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Characterization of ternary $(Na_{0.5}K_{0.5})_{1-x}Li_xNbO_3$ lead-free piezoelectric ceramics prepared by molten salt synthesis method

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Abstract $(Na_{0.5}K_{0.5})_{1-x}Li_xNbO_3$ powders and ceramics were prepared by molten salt synthesis method. Pure perovskite-phase powder was obtained at a low temperature of 740 °C with a grain size of below 800 nm. The effects of the $LiNbO_3$ on phase transition, microstructure, electrical properties, and temperature stability were investigated. A morphotropic phase boundary was identified. The scanning electron microscopy indicated that the $(Na_{0.5}K_{0.5})_{1-x}Li_xNbO_3$ powders and ceramics obtained by the molten salt synthesis method have a relatively uniform particle size and microstructure. The results indicate that these materials are promising candidates for lead-free piezoelectric ceramics for practical applications.

Introduction

Currently, piezoelectric ceramics based on lead zirconate titanate (PZT) system are widely used for piezoelectric actuators, sensors, and transducers due to their excellent piezoelectric properties [1, 2]. However, these piezoelectric ceramics contain more than 60 wt% lead [3–5], so piezoelectric components made by PZT may cause continuous damage to environment and human health because of the toxicity of lead oxide. Therefore, it is necessary to replace lead-based ceramics rapidly by developing lead-free piezoelectric ceramics with good piezoelectric properties.

The search for alternative piezoelectric materials is now being focused on alkali noibate, modified bismuth titanate [6–11]. Among them, $Na_{0.5}K_{0.5}NbO_3$ (abbreviated as KNN) [12, 13] has been considered a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity and ferroelectricity.

However, pure KNN ceramics sintered by ordinary sintering method show relatively lower electrical properties ($d_{33} \sim 80$ pC/N, $k_p \sim 36\%$) due to the difficulty in the processing of dense ceramics [14, 15]. There are two reasons for this problem. First, the phase stability of pure KNN ceramics is limited to 1140 °C according to the phase diagram for $KNbO_3$–$NaNbO_3$ [16]. Therefore, high sintering temperature is impossible. In addition, Na_2O and K_2O easily evaporate at high temperature, which change the stoichiometry of KNN ceramics and lead to the formation of extra phase [17]. Varieties of additions have been made to KNN to form new KNN-based ceramics with improved relative density and piezoelectric properties. These include the formation of solid solutions of KNN with other ferroelectrics or nonferroelectrics, such as KNN–$LiTaO_3$ [18], KNN–$LiNbO_3$ [19], KNN–$LiSbO_3$ [20], KNN–$Li(Nb,Ta,Sb)O_3$ [21], KNN–$Bi_{0.5}Na_{0.5}TiO_3$ [22], KNN–$LiSbO_3$–$CaTiO_3$ [23, 24], as well as the use of sintering aids, such as $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ [25]. All of the modifications were reported to exhibit enhanced piezoelectric properties due to the presence of the polymorphic phase transition from the orthorhombic to tetragonal phase (abbreviated as PPT) near or at room temperature [26–28].

Among above new solid solution, KNN–$LiNbO_3$ ceramics were considered as an excellent candidate for lead-free piezoelectric ceramics because of high piezoelectric properties such as $d_{33} = 220$–300 pC/N [19]. Many authors have reported the research development of this system such as phase structure [19], the effect of Ta substitution [29], and the effect of the sintering temperature on the properties [30]. Ringgard and Wurlitzer [16] have

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evaluated the material constants with respect to the application of industrial applications in pulse-echo measurement devices.

In previous studies [11–30], KNN-based ceramics were mainly fabricated using a conventional mixed oxides (CMOs) method at higher temperature (synthesized at around 900 °C and sintered at around 1110 °C [20, 24]). Because of Alkali easy evaporating at high processing temperature, the CMO method not only lead to rather coarse and agglomerated particles with a broad particle size distribution, but also rendered compositional fluctuation and structural inhomogeneities in the final products. It is well known that the macroscopic properties of ceramics are directly related to their phase composition, grain size, homogeneity, and microstructure, while these compositional and structural parameters are substantially influenced by the method of their preparation and the starting materials. Research effort has been devoted to the preparation of the material by various simple and reproducible low temperature synthesis techniques, such as sol–gel method [31], citrate method [32], hydrothermal process [33], and MSS method [34]. The MSS method is a simple and cost-effective technique for preparing single-crystalline particles with the desired composition in a low-melting point flux. Some ceramic powders, such as $Sr_2Nb_2O_7$ [35], $BaFe_{12}O_{19}$ [36], $BaNd_2Ti_4O_{12}$ [34], and BNBT6 [37], have been obtained by MSS techniques. Advantages of MSS are as follows: (1) the preparation temperature of MSS is lower, and reaction time is shorter than CMO because of the high diffusivities of the components [38]; (2) obtaining pure and agglomerate-free powders and grain-oriented ceramics [21]. The powders obtained by the MSS method have several unique characteristics, which are determined mainly by the chemical and crystallographic constraints given by the salt. In many cases, several eutectic compositions have been used to reduce the melting point of the salt. Until now, however, there is no report on molten flux-synthesized KNLN, although this method readily provides the desired composition and aggregate-free powder.

