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Low-temperature sintering and electrical properties of (K, Na)NbO$_3$ based lead-free ceramics with high Curie temperature

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Abstract

Lead-free ceramics $(1-x)(K_{0.48}Na_{0.52})NbO_3$–$(x/5.15)K_{2.9}Li_{1.95}Nb_{5.15}O_{15.3}$ ($x = 0.3$–0.6, KNN–KLN100x) were prepared by conventional sintering technique at a low temperature of 960 °C. The effects of KLN contents on microstructure, dielectric, and piezoelectric properties were investigated. After the addition of KLN, the sintering performance and Curie temperature of the ceramics were markedly improved. The ceramics with $x = 0.3$ exhibited very good piezoelectric properties: $d_{33} = 138$ pC/N, $k_p = 45.03\%$, $T_c = 495$ °C, the dielectric constant at room temperature ε_r (RT) = 478 and the maximum dielectric constant ε_r (max) = 5067. These results indicated that the KNN–KLN100x lead-free ceramics sintered at low temperatures are promising for high temperature piezoelectric applications.

Keywords: A. Sintering; C. Dielectric properties; C. Piezoelectric properties; Low-temperature sintering

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1. Introduction

Recently, considerable attention has been given to lead-free materials for replacing lead-based materials due to the growing demands for environmental protection. Among the lead-free materials, $(K_{1-x}Na_x)NbO_3$ (abbreviated as KNN) is the most studied system following the work of Saito et al. [1], because of its excellent piezoelectric properties and high Curie temperature T_c [2–11]. However, pure KNN ceramics sintered by conventional solid-state reaction showed that poor performance resulted from the difficulty of densification and hygroscopicity [2]. Numerous studies have been carried out in order to improve the piezoelectric properties of KNN-based ceramics. These included the chemical modifications to prepare compositions close to an MPB or shift the orthorhombic to tetragonal phase transition ($T_{O\text{-}T}$) to near or below room temperature, such as KNN-Li(Nb, Sb, Ta)O$_3$ [3–5], KNN-Ag(Nb, Sb, Ta)O$_3$ [6], KNN-AETiO$_3$ (AE = Mg, Ca, Sr, Ba) [7], and KNN-(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ [8]. Others have employed new sintering processes, such as hot-press [9], spark plasma sintering [10], and sintering aids like CuO [11]. Unfortunately, the improvement of the piezoelectric properties is usually at the cost of the decrease of the Curie temperature in these studies.

Therefore, it is important to prepare the lead-free piezoelectric materials with high Curie temperature and good piezoelectric properties. In this work, $(1-x)(K_{0.48}Na_{0.52})NbO_3$–$(x/5.15)$ $K_{2.9}Li_{1.95}Nb_{5.15}O_{15.3}$ ceramics ($x = 0.3$–0.6) with high Curie temperature were obtained by the conventional sintering method. The effects of KLN on the microstructure and piezoelectric properties of the ceramics were investigated. Since the ideal stoichiometric $K_3Li_2Nb_5O_{15}$ phase does not exist according to the phase diagram of the ternary system K_2O–Li_2O–Nb_2O_5, excess amount of Nb_2O_5 is required to stabilize the structure [12]. Thus the tungsten bronze structure $K_{2.9}Li_{1.95}Nb_{5.15}O_{15.3}$ with a composition of $K_2O = 29$ mol.%, $Li_2O = 19.5$ mol.%, $Nb_2O_5 = 51.5$ mol.% was chosen as the dopant [13].

2. Experimental

K_2CO_3 (99.94%), Na_2CO_3 (99.56%), Li_2CO_3 (98.0%), Nb_2O_5 (99.5%) were used to prepared KNN–KLN100x ($x = 0.3$–0.6) ceramics by conventional solid-state reaction method. Firstly, the KNN and KLN precursor powders were calcined at 700 °C and at 960 °C for 6 h, respectively. The

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calcined powders were then mixed with different KNN/KLN molar ratios. The obtained powders were again mixed thoroughly with a polyvinyl alcohol binder solution and pressed into disks with 15 mm in diameter. After burning off the binder, the green pellets were sintered at 960–1070 °C for 3 h in air. Silver electrodes were applied on both sides of the samples and fired at 700 °C for 60 min. The samples were poled in a silicone oil bath under a DC field of 4 kV/mm at 120 °C for 20 min.

