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Hardening characteristics and compositional dependence of piezoelectric properties in Cu^{2+} modified $0.52NaNbO_3$–$(0.48-x)KNbO_3$–$xLiNbO_3$ ceramics

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ABSTRACT

The phase transition and compositional dependence of piezoelectric properties were investigated for ternary lead-free $NaNbO_3$–$KNbO_3$–$LiNbO_3$ system where Li^+ is solely substituted for K^+. An orthorhombic–tetragonal phase transition near room temperature was identified when 2–4 mol% K^+ was replaced by Li^+. The hardening behavior of piezoelectric properties was induced by adding a few amount of CuO, but remarkably influenced by the content of Li^+ in the composition. Mechanisms concerning the phase transition diffuseness, grain morphology and defect dipoles were discussed in combination with the variation of electrical properties.

1. Introduction

Solid solutions of antiferroelectric $NaNbO_3$ (NN) and ferroelectric $KNbO_3$ (KN) near their morphotropic phase boundary exhibit excellent dielectric and piezoelectric properties [1,2]. The further modified compositions such as $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$xLiNbO_3$ (NKN–xLN) own significantly improved piezoelectric properties through shifting a polymorphic phase transition (PPT) between orthorhombic and tetragonal phases toward room temperature [3]. Furthermore, it was reported that $(1-x)$NN–xLN compositions own several phase transitions [4,5]. There exists a two-phase coexistence zone at room temperature between orthorhombic and tetragonal ferroelectric phases at $x{\sim}0.12$, near which enhanced piezoelectric properties were achieved [6].

Therefore, it is possible to make new compositions in NN–KN–LN ternary systems by substituting Li^+ only for K^+, rather than conventionally for both K^+ and Na^+ in equal mole [3]. This could reduce the content of K^+ in the total composition, and simultaneously generate a two-phase coexistence zone at room temperature. It is known that K^+ not only tends to volatilize seriously at high temperature, but also causes the deliquescence of the samples in air.

As far as electrical properties are concerned, alkaline niobate ceramics exhibit typical softening characteristics. Their high dielectric loss and small Q_m values make them hard to be applied for high-power device applications. The addition of CuO as a frequently used acceptor dopant could obviously induce hardening characteristics in pure NKN ceramics [7]. However, this seems not to work well in modified NKN based samples where Q_m values are considerably low [8–10] although these compositions may have relatively high piezoelectric constants. It appears that the hardening effect in these systems doped with Cu^{2+} is closely related to the composition of the materials. In addition, the hardening features associated with domain switching behaviors could be related to the point defects in the compositions, to the phase coexistence as well as to the grain boundaries based on different domain stabilization mechanisms [11–13].

The purpose of this study is thus to investigate the phase transition and the compositional dependence of various electrical properties for ternary 0.52NN–$(0.48-x)$KN–xLN (NKLNx) lead-free ceramics. The 1 mol% CuO was used to improve the densification behavior and specially to explore the influence of Li^+ content on hardening effects in CuO doped NKN based compositions. The grain morphology, densification and various electrical properties will be explored in detail. The mechanism of how the hardening effect is correlated to the content of Li^+ and Cu^{2+} was discussed.

2. Experimental

High-purity oxides and carbonates, Nb_2O_5 (99.5%), Ta_2O_5 (99.9%), Sb_2O_3 (99.9%), CuO (99.0%), Na_2CO_3 (99.8%), K_2CO_3 (99.0%) and Li_2CO_3 (99.9%), were used as the starting materials. After calcinations at 850–900 °C, 1 mol% CuO and 0.5 wt% PVB binder were added, followed by a mill process for 24 h together with. Disk specimens were sintered in air at 1010–1100 °C for 3 h. For electrical measurements, silver paste was screen printed and then fired at 550 °C for 30 min. The electric poling was performed at 110 °C in a silicone oil bath by applying a dc

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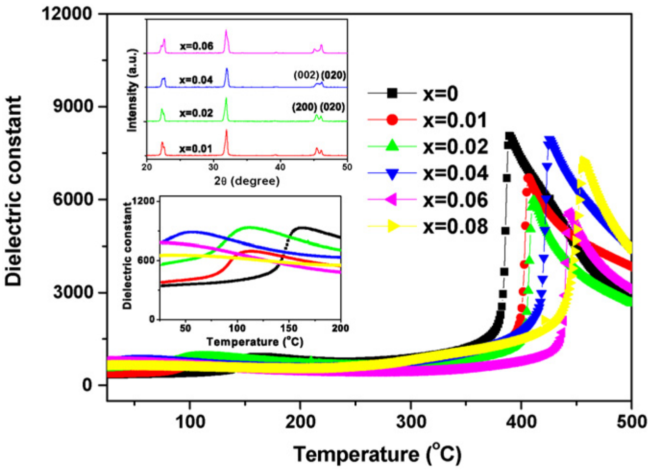

Fig. 1. Dielectric constants at 1 kHz as a function of temperature for 1 mol% CuO doped NKLN*x* ceramics. Insets are locally magnified dielectric constant versus temperature curves (lower) and XRD results for samples with different *x* (upper).