In this study, $LiNbO_3$ (abbreviated as LN) modified $(Na_{0.5}K_{0.5})_{1-x}Li_xNbO_3$ (abbreviated as KNLN) lead-free piezoelectric ceramics were prepared by MSS method, and the effect of amount of $LiNbO_3$ addition on the crystal structure, phase transition behavior, and dielectric and piezoelectric properties are investigated.

Experimental

Preparation of sample

A composition of $(Na_{0.5}K_{0.5})_{1-x}Li_xNbO_3$ ($x = 0$, 0.04, 0.06, and 0.08) were prepared by the MSS method. The starting materials used in this study were K_2CO_3, Na_2CO_3, Nb_2O_5, and Li_2CO_3 of 99.9% purity. K_2CO_3–Na_2CO_3 salt with a molar ratio of 0.45:0.55 was used as the eutectic composition; its melting point is about 710 °C. The weight ratio (W) of salts to oxides was 1:1.3 mol%, and excess K_2CO_3 and Na_2CO_3 were used to avoid severe composition fluctuation, owing to the volatilization of potassium and sodium. First, the oxide sources and the Na_2CO_3–K_2CO_3 flux were co-mixed and ball-milled in ethanol for 6 h. Then, the dried slurry calcined at 740 °C for 2 h. The calcined powders were washed using hot ethanol. After drying, powders were mixed with 5 wt% polyvinyl alcohol (PVA) solution, and then were pressed into pellets with a diameter of 22 and 2-mm thickness under 100 MPa pressure. After burning off PVA, the green plates were sintered at 1000 °C for 2 h. Relative densities (for samples with $x = 0$–0.08) higher than 97% of the theoretical density were obtained.

Silver electrodes were formed by painting on both surfaces of each sintered disk, and the samples were immersed in silicon oil and poled in a 30 kV/cm direct current field for 30 min at 150 °C. All electrical measurements were carried out about 24 h after poling.

Characterization of properties

The calcined powders were examined by X-ray diffraction (XRD, Model D/MAX-2500X, Japan). The microstructure of calcined powders and sintered bodies was observed using a scanning electron microscope (SEM, Model XL30-DX-4, Philips, Holand). Apparent sintered densities were measured by the Archimedes method with ethanol. Dielectric properties were obtained by measuring the capacitance and loss at 1 kHz using an LCR meter (HP 4294A). The Curie temperature (T_C) was determined by temperature dependence of the dielectric constant at 1 kHz. The piezoelectric constant (d_{33}) was measured using a quasi-static piezoelectric d_{33} meter (Model ZJ-3d, China). The planar coupling coefficient (k_p) and thickness (k_t) were calculated by the resonance–antiresonance method on the basis of IEEE standards using an impedance analyzer (HP4194A) based on the following relations and IEEE standards [39]:

$$K_p = \left[\frac{\eta_1^2 - \left[1-(\sigma^E)^2\right]}{2(1+\sigma^E)} \times \frac{f_a^2 - f_{s1}^2}{f_a^2}\right]^{1/2} \quad (1)$$

$$K_t = \left[\frac{\pi f_{s1}}{2 f_a} \tan\frac{\pi(f_a - f_r)}{2 \quad f_a}\right]^{1/2} \quad (2)$$

$$\sigma^E = \frac{5.332 f_r - 1.867 f_{s1}}{0.6054 f_{s1} - 0.1910 f_r} \quad (3)$$

$$\eta_1 = 1.867 + 0.6054\sigma^E \tag{4}$$

where f_a is the antiresonant frequency, f_r is the resonant frequency, and f_{s1} is the first overtone resonant frequency, which were measured using an HP4194A impedance bridge. σ^E is the Poisson's ratio (the superscript "E" means the boundary conditions are short circuited), and η_1 is the frequency constant of a disk resonator.