The crystalline phases of the ceramics were studied by X-ray diffraction using Cu-Kα radiation (D/Max-2550 V, Rigaku, Tokyo, Japan). The bulk densities of the sintered samples were measured by the Archimedes method. The microstructure was observed via an electron microprobe microscopy analysis (JXA-8100, JEOL, Japan). The temperature dependence of dielectric constant and dissipation factor was examined using a LCR meter (HP 4284A, Agilent Technology Co. Ltd., USA). The piezoelectric constant d_{33} was measured by a quasi-static d_{33} meter (Model ZJ-3A, Institute of Acoustics, China). The planar-mode electromechanical coupling factors k_p and mechanical quality factor Q_m were determined by the resonance and antiresonance method on the basis of IEEE standards using an impedance analyzer (HP 4294A, Toyo Corp., Japan).

3. Results and discussion

With the increase of x, the optimal sintering temperature decreased from 1120 °C for pure KNN to 960 °C with $x = 0.6$ due to formation of a liquid phase [5]. The decrease of the sintering temperature is beneficial to lower the volatilization of K and thus improved the sintering performance of the ceramics. As measured by the Archimedes method, all the ceramics possessed a density higher than 95% of the theoretical density.

Fig. 1(a) shows the room temperature XRD patterns of the precursor powders of KNN and KLN calcined at 700 °C and at 960 °C for 6 h, respectively. It can be seen that pure KNN powders with orthorhombic perovskite phase and KLN powders with a tetragonal tungsten bronze structure were formed. Fig. 1(b) shows the XRD patterns of KNN–KLN100x ceramics with $x = 0.3$–0.6. All ceramics showed that the perovskite phase KNN and a secondary phase of tungsten bronze KLN coexisted, indicating that KLN was partially diffused into KNN lattices. Moreover, the intensity of the KLN phase increased progressively with the increase of x, and KLN phase became the primary phase at $x = 0.6$. This may be attributed to the solubility limit of Li^+ in the A site of KNN ceramics [3]. The existence of the second phase is considered to affect the dielectric and piezoelectric properties.