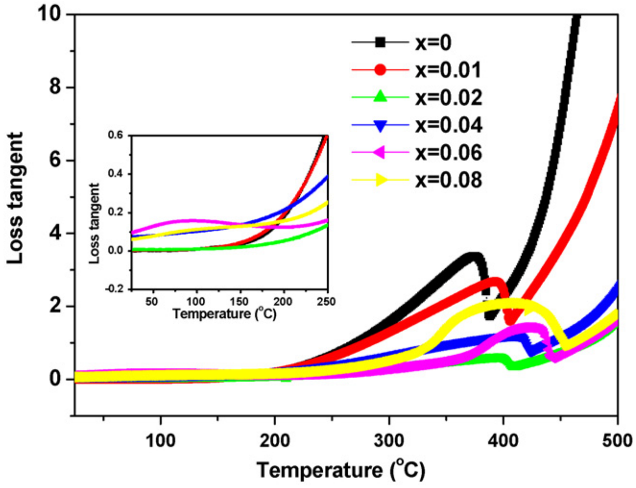

Fig. 2. Loss tangent values at 1 kHz as a function of temperature for 1 mol% CuO doped NKLN*x* ceramics. Inset is locally magnified curves in the temperature range of 25–250 °C.

field of 3–5 kV/mm for 20 min and the electric field was maintained during cooling.

The crystal structure was examined by an X-ray diffractometer (XRD, D/Mzx-rB, Rigaku, Japan) using a Cu Ka radiation. The microstructure was observed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, Santa Clara, CA) equipped with a temperature box. Polarization was measured under an alternating electric field using a ferroelectric measuring system (Precision Premier II, Radiant Technologies, Albuquerque, NM). The piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by a resonance–antiresonance method with an impedance analyzer (Impedance Analyzer, PV70A, Beijing, China).

3. Results and discussion

It can be seen from Fig. 1 that the PPT of the $Na_{0.52}K_{0.48}NbO_3$ composition was gradually moved downwards with the addition of Li^+. At $x = 0.02$–0.04, the PPT approximately locates near room temperature. Furthermore, the phase transition behavior near room temperature was identified by XRD (see inset). A phase transition zone between orthorhombic and tetragonal ferroelectric phases can be identified within $x = 0.02$–0.04. The dielectric-temperature measurements keep agreement with the XRD results. Compared to previous studies [3] where Na^+ and K^+ in equal molar were together substituted by Li^+, less Li^+ in this study is needed to induce the phase structure transition near room temperature. Although all compositions were mixed with 1 mol% CuO, yet all of them exhibit a perovskite structure. On the other hand, T_c increases with the substitution of more K^+ by Li^+. The change of phase transition temperatures indicates that the Li^+ substitution tends to stabilize the tetragonal ferroelectric phase. Although Li^+ has similar electron configurations to Na^+ and K^+ (in the same group of Periodic Table of the Elements), yet Li^+ tends to form an ilmenite structure rather than a perovskite structure possibly owing to different ionic radius (CN = 12, $R_{Li} = 1.25$ Å, $R_{Na} = 1.39$ Å and $R_K = 1.64$ Å) [14], because Li^+ is too small to fit A-site of a perovskite structure. Therefore, $LiNbO_3$ with an ilmenite structure will cause lattice distortion after it enters into NKN perovskite lattices. This kind of structural distortion could become the reason for the above-mentioned phase transition. In addition, loss tangent values of Cu^{2+} and Li^+ co-doped NKN ceramics were measured as a function of temperature, as shown in Fig. 2. In general, loss values increase with increasing temperature and reach maxima at the ferroelectric–paraelectric phase transition temperatures. However, they slightly increase with increasing the content of Li^+ in the composition. Owing to that the doping level of CuO is fixed at 1 mol%, the change of loss values with the content of Li^+ could be thus partially attributed to the densification. The influence of Cu^{2+} and Li^+ co-doping on the microstructure and sample density will be mentioned later.