Result and discussion

Phase transition behavior

Figure 1 shows the X-ray powder diffraction patterns of KNLN ceramics at room temperature. It is found that a complete solid solution is difficult to form between KNN and LN. As we all known, although both KNN and LN have octahedral basic structure units (NbO_6 and LiO_6), they belong to different structures. KNN has the perovskite structure, LN, however, has the lithium niobate structure, which can be described as a heavily distorted perovskite or an ordered phase derived from the lithium niobate structure. Different structures prevent the formation of a complete solid solution between KNN and LN. As presented in Fig. 1, KNLN ceramics ($x \leq 0.06$) show pure perovskite phases and no secondary phases could be certified. The results indicate that the Li^+ has completely diffused into the KNN lattice to form a new solid solution. However, at $x = 0.08$, the solubility of Li^+ in the A site of ABO_3 perovskite structure becomes difficult due to the different ways that $LiNbO_3$ and NKN crystallize, a $K_3Li_2Nb_5O_{15}$ phase (ICDD: 52-0157) with tetragonal tungsten bronze structure begins to appear. The structure of solid solution transforms from orthorhombic to tetragonal symmetry due to the large distortion caused by Li^+. The variation of lattice parameters as a function of the LN content is shown in Fig. 1. The lattice distortion may affect the electrical properties of the ceramics, which will be discussed later.

Figure 2 shows the XRD pattern of KNLN powder with different amounts of LN addition in the 2θ range of 44°–47°. It can be seen from Fig. 2 that the ceramics are orthorhombic phase at $x \leq 0.04$, and the tetragonal phase appears and increases continuously with increasing x. The tetragonal and orthorhombic phase is characterized by (002)/(200) and (202)/(020) peak splitting about 45° [30]. It can be concluded from Figs. 1 and 2 that the orthorhombic and tetragonal ferroelectric phases of the ceramics coexisted in the composition range of $0.4 < x < 0.6$ at room temperature. Previous research report that the orthorhombic and tetragonal phase co-exist in KNLN ceramics when $x = 0.06$ [19, 30]. At the same time, it can be seen from Fig. 2 that the diffraction peaks become sharper and shift to lower 2θ angles with the increase in the content of $LiNbO_3$. It is obvious that the grain size (D) which is judged by Scherrer's equation $D = k\lambda/(\beta\cos\theta)$ (k is Scherrer contant, λ is X-ray wave length, β is peak width at half height, and θ is angle of diffraction) becomes larger [40]. Figure 2 also indicates that the intensity of diffraction changes with the increase in the content of LN, which means the grain orientation alternated because of the change of different phase contents.

Morphological development and microstructure

Figure 3 shows the micrographs of the KNLN powders with different amounts of LN addition calcined at 740 °C for 2 h. The mean grain size could be quantitatively

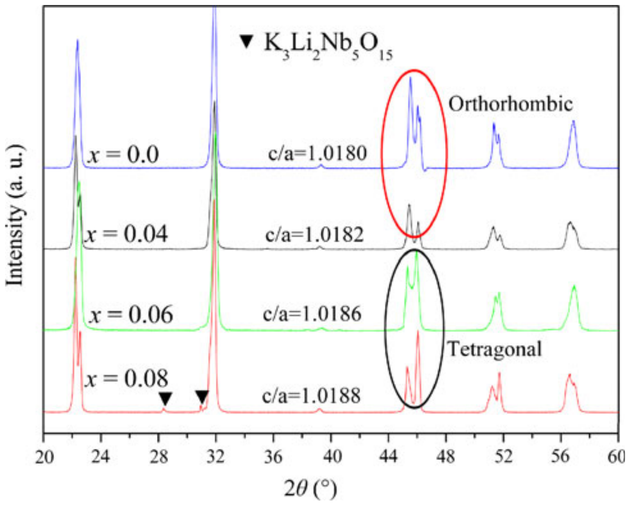


Fig. 1 The XRD of KNLN powder with different amounts of LN addition

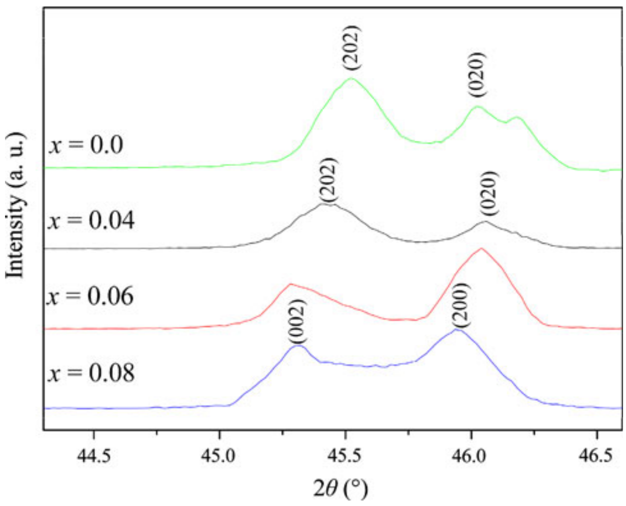


Fig. 2 The XRD of KNLN powder with different amounts of LN addition in the 2θ range of 44°–47°