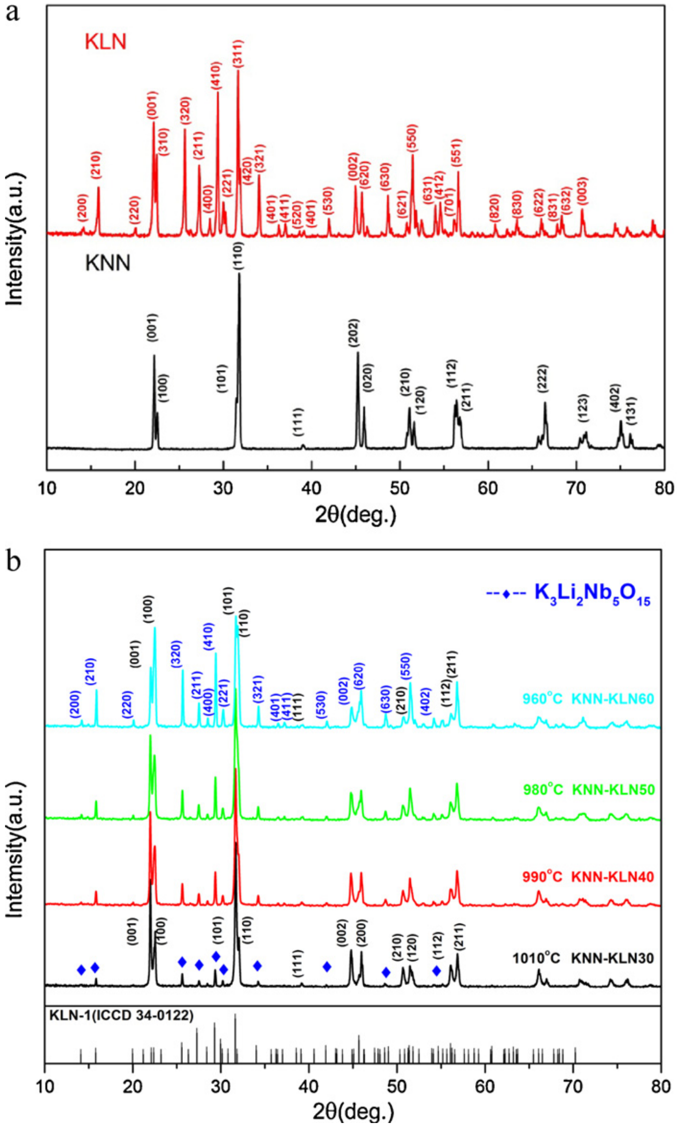

Fig. 1. The room temperature XRD patterns of: (a) the KNN powders calcined at 700 °C and KLN powders calcined at 960 °C, for 6 h; (b) KNN–KLN100x ceramics with $x = 0.3$, 0.4, 0.5, 0.6 sintered at different temperatures from 1010 °C to 960 °C, for 3 h, respectively.

The microstructure of KNN–KLN100x ceramics with $x = 0.3$–0.6 was shown in Fig. 2. A characteristic quasi-cubic morphology of the grains can be seen in the samples. Abnormal grain growth (AGG) behavior was observed at $x = 0.3$ (Fig. 2(a)). Among those, some had a larger size about 10 μm, while some were smaller about 1–2 μm. By increasing x to 0.4, the AGG can also be observed, but the difference between the grain sizes became relatively smaller (Fig. 2(b)). The AGG behavior disappeared and the average grain size decreased to about 1–2 μm with increasing x to 0.5 and 0.6, and the ceramics showed a relatively uniform microstructure (Figs. 2(c) and (d)). It is beneficial to the practical application because it is known that the fine grain and homogenous microstructure would lead to high mechanical strength for the piezoelectric ceramics [10]. According to the above results, KLN was effective in suppressing the grain growth due to the change in the critical driving force for rapid grain growth in the structure of the faceted interfaces or boundaries [3,4]. By increasing x and decreasing the sintering temperature, the critical driving force for rapid grain growth decreased. As a