Fig. 3 shows that the addition of 1 mol% CuO has induced an evident hardening effect in all compositions as indicated by double hysteresis-like curves [7]. The remnant polarization P_r becomes smaller (approximately 3 $\mu C/cm^2$ in this study, usually 15 $\mu C/cm^2$ for un-doped NKN ceramics [2]) and the coercive field E_c increases (>1600 V/mm in this study, usually 950–1000 V/mm for un-doped NKN ceramics [2]). However, the hardening effect induced by adding 1 mol% CuO was found to depend on the content of Li^+, although both P_r and E_c slightly fluctuate with *x*. This is probably because there are so many factors influencing both parameters (P_r and E_c), for examples, the density, microstructure (grain morphology) and phase structures, in addition to the domain structure. Compared to Na^+, K^+ and Li^+, Cu^{2+} is too small to fit A-site of a perovskite structure (CN = 6, $R_{Cu} = 0.73$ Å, $R_{Nb} = 0.64$ Å), but could occupy B-site, thus replacing Nb^{5+} as an acceptor dopant.

The piezoelectric and electromechanical properties of the samples with various compositions were shown in Table 1. On the one hand, it can be found that the addition of a small amount of Li^+ tends to increase d_{33} and k_p to optimum values, as the composition approaches a two-phase coexistence zone. On the other

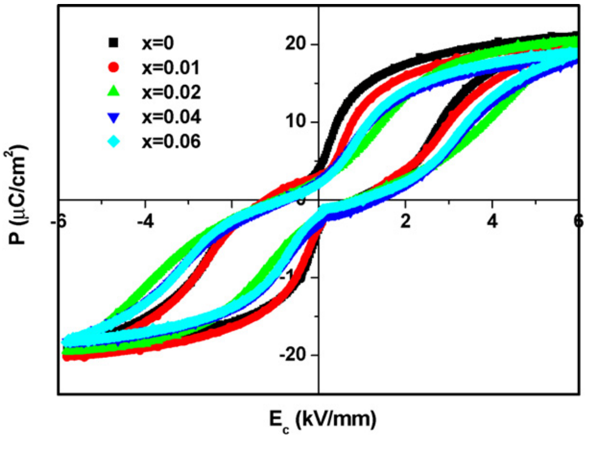

Fig. 3. Hysteresis loops of polarization versus electric field for 1 mol% CuO doped NKLN*x* ceramics.

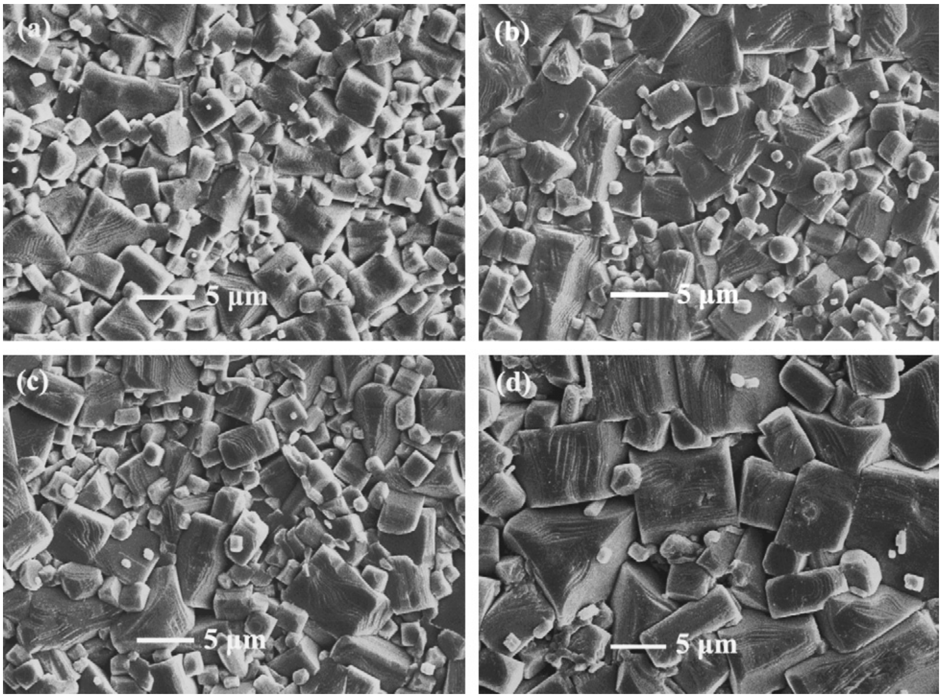

Fig. 4. Scanning electron microscopy images of NKLNx ceramics sintered at 1050 °C: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$ and (d) $x = 0.06$.