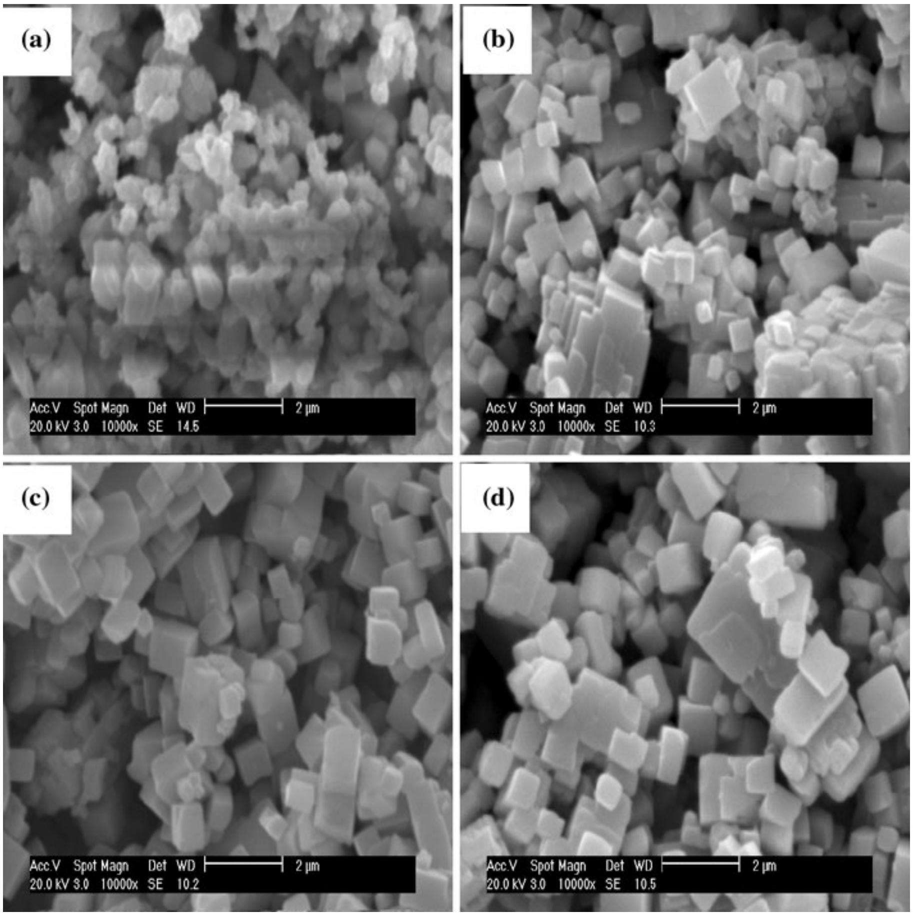


Fig. 3 SEM of KNLN powders with different amounts of LN addition calcined at 740 °C for 2 h: **a** $x = 0.0$; **b** $x = 0.04$; **c** $x = 0.06$; and **d** $x = 0.08$

obtained by line intercept method from Figs. 3 and 4. It is shown that with an increase of amount of LN addition, the particle sizes became larger. High quality ceramics require pure and agglomerate-free powders [21, 38]. An average particle size about 300 nm with a relatively uniform size distribution was obtained at 740 °C for 2 h (Fig. 3b, c, and d). No large agglomerates were found in these powders except ($x = 0.0$) sample (Fig. 3a).

