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ARTICLE

Piezoelectric Thermal Stability of $(K_xNa_{1-x})NbO_3$ Based Ceramics

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Abstract: Lead-free piezoelectric ceramics $(K_xNa_{1-x})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ (x=0.40~0.60; y=0.03, 0.035, 0.04) were prepared by a conventional solid-state reaction method, and the thermal stability of piezoelectric properties was investigated. Results show that samples in the researched compositional range have high piezoelectric constant of d_{33}=250 pC/N and k_p=50%. In the thermal aging test up to the Curie temperature of approximately 325 °C, d_{33} and k_p of the ceramics remain almost unchanged although there is polymorphic phase transition (PPT) near room temperature. Moreover, the ceramics present the very good piezoelectric temperature stability and k_p shows a weak temperature dependence over a wide measured temperature range from −50 ℃ to 120 ℃. The excellent thermal stability was discussed from the aspect of temperature range of phase coexistence.

Key words: lead-free ceramics; piezoelectric property; K/Na ratio; temperature stability

$Pb(Zr,Ti)O_3$-based piezoelectric ceramics have been widely used in the manufacture of actuators, sensors, transducers and other electromechanical devices because of their excellent piezoelectric properties. However, due to the toxicity of the lead oxide used in the production process, there are increasing demands to replace these ceramics with environmentally benign lead-free alternatives. Recently, significant progress has been reached in KNN-based ceramics, which showed that they might be the promising candidates as lead-free piezoelectric materials[1-9], especially the latest reported ceramics with a giant d_{33} of ~490 pC/N associated with R-T phase boundary, which points out the direction for the development of enhanced lead-free ceramics[10,11]. Interestingly, most of investigations on KNN based ceramics have been carried out based on the equal or nearly equal molar ratio of K to Na. This situation might be explained as these researches were influenced to a great extent by the historical results. It was reported that k_p and d_{33} of $K_xNa_{1-x}NbO_3$ ceramics prepared by the conventional solid-state reaction method and hot pressing method all exhibited the value peaks around $K_{0.5}Na_{0.5}NbO_3$[12–14]. Since then, the equal molar ratio of K/Na has been widely believed to be the essential condition to obtain excellent piezoelectric properties in the KNN-based ceramics, and it is frequently ascribed to the existence of a morphotropic phase boundary (MPB), which separates two orthorhombic phases with a slight discontinuity in lattice parameters at x=0.475[15,16].

Nevertheless, previous investigations on $K_xNa_{1-x}NbO_3$ (KNN)[17], $(K_xNa_{0.96-x}Li_{0.04})(Nb_{0.91}Ta_{0.05}Sb_{0.04})$[18] ceramics and recently reported ceramics $(1-x)(K_{1-y}Na_y)(Nb_{1-z}Sb_z)O_3$-$x$$Bi_{0.5}(Na_{1-w}K_w)_{0.5}ZrO_3$[10] show that the speculated MPB associated with K/Na ratios can be hardly observed and its influence on the high piezoelectric performance is very limited, the d_{33} and k_p values are nearly independent of the K/Na ratio within the wide compositional range. To further verify the conclusion, in the present paper we prepared $(K_xNa_{1-x})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ (KNLNT, x=0.40~0.60; y=0.03, 0.035, 0.04) ceramics by the conventional solid state reaction method and investigated their dielectric and piezoelectric properties, phase transitions and temperature stabilities with different K/Na ratios systemically. The result we gained is very important to further design and develop the new KNN-based piezoelectric materials with high piezoelectric performance.