Table 1
Various electrical and physical properties of 1 mol% CuO doped NKLNx ceramics sintered at 1050 °C.

x	Density (g/cm^3)	$\varepsilon_{33}{}^{T}$	d_{33} (pC/N)	k_p	Q_m
0	4.25	1397	104	0.34	834
0.01	4.33	1287	109	0.36	1023
0.02	4.27	1173	99	0.31	410
0.04	4.26	1154	94	0.24	193
0.06	4.23	1238	91	0.17	164

hand, the mechanical quality factor Q_m changes remarkably with the Li$^+$ content in the compositions doped with 1 mol% CuO. It was reported that the Q_m for pure NKN ceramics is approximately 150, but significantly increases to 2400 after the addition of CuO [10]. In this study, the samples could still have an improved Q_m when x is small; however, the samples with more Li$^+$ have a much less improved Q_m. It is indicated that the content of Li$^+$ has an effect on the hardening behavior of CuO doped NKN based compositions. By comparison, Ta^{5+} or Sb^{5+} behaviors differently from Li$^+$ because the Q_m of the CuO modified $(Na_{0.5}K_{0.5})(Nb_{1-x}Ta_x)O_3$ and $(Na_{0.5}K_{0.5})(Nb_{1-x}Sb_x)O_3$ ceramics is over 1300 [15,8].

According to the symmetry-conforming property of point defects [12], whether the phase transition is diffuse or not will influence the rotation of polarization vectors and defect dipole moments under an electric field. In a diffuseless process (as discussed above, the material becomes a solely tetragonal ferroelectric for $x > 0.04$), the defect symmetry or defect dipole moments cannot be rotated, providing a restoring force or an internal bias field to favor a reverse domain switching when the electric field is removed. Therefore, the P_r becomes very low after such a measurement. However, for compositions with $x < 0.02$, the materials undergo a diffuse tetragonal–orthorhombic phase transition near room temperature, suggesting that defects may migrate and settles in a distribution with the same symmetry as the crystal after the transformation. Therefore, the difference of polymorphic phase transition temperatures owing to the addition of Li$^+$ may induce different hardening processes based on the variation of the aging time.

Moreover, it is also believed that defect complexes due to the formation of oxygen vacancies can be oriented parallel to the spontaneous polarization to stabilize the spontaneous polarization, thus leading to hardening effects [11]. If so, hardening effects should increase with the oxygen concentration. Unfortunately the increased Q_m values were not observed in samples doped with increasing contents of Cu^{2+} [9].

To further clarify the above issues, the grain morphology for different samples was shown in Fig. 4. It is believed that the domain size increases with increasing the grain size [16]. Therefore, less bias field could be formed in samples with a larger grain size because a long-range diffusion is needed across bigger domains. Therefore, the Q_m for samples with $x = 0.06$ becomes quite low. In addition, in the phase transition zone ($x = 0.02$–0.04), the two-phase coexistence tends to induce a softening effect because more numbers of spontaneous polarization vectors make the domain switching easier with the external field. On the other hand, evident grain growth (Fig. 4) and relatively low density (Table 1) for Cu doped NKN with larger content of Li$^+$ could also contribute to the increase in loss values (Fig. 2).

It can be seen that for samples with larger contents of Li$^+$, an evident grain growth tends to counteract the hardening effect from oxygen vacancies. A few compounds with low melting points and a few eutectic points can be formed between Li_2O and CuO [17]. The formed liquid phases promote the densification and simultaneously speed up the grain growth. Therefore, it is essential to consider how to effectively control the grain growth when Cu^{2+} is applied to make lead-free piezoelectric ceramics with a large Q_m for high-power application. Noticeably, it is still of value in future to investigate the domain structures of CuO doped alkaline niobate based ceramics to see if and how the content of Li$^+$ affects the domain morphology.

4. Conclusion

Ternary NKLNx lead-free ceramics were prepared by substituting Li$^+$ for K$^+$. Their phase transition behavior and compositional dependence of piezoelectric properties were investigated. The polymorphic phase transition between orthorhombic and tetragonal phases was shifted toward room temperature as only 2–4 mol% K^+ was substituted by Li^+. The addition of 1 mol% CuO induces an evident hardening effect; however it is found to be dependent on the content of Li^+ in the composition. Various mechanisms concerning the phase transition diffuseness, grain morphology and defect dipoles were discussed in combination with the variation of electrical properties.

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