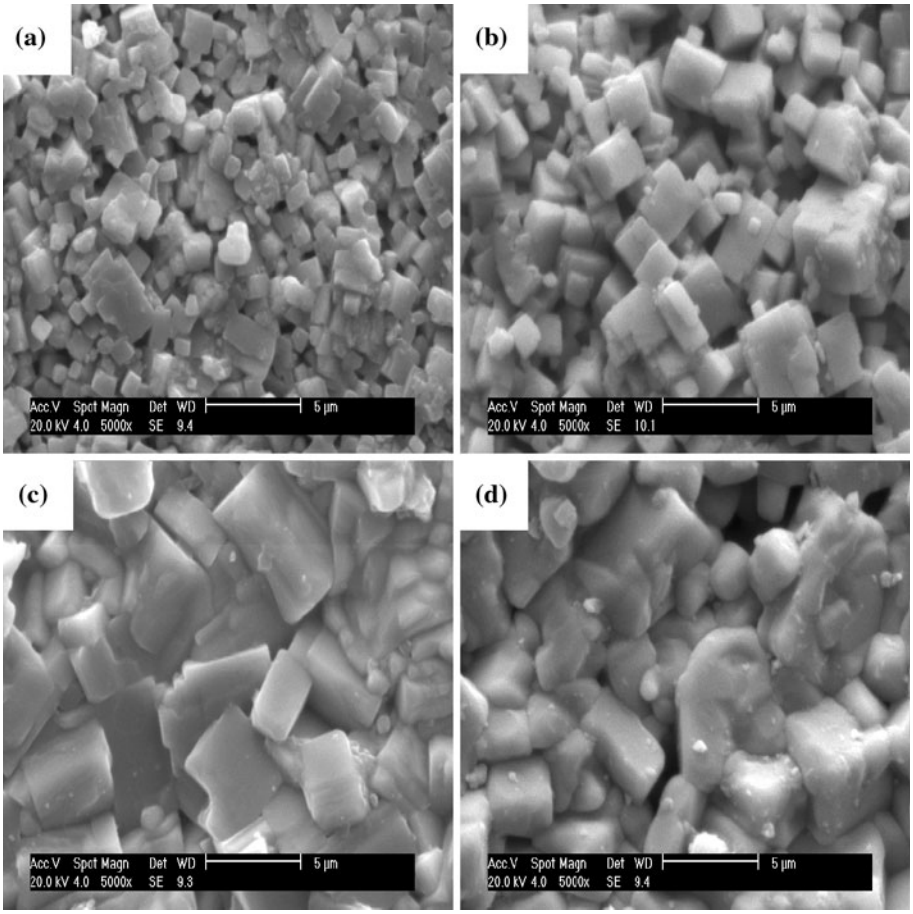
Figure 4 shows the SEM micrograph of free surfaces of the specimens with the different amounts of LN addition sintered at 1000 °C for 2 h. The grain becomes bigger with increasing the amount of LN addition ($x \leq 0.06$). The microstructure of sample ($x = 0.06$) is much uniform and fine, the grain boundary is clear, their microstructure is dense, and the average grain size is about 300 nm. It is obvious that the radius of Li^+ (0.60 Å) ions is smaller than K^+ and Na^+ (1.33 and 0.95 Å) [40]. In view of the radius, Li^+ ions entering to the pattern may cause lattice distortion of lattice [41]. The loose structure can be sintered easily, and this makes the grain size increase (Fig. 4a, b, and c). A consecutive increase of amount of LN addition would make the grain size decrease (Fig. 4d), because the growth of grains was significantly inhibited by the excessive content of LN segregating at grain boundaries which exerted a drag force against the grain boundary movement [42]. It can be seen from Fig. 4 that the addition of LN causes a significant change in the grain size, which influences the domain wall motion. The motions of domain wall affect the electrical properties of piezoelectric ceramics deeply [43].

Figure 5 shows the variation of density of KNLN ceramics with the amount of LN addition. The density values of samples increase at first and approached the maximum value 4.38 g/cm^3 with the amount of LN addition is 6 mol%, then dropped. This should ascribe to the formation of $K_3Li_2Nb_5O_{15}$ with the lower density (theoretical density: 4.376 g/cm^3) [19]. The maximum density is proximity to the theoretical density of about 97% theoretical density of NKN (~4.5 g/cm^3). It can be concluded from the above observations and analysis that the addition of LN prompted the sintering and makes KNLN ceramics more compact.

Dielectric and piezoelectric properties

The variation of dielectric constant (ε_r) for the unpoled KNLN ceramics as a function of temperatures at 1 kHz with different amounts of LN addition is shown in Fig. 6.

Fig. 4 SEM micrographs of samples with different amounts of LN addition sintered at 1000 °C for 2 h: **a** $x = 0.0$; **b** $x = 0.04$; **c** $x = 0.06$; and **d** $x = 0.08$



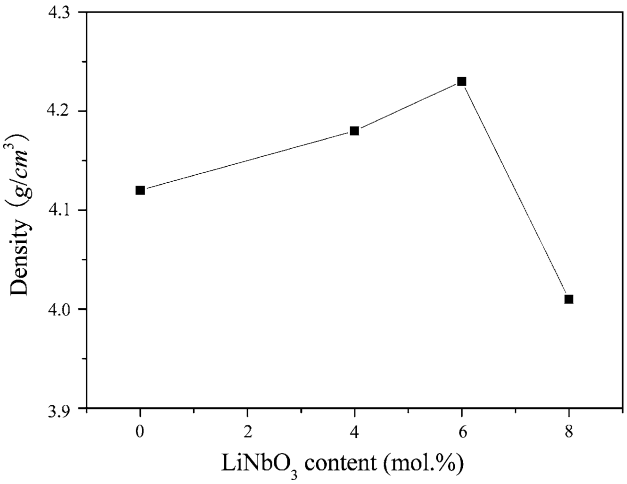


Fig. 5 Variation of density with different amounts of LN addition sintered at 1000 °C for 2 h