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1 Experiment

$(K_xNa_{1-x})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ (KNLNT, y=0.03, 0.035, 0.04, and x =0.4~0.6) were prepared by the conventional solid-state reaction technique, using starting materials of K_2CO_3(99.0%), Na_2CO_3 (99.8%), Li_2CO_3 (99.9%), Ta_2O_5 (99.5%) and Nb_2O_5 (99.5%). The raw materials were dried in a vacuum oven at 120 ℃ for at least 8 h to remove the absorbed moisture. Then, they were weighed according to the stoichiometric ratio, ball mixed in alcohol, and calcined at 920 ℃ for 2 h. The calcined mixture was again ball milled and pressed into pellet disks of 15 mm in diameter and 1.5 mm in thickness. Sintering was carried out in ambient at the optimum sintering temperature for 2 h, and the optimum temperature of each composition is listed in Table 1, which is determined by measuring the maximum mass density. It can be seen that the sintering temperature decreases with the increasing K content. To avoid the possible alkali evaporation, the specimens were buried in the KNN powders of the same compositions during the sintering. For electrical characterization, they were coated with silver paint on the upper and lower surfaces and heated at 575 ℃ for 20 min.

Microstructures were characterized on a HITACHI S-520 scanning electronic microscope (SEM). Crystalline structures were investigated at room temperature by X-ray diffraction (XRD) with Cu Kα radiation using a D8 ADVANCE diffractometer. For dielectric and piezoelectric measurements, poling was accomplished in silicon oil using a DC power supply under the conditions of temperature 140 ℃ and voltage 4.0~6.0 kV mm^{-1} for 30 min. Measurements were carried out at least 18 h after the poling by employing an Agilent 4294A precision impedance analyzer. The d_{33} values were measured using a Berlincourt-type d_{33}-meter (YE 2730A). The k_p values were obtained from the resonance-antiresonance frequencies. Piezoelectric temperature stability was evaluated in an Espec SU-261 chamber. Thermal aging stability test was carried out in the following way. The specimen was first cooled or raised to the designed temperature and kept for 1 h, and the piezoelectric measurement was performed after being restored to room temperature.

2 Results and Discussion

2.1 Piezoelectric properties

We firstly investigated the piezoelectric properties with different K/Na ratios at room temperature in $(K_xNa_{1-x})_{1-y}Li_y$-$Nb_{0.80}Ta_{0.20}O_3$ (KNLNT, x=0.40~0.60; y= 0.03, 0.035, 0.04) ceramics. The data are shown in Fig.1. For comparison, the d_{33} values of pure $K_xNa_{1-x}NbO_3$ (KNN) ceramics are also marked in Fig.1. From the figure, it is easily seen that the Li/Ta addition to the pure KNN ceramics can strongly enhance their piezoelectric properties. These KNLNT ceramics present high piezoelectric constants d_{33} (~250 pC/N) and k_p (~50%). Moreover, it's also can be seen that d_{33} values are almost independent of the alkali ratio in the compositional range of x=0.40~0.60 in KNLNT ceramics, which is very similar to that of pure KNN ceramics reported before [15]. Meanwhile, the k_p curves show a similar variation tendency to d_{33} values, and also change little with different alkali ratios in the same compositional range. From the result, we can get the conclusion that these ceramics not only present outstanding piezoelectric performance, but also these properties almost keep unchanged with different K/Na ratios in the wide compositional range.

Table 1 Optimum sintering temperature of KNLNT alloys (°C)

Li content, y	x=0.40	x=0.45	x=0.50	x=0.55	x=0.60
0.03	1140	1140	1140	1120	1120
0.035	1130	1120	1120	1120	1110
0.04	1140	1140	1130	1130	1120

Fig.2 shows XRD patterns of three typical KNLNT ceramics and pure $K_{0.5}Na_{0.5}NbO_3$ ceramics. From the XRD patterns, we can seen the ceramics present perovskite structure; no obvious secondary phase is detected. In comparison with pure KNN ceramic that obviously exhibits typical orthorhombic perovskite structure at room temperature, KNLNT ceramics exhibit the structure change with the increasing Li content from a polymorphic phase transition (PPT) to a tetragonal symmetry, and the surface indexes of diffraction

