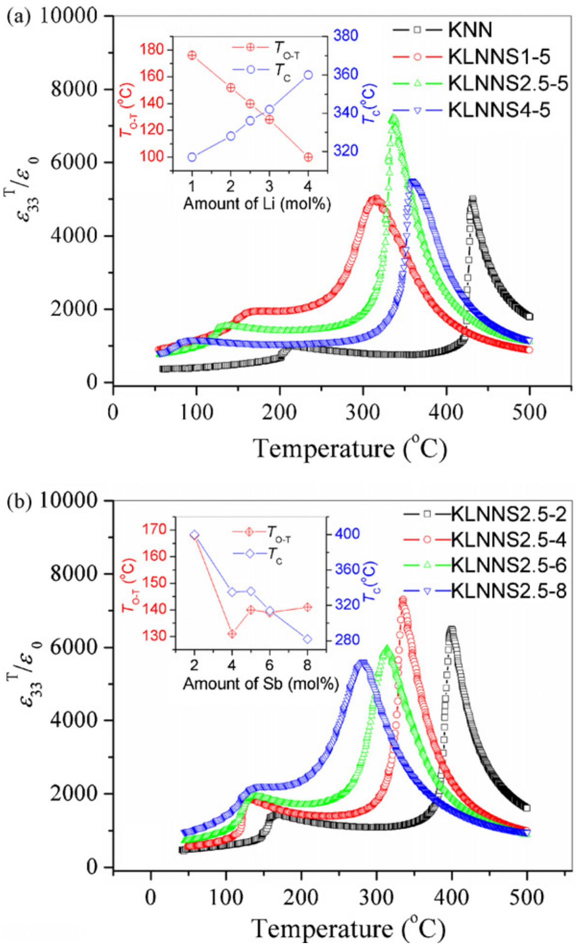

Fig. 4. Temperature dependence of $\varepsilon_{33}^T/\varepsilon_0$ of (a) KLNNS*x*–5 ceramics and (b) KLNNS2.5–*y* ceramics at 10 kHz (the insets are the variations of their $T_{O–T}$ and T_C values with *x* and *y*, respectively).

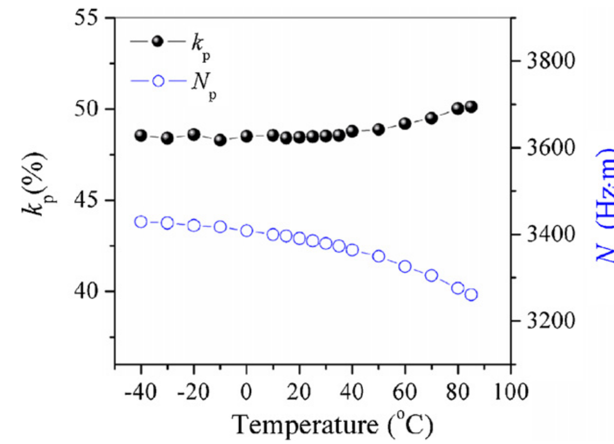

Fig. 5. Temperature dependence of k_p and N_p in the temperature range of −40 to 85 °C for KLNNS2.5–5 ceramic.

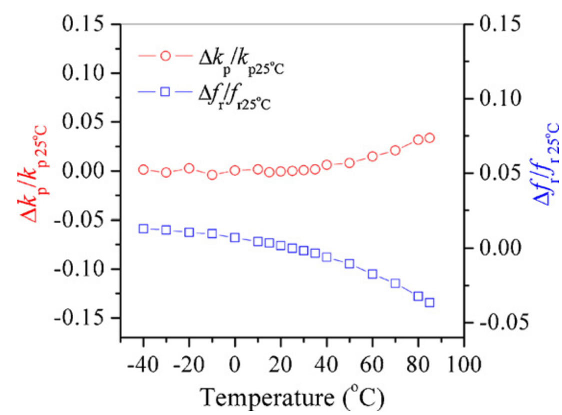

Fig. 6. Variations of $\Delta k_p/k_{p\,25\,°C}$ and $\Delta f_r/f_{r\,25\,°C}$ in the temperature range of −40 to 85 °C for KLNNS2.5–5 ceramic.