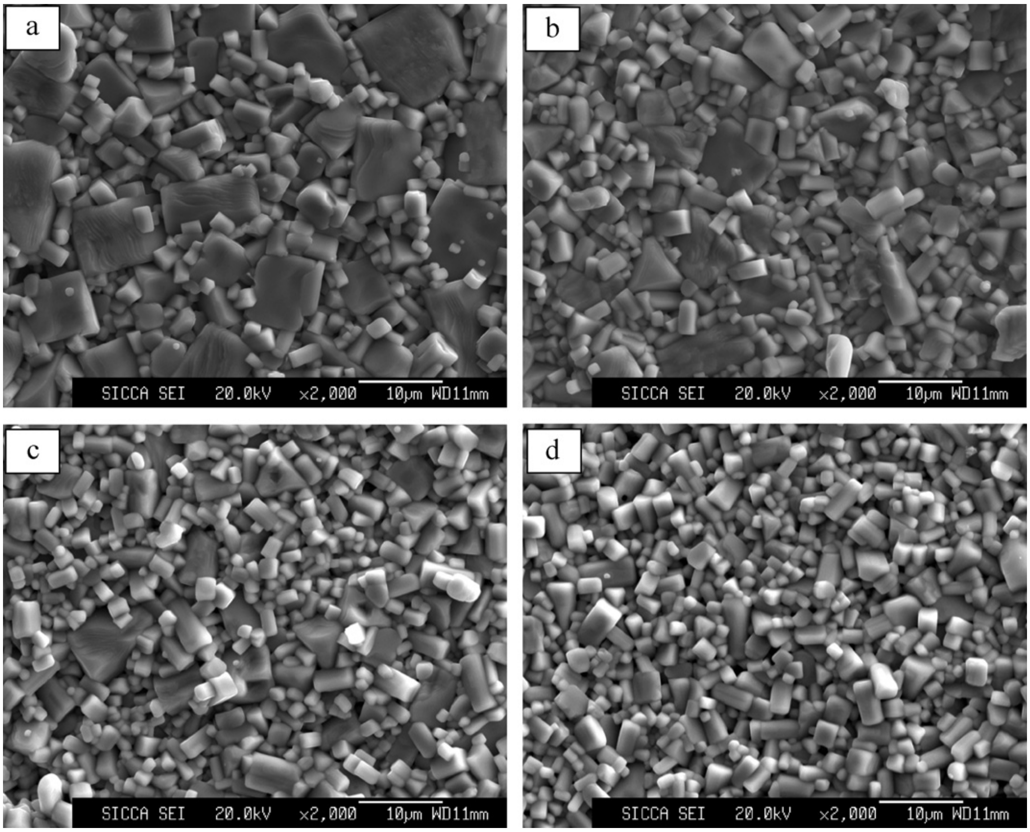

Fig. 2. SEM micrograms of the sintered KNN–KLN100x ceramics with (a) $x = 0.3$, (b) $x = 0.4$, (c) $x = 0.5$ and (d) $x = 0.6$.

consequence, the number of grains that show abnormal growth decreased and then disappeared.

Fig. 3 shows the temperature dependence of the dielectric constant ε_r and loss $\tan\delta$ at 100 kHz for KNN–KLN100x ceramics. As shown in Fig. 3, only one peek corresponding to the phase transitions of cubic to tetragonal at T_c was observed. It was found that ε_r and $\tan\delta$ for all samples were nearly temperature independent from room temperature to 400 °C, which was important for high-temperature application.

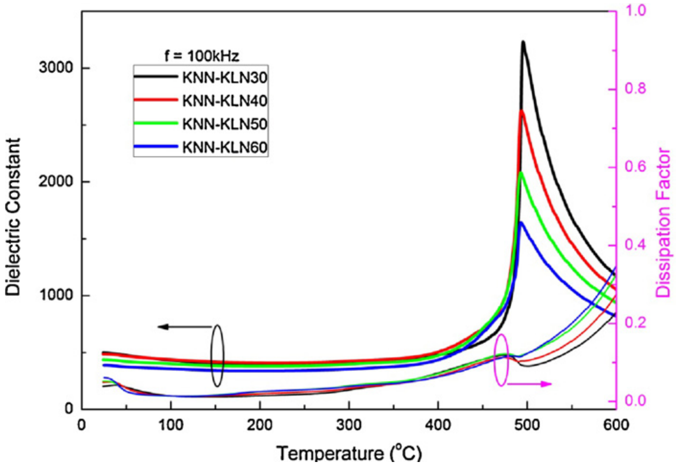

Fig. 3. The temperature dependence of the dielectric constant (ε_r) and dissipation factor ($\tan\delta$) at 100 kHz for KNN–KLN100x ceramics with $x = 0.3$, 0.4, 0.5 and 0.6.

Figs. 4 and 5 show the dielectric and piezoelectric properties of the KNN–KLN100x ceramics as a function of x, respectively. As shown in Fig. 4, dielectric constant at room temperature ε_r (RT) and the maximum dielectric constant ε_r (max) decreased with the increase of x. The similar trends were observed in $\tan\delta$ and T_c. It was noted that T_c reached the maximum value of 495 °C at $x = 0.3$, which was much higher than the previous reports [2–11]. Both d_{33} and k_p decreased with increasing x, giving a maximum value of 138 pC/N and 45.03% at $x = 0.3$, respectively (Fig. 5). On the contrary, Q_m increased with increasing x. Moreover, the obtained d_{33} value at $x = 0.3$ was higher compared with pure KNN ceramics sintered in air [2], and reached the same level of hot-pressing or spark plasma sintering KNN ceramics [8]. The electrical properties may be related to the microstructures including densification, grain shape, grain size, and size distribution. Moreover, domain rotation is easy for large grains, the enlarged grain size was also considered to benefit the improvement of d_{33} values [3,4]. Thus the variation of microstructures with the KLN content may be the main reason for the variation of the properties of the KNN–KLN100x ceramics.