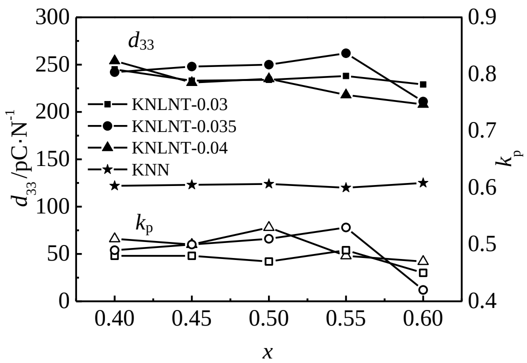

Fig.1 Changes of d_{33} and k_p with different K/Na ratios

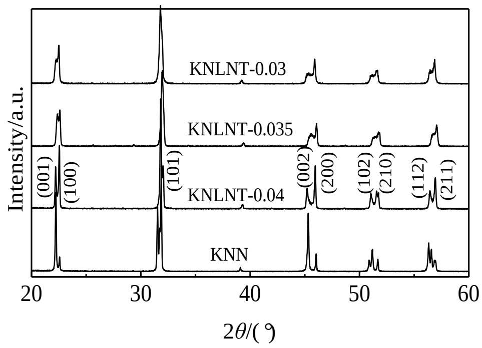

Fig.2 XRD patterns of KNLNT ceramics obtained at room temperature

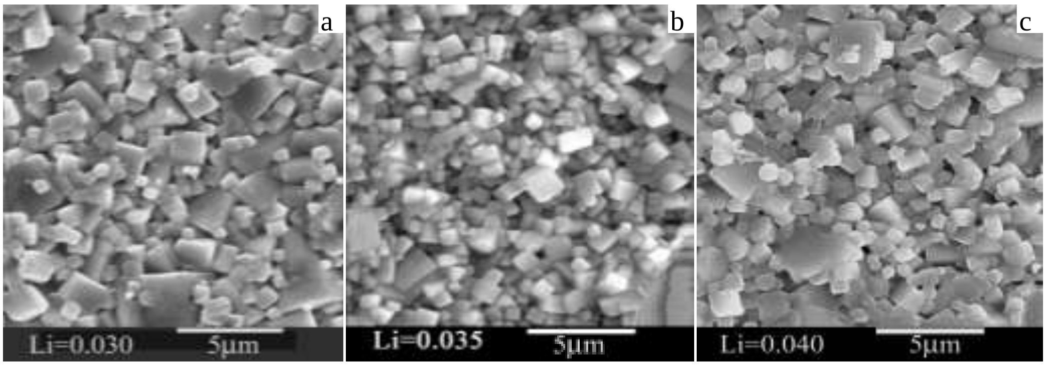

Fig.3 SEM images of three typical KNLNT (y=0.03, 0.035, 0.04) ceramics (x=0.50): (a) y=0.03, (b) y=0.035, and (c) y=0.04

peaks are also presented. So it is believed that the coexistence of orthorhombic and tetragonal phases plays an important role in the observed high piezoelectric properties of our KNLNT ceramics as in other KNN-based ceramics [3-9, 18-27].

As we all know, the microstructure has an important influence on the physical properties of potassium sodium niobate. So the microstructures of samples were researched and the SEM images of three typical KNLNT (y=0.03, 0.035, 0.04) ceramics with x=0.50 are given in Fig.3.

Within the compositional range, they resemble each other and do not show a significant change with the x value. This is one of the reasons that the piezoelectric performance of the ceramics shown in Fig.1 is almost the same in this compositional range. Ceramics exhibit a bimodal grain size distribution and the average grain size is between 1.0 and 2.0 μm. In Fig.3, the size difference between fine and large grains gets smaller with the increasing Li content, which indicates Li can promote uniformity of grain growth.