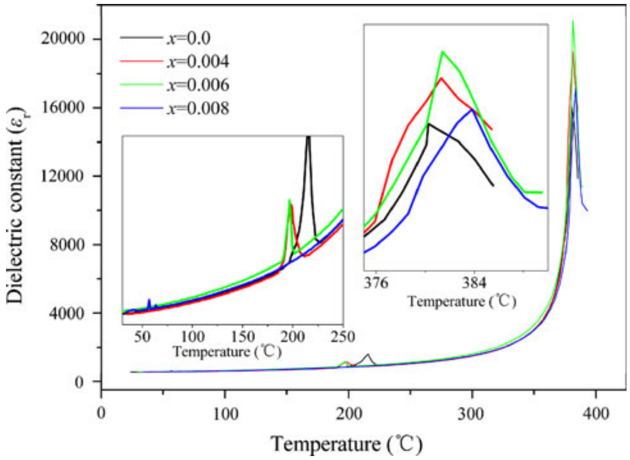


Fig. 6 Temperature dependence of ε_r with $x = 0.0$, 0.04, 0.06, and 0.08 at 1 kHz

All samples show two dielectric peaks, which correspond to the phase transitions from orthorhombic to tetragonal ($T_{O\text{–}T}$) and from tetragonal to cubic (T_C). For pure KNN ceramics, $T_{O\text{–}T}$ and T_C are 200 and 420 °C, respectively [18, 19]. It should be noted that all the samples still show classic ferroelectric behavior after the addition of LN. It can be seen from the Fig. 6 that $T_{O\text{–}T}$ decreases and T_C increases with increasing LN content. The $T_{O\text{–}T}$ shifts from 200 °C for pure KNN to 63.5 °C for the ceramics ($x = 0.08$). This is because partial substitution of A-site ions $(Na_{0.5}K_{0.5})^+$ by Li^+ can cause T_C to increase while $T_{O\text{–}T}$ decreases [19]. $LiNbO_3$ has the highest T_C (1210 °C) among the ferroelectrics, so it is understandable that the T_C shifts to higher temperature as amount of LN addition increases. The T_C of KNLN ceramics prepared by MSS is lower than the reported value [18, 19]. It is also observed that all the samples still show no frequency dispersion of permittivity or variations of T_C near the maxima dielectric constant. This indicates a high quality dielectric with no major macrochemical inhomogeneity in the samples.

Figure 7 shows the temperature dependence of dielectric loss (tan δ) for the unpoled KNLN ($x = 0.06$) ceramics with 6 mol% LN addition at 1 kHz. It was found that the tan δ value varies from the minimum 1.8 to 10%, indicating that the ceramics have not significant conductivity appearance even at temperature as high as 375 °C. As a result, the KNLN ($x = 0.06$) lead-free piezoelectric ceramics in present study possess high T_C (379.4 °C) along with good dielectric properties, it is suitable for higher temperature application.

Figure 8 shows ε_r, tan δ of poled KNLN ceramics samples as a function of amount of LN addition at room temperature. It can be seen that ε_r increases the former three compositions, but decreases for the fourth composition. At the same time, the variation of tan δ with the amount of LN addition is opposite to that of ε_r. When amount of LN addition is 6 mol%, the tan δ and ε_r reach the maximum and minimum value of 585 and 1.8%, respectively. The high ε_r and low tan δ loss are due to the improvement of the bulk density.

Figure 9 shows that the d_{33}, k_p, and k_t of the KNLN as a function of amount of LN addition sintered at 1000 °C. It is clear that the d_{33}, k_p, and k_t values of samples increased at first and approached the maximum value ($x = 0.06$), then dropped. The piezoelectric properties decrease rapidly due to excessive Li that may result in inhibiting grain growth, existence of secondary phase, and poor microstructural homogeneity. Figure 9 indicates that the ceramics with $x = 0.06$ possess good piezoelectric and dielectric properties ($d_{33} = 213$, $k_p = 35\%$, $k_t = 46\%$, $\varepsilon_r = 585$, and tan $\delta = 1.8\%$). It was reported that the PPT at or near room temperature is responsible for the improvement in the piezoelectric properties of KNN-based lead-free ceramics [26–28]. The phase structure of KNLN ($x = 0.06$) ceramics near PPT is the coexistence of orthorhombic and tetragonal phases (Fig. 1). In general, a large number of thermodynamically equivalent states near the PPT allow a high degree of alignment of ferroelectric dipoles. This high degree of alignment and enhanced polarizability result in an enhancement of electrical properties near the PPT. In addition, it was thought that good piezoelectric properties of the ceramics with $x = 0.06$ should be attributed to the optimum Li content in the ceramics. The ceramics with an optimum Li content possess appropriate lattice distortion. This kind of lattice distortion introduces higher densification microstructure (Figs. 3, 4, 5).