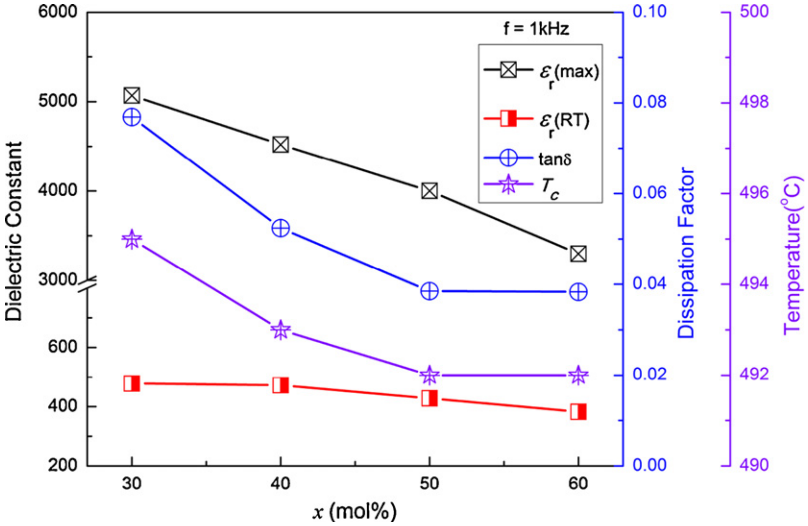

Fig. 4. The dielectric properties of KNN–KLN100x ceramics as a function of x.

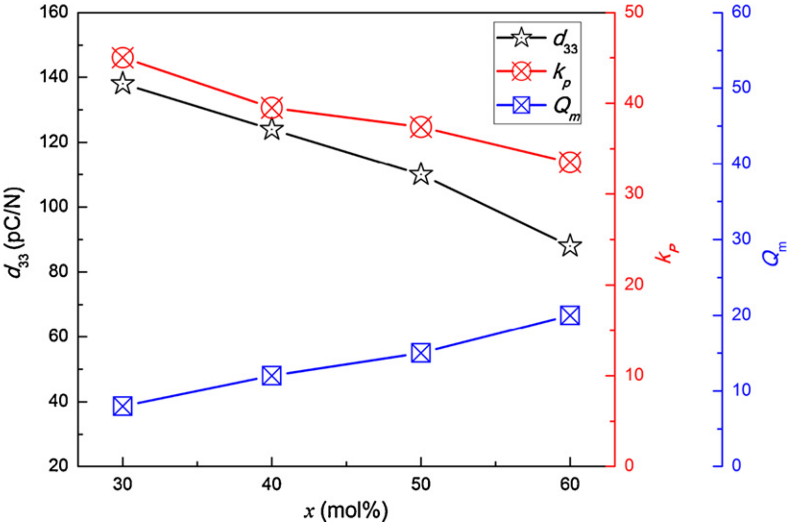

Fig. 5. The piezoelectric properties of KNN–KLN100x ceramics as a function of x.

4. Conclusions

The $(1-x)(K_{0.48}Na_{0.52})NbO_3$–$(x/5.15)K_{2.9}Li_{1.95}Nb_{5.15}O_{15.3}$ ($x = 0.3$–0.6) lead-free piezoceramics possessed high Curie temperature were investigated. The addition of KLN decreased the sintering temperature to as low as 960 °C, and effectively increased the Curie temperature of the ceramics. Enhanced dielectric and piezoelectric properties were obtained at $x = 0.3$: $d_{33} = 138$ pC/N, $k_p = 45.03\%$, $T_c = 495$ °C, $\varepsilon_r(\mathrm{RT}) = 478$ and $\varepsilon_r(\max) = 5067$. These results indicated that KNN–KLN100x ceramics are promising lead-free piezoelectric candidates for high temperature applications.

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