3260 Hz m as the temperature increases from −40 to 85 °C. The variations of $\Delta k_p/k_{p\,25\,°C}$ and $\Delta f_r/f_{r\,25\,°C}$ in the temperature range of −40 to 85 °C for the KLNNS2.5–5 ceramic are shown in Fig. 6. The $\Delta k_p/k_{p\,25\,°C}$ value exhibited a negative maximum of −0.004 and a positive maximum of 0.033 at −10 and 85 °C, respectively. In addition, the $\Delta f_r/f_{r\,25\,°C}$ with a positive maximum value of 0.013 was obtained at −40 °C and with a negative maximum value of −0.036 was obtained at 85 °C. It is known that the temperature stability of f_r is mainly related to the variation of elastic constant. The change in the crystal structure results in the variation of elastic constant with increasing temperature. In general, two phase coexistence would greatly improve some properties such as piezoelectric and elastic properties. This phenomenon has been observed in $Pb(Mn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ single crystals.[25] Therefore, the increase in the elastic constant leads to a decrease in the f_r with increasing temperature towards the $T_{O–T}$. Meanwhile, $\Delta f_r/f_{r\,25\,°C}$ values increase with increasing temperature resulting in the degradation of the temperature stability. It has been reported that the 0.948KNN–0.052$LiSbO_3$ ceramic exhibits excellent piezoelectric properties with k_p = 50% and d_{33} = 265 pC/N, but it possesses a low $T_{O–T}$ of 35 °C.[12] The $T_{O–T}$ near room temperature may limit its applications greatly because of the property

Table 1
Properties of $(K_{0.5-x}Li_x)Na_{0.5}Nb_{1-y}Sb_yO_3$ (KLNNS*x*–*y*) ceramics at room temperature

Compositions	ρ (g/cm³)	k_p (%)	k_{31} (%)	d_{33} (pC/N)	Q_m	N_p (Hz m)	$\varepsilon_{33}^T/\varepsilon_0$	tan δ	$T_{O–T}$ (°C)	T_C (°C)
KNN	4.25	35	21	102	79	3180	353	0.237	215	430
KLNNS2–5	4.55	45	27	156	152	3360	614	0.041	152	328
KLNNS2.5–5	4.57	49	30	155	193	3390	543	0.019	140	336
KLNNS3–5	4.47	43	26	151	143	3370	637	0.027	128	342
KLNNS2.5–4	4.49	45	27	144	174	3350	533	0.025	131	335
KLNNS2.5–6	4.50	42	25	164	116	3400	797	0.044	139	314

Dielectric properties were measured at 1 kHz.

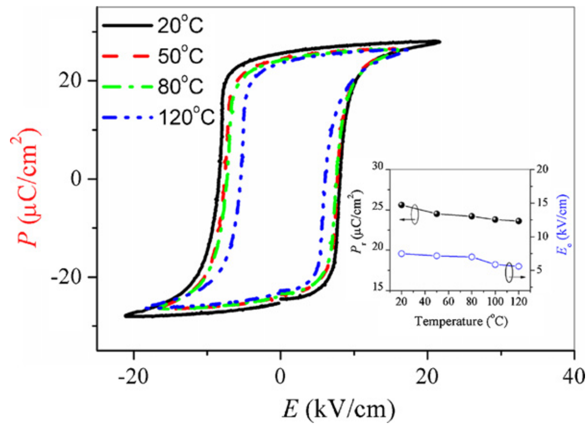

Fig. 7. *P*–*E* hysteresis loops of KLNNS2.5–5 ceramic at different temperatures. The inset is the remnant polarization and coercive field of the KLNNS2.5–5 ceramic as a function of temperature.

variation and domain instability during thermal cycling between the two ferroelectric phases (the electromechanical coupling factors were decreased by 10% with the thermal cycling for the 0.948KNN–0.052LiSbO_3 ceramic).[12,26] In this study, although the piezoelectric properties of the KLNNS2.5–5 ceramic are lower than those reported results of other KNN-based ceramics, the sample possesses better temperature stability in the temperature range of −40 to 85 °C. Moreover, the resonance frequency, piezoelectric, and dielectric properties of the KLNNS2.5–5 ceramic almost keep unchanged after 12 weeks, which suggests that the sample also possesses good aging characteristics.

The *P*–*E* hysteresis loops of the KLNNS2.5–5 ceramic were also measured at different temperatures, as shown in Fig. 7. The inset in Fig. 7 is the remnant polarization (P_r) and coercive field (E_c) of the sample as a function of temperature. It can be observed from Fig. 7 that well-saturated hysteresis loops were obtained, which confirms the good ferroelectric nature of the ceramics. The P_r was found to be 25.6 μC/cm^2 with an E_c of 7.48 kV/cm at room temperature, decreasing to 23.6 μC/cm^2 with an E_c of 5.60 kV/cm at 120 °C. These results indicate that the ferroelectric properties of the KLNNS2.5–5 ceramic also possess good temperature stability in the measured temperature range.