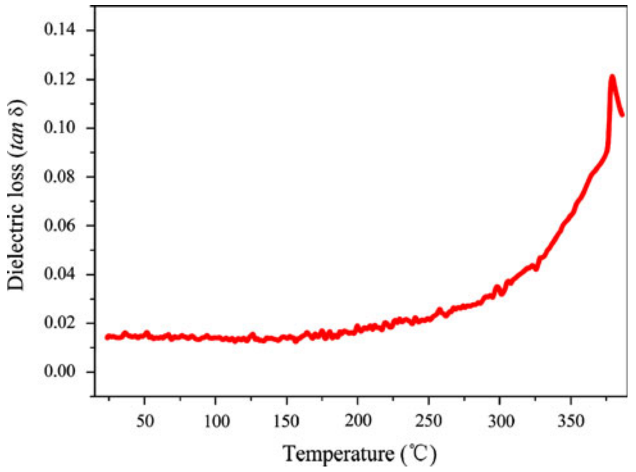


Fig. 7 Temperature dependence of tan δ for the samples with 6 mol% LN at 1 kHz

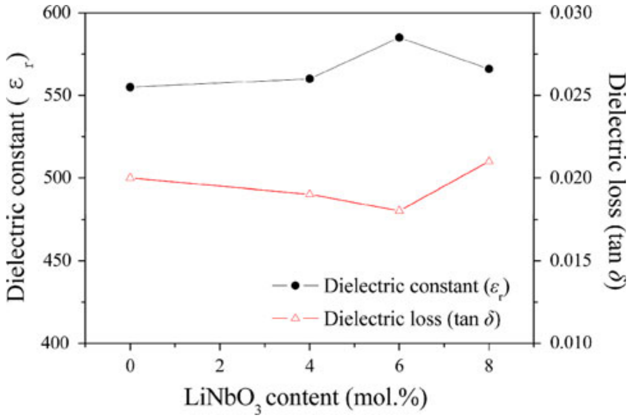


Fig. 8 ε_r, tan δ as a function of amount of LN addition sintered at 1000 °C for 2 h

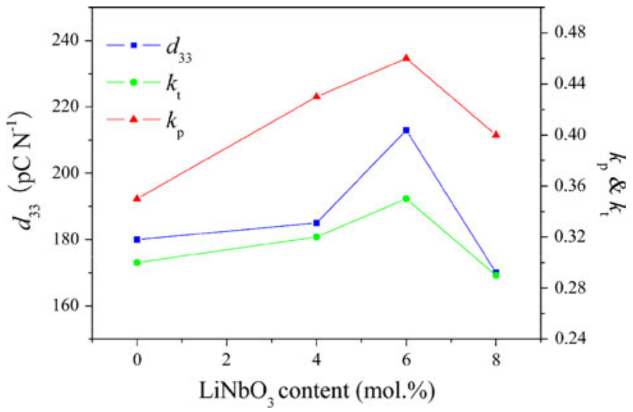


Fig. 9 d_{33}, k_p, and k_t as a function of amount of LN addition

Conclusions

A molten salt synthesis method is an effective method to synthesize powders and ceramics of ternary $(Na_{0.5}K_{0.5})_{1-x}Li_xNbO_3$. K_2CO_3–Na_2CO_3 eutectic mixtures were used as the flux with the ratio of molten salt content, and raw material was 8 wt%. The addition of LN prompted the sintering and made KNLN ceramics more compact. The calcination temperature of 740 °C and sintering temperature of 1000 °C are much lower compared to the traditional ceramics process. The phase structure in all samples is perovskite phase. The orthorhombic and tetragonal ferroelectric phases of the ceramics coexisted in the composition range of $0.4 < x < 0.6$ at room temperature. The addition of Li makes the orthorhombic–tetragonal phase transition temperature (T_{O-T}) decreases and Curie temperature (T_C) increases with increasing LN content. 094NKN–0.06LN exhibited high piezoelectric properties and the performance. The optimum values of ε_r, tan δ, d_{33}, Q_m (mechanical quality factor), K_p, K_t, and T_C are 585, 1.8%, 213 pC/N, 500, 35%, 46% and 381.4 °C, respectively. Comparable with the other KNN-based ceramics, it is suitable for a wide range of electromechanical transducer applications.