The KLNNS2.5–5 ceramic possess good temperature stability of the electrical properties, which was selected as the materials for fabricating superthin buzzers. The superthin buzzers were prepared using the KLNNS2.5–5 ceramic membranes with diameters of 15–16 mm and thicknesses of 0.10–0.11 mm obtained by the roll forming process. The photographs of the KLNNS2.5–5 ceramic membranes and buzzers are shown in Fig. 8. The electrical properties of the piezoceramic membranes are $k_p = 0.44$–0.45, $\varepsilon_r = 450$–550 (120 Hz), and $\tan\delta = 0.020$–0.035 (120 Hz). Besides, the f_r of the superthin buzzer disks is 4.60–4.70 kHz. Fig. 9 shows the sound pressure level (SPL) of the lead-free superthin buzzers as a function of frequency in the range of 20–20,000 Hz. It was found that the SPL reaches 84.2 dB at 2 kHz, which is slightly lower than that (SPL ≥ 85 dB) of the lead-based buzzers. In addition, a maximum value (∼88.8 dB) of SPL was obtained at 2.81 kHz. The

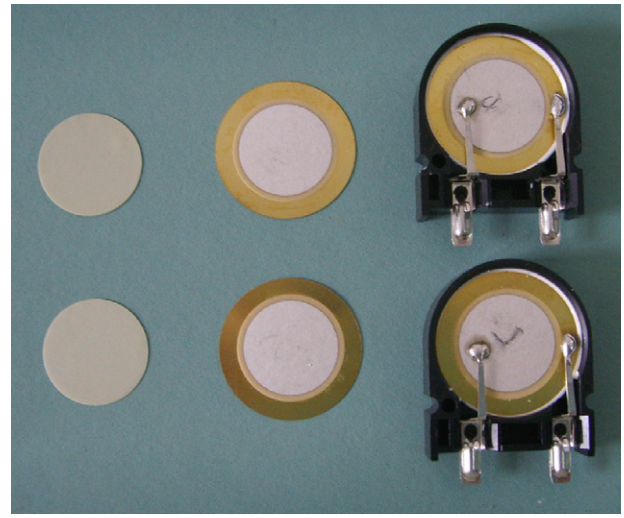

Fig. 8. Photographs of KLNNS2.5–5 ceramic membranes and buzzers.

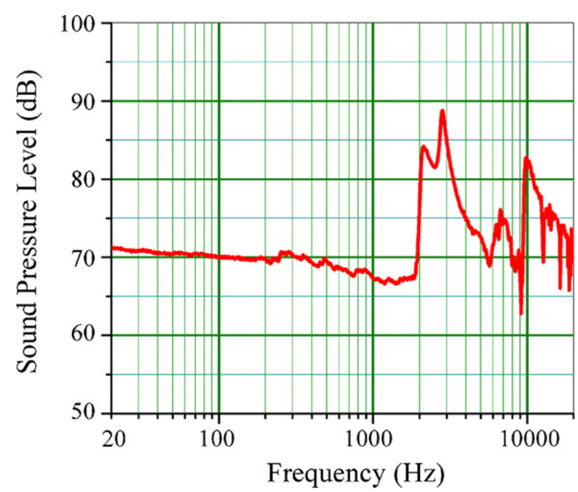

Fig. 9. Sound pressure level of KLNNS2.5–5 based superthin buzzers as function of frequency in range of 20–20,000 Hz.

results show that the lead-free buzzers have good electroacoustic properties which can basically satisfy the requirements of practical applications, e.g., microwave ovens.

4. Summary

$(K_{0.5-x}Li_x)Na_{0.5}Nb_{1-y}Sb_yO_3$ lead-free piezoelectric ceramics with dense microstructure and good temperature stability have been prepared by ordinary sintering process. XRD analysis revealed that single perovskite phase with orthorhombic structure was obtained in all ceramic samples. The ceramics exhibited improved densification and electrical properties by adding a proper amount of Li and Sb to KNN without decreasing the T_{O-T} greatly. The electromechanical factors and dielectric properties of the KLNNS2.5–5 ceramic were found to be $k_p \sim 49\%$, $k_{31} \sim 30\%$ and $\varepsilon_{33}^T/\varepsilon_0 \sim 543$, $\tan\delta \sim 0.019$, respectively, with good temperature stability in the temperature range of −40 to 85 °C. Besides, buzzers based on the KLNNS2.5–5 ceramic have good electroacoustic properties which can basically satisfy the requirements of practical applications, and the preparation techniques are very convenient to make their industrial production possible. Results show that the KLNNS2.5–5 ceramic is a promising lead-free material for practical application in buzzers.

Acknowledgements

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