References

1. Abraham T (2000) Am Ceram Bull 9:45
2. Tani T, Kimura T (2006) Adv Appl Ceram 105:55
3. Cross E (2004) Nature 432:24
4. Kosec M, Bobnar V, Hrovat M, Bernard J, Malic B, Holc J (2004) J Mater Res 19(6):1849
5. Yoo J, Oh D, Jeong Y, Hong J, Jung M (2004) Mater Lett 58:3831
6. Chiang YM, Farrey GW, Soukhojak AN (1998) Appl Phys Lett 73:3683
7. Chu B, Chen D, Li G, Yin Q (2002) J Eur Ceram Soc 22:2115
8. Park SE, Chung SJ (1996) J Am Ceram Soc 79:1290
9. Kakimoto K, Masuda I, Ohsato H (2003) Jpn J Appl Phys 42:6102
10. Guo Y, Kakimoto K, Ohsato H (2004) Solid State Commun 129:279
11. Lin D, Xiao D, Zhu J, Yu P, Yan H, Li L (2004) Mater Lett 58:615
12. Jaeger RE, Egerton L (1962) J Am Ceram Soc 45:209
13. Haertling GH (1967) J Am Ceram Soc 50:329
14. Wang XX, Chan HL, Choy CL (2003) J Am Ceram Soc 86(10):1809
15. Takenaka T, Sakata K (1980) Jpn J Appl Phys 19:31
16. Ringgaard E, Wurlitzer T (2005) J Eur Ceram Soc 25:2701
17. Maeder MD, Damjanovic D, Setter N (2004) J Electroceram 13:385
18. Guo Y, Kakimoto K, Ohsato H (2005) Mater Lett 59:241
19. Guo Y, Kakimoto K, Ohsato H (2004) Appl Phys Lett 85:4121
20. Wu JG, Xiao DQ, Wang YY, Zhu JG, Yu P, Jiang YH (2007) J Appl Phys 102:114113
21. Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T, Nakamura M (2004) Nature 432:84
22. Zuo RZ, Ye C (2007) Appl Phys Lett 91:062916
23. Zhang SJ, Xia R, Shrout TR (2007) Appl Phys Lett 91:132913
24. Wu JG, Xiao DQ, Wang YY, Wu WJ, Zhang B, Li J, Zhua JG (2008) Scr Mater 59:750
25. Matsubara M, Kikuta K, Hirano S (2005) J Appl Phys 97:114105
26. Zhang SJ, Xia R, Shrout TR, Zang GZ, Wang JF (2007) Solid State Commun 141:675
27. Wu JG, Xiao DQ, Wang YY, Zhu JG, Wu L, Jiang YH (2007) Appl Phys Lett 91:252907
28. Wu JG, Wang YY, Xiao DQ, Zhu JG, Pu ZH (2007) Appl Phys Lett 91:132914
29. Hollenstein E, Davis M, Damjanovic D, Setter N (2005) Appl Phys Lett 87:182905
30. Du HL, Tang FS, Luo F, Zhu DM, Qu SB, Pei ZB, Zhou WH (2007) Mater Res Bull 42:1594
31. Hou J, Qu Y, Ma W (2007) J Mater Sci 42:6787. doi:10.1007/s10853-006-1429-1
32. West DL, Payne DA (2003) J Am Ceram Soc 86:192
33. Pookmanee P, Rujijanagul G, Ananta S, Heimann RB, Phanichphant S (2002) J Eur Ceram Soc 24:517
34. Katayama K, Azuma Y, Takahashi Y (1999) J Mater Sci 34:301. doi:10.1023/A:1004405605913
35. Brahmaroutu B, Messing GL, Trolier-McKinstry S (1999) J Am Ceram Soc 82:1565
36. Arendt RH (1973) J Solid State Chem 8:339
37. Chen WW, Kume S, Watari K (2005) Mater Lett 59:3238
38. Arent RH, Rosolowski ZH, Szymaszek JW (1979) Mater Res Bull 14:703
39. The Institute of Electrical and Electronics Engineers (IEEE), Standards on Piezoelectricity, American National Standards Institute, ANSI/IEEE Std. (1987) p 176
40. Cotton FA, Wilkinson G, Gaus PL (1995) Basic inorganic chemistry. Wiley, New York
41. Li LT, Yao YJ, Mu ZH (1980) Ferroelectrics 28:403
42. Hou YD, Zhu MK, Gao F, Wang H, Wang B, Yan H, Tian CS (2004) J Am Ceram Soc 87:847
43. Randall CA, Kim N, Kucera JP, Cao W (1998) J Am Ceram Soc 81:677