2.2 Thermal stability

Besides excellent piezoelectric activity, other properties are also found to be very stable in the severe thermal aging test, as given in Fig.4. It delineates representatively the changes of d_{33} and k_p data in $(K_{0.5}Na_{0.5})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ (y=0.03, 0.035, 0.04) ceramics with the thermal aging temperature. It can be seen that d_{33} and k_p remain nearly unchanged within the broad temperature range from the low experimental temperature limit of −150 °C to high temperature close to T_C =325 °C (Curie temperature), which is quite similar to what was observed in $(K_{0.40}Na_{0.60})_{0.96}Li_{0.04}Nb_{0.80}Ta_{0.20}O_3$ and $(K_{0.55}Na_{0.45})_{0.965}$-$Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramics in the previous work[17,24]. The other compositional ceramics we investigated in the work also present the same curve, which proves again that the equal molar ratio of K/Na is not the essential condition to obtain excellent piezoelectric properties in KNN-based ceramics.

Fig.5 shows the piezoelectric temperature stability of three typical compositions in terms of k_p data with various temperatures. In contrast to the results previously obtained in other KNN-based ceramics[19,24-30], k_p in the work shows the weak temperature dependence over a wide measured temperature

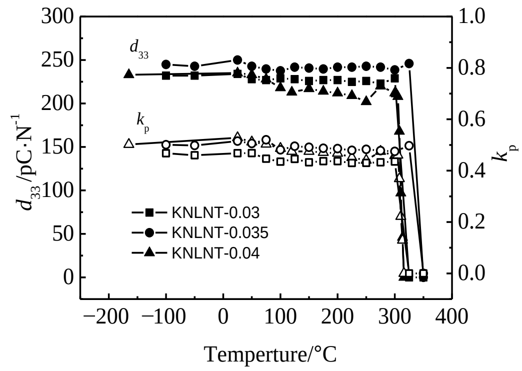

Fig.4 Variations of d_{33} and k_p with thermal aging temperature

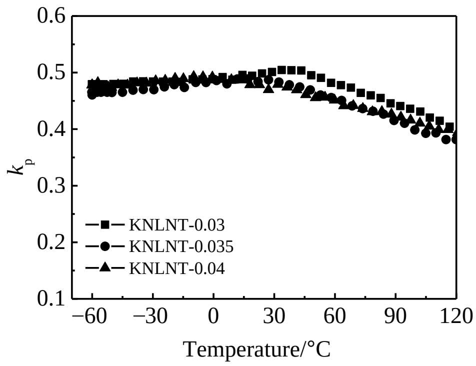

Fig.5 Variations of k_p with temperature

range from −50 ℃ to 120 ℃. In particular, as shown in Fig.5, very few changes of k_p with temperature are seen within the common usage temperature range between −50 ℃ and 80 ℃, where the k_p values keep larger than 0.45. Generally, in comparison with $CaTiO_3$-modified (Na,K,Li) (Nb,Ta,Sb)O_3 and $BiFeO_3$-modified (Na,K,Li) (Nb,Ta,)O_3 ceramics [28,31,32], the KNLNT ceramics show the quite closed piezoelectric temperature stability but the similar or higher d_{33} values. Therefore, the KNLNT ceramics possess not only the high piezoelectric properties but also the very good piezoelectric temperature stability and the excellent thermal aging stability.

We know that the excellent piezoelectric performance of

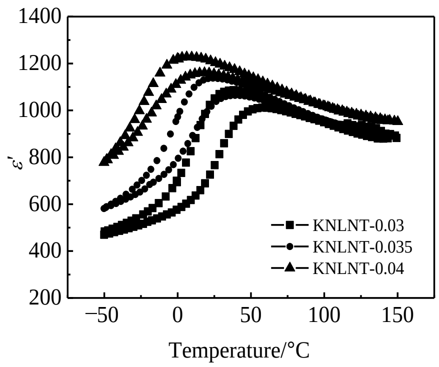

Fig.6 Thermal hysteresis of ε'

the KNLNT ceramics is caused by the phase transition temperature between orthorhombic and tetragonal decreasing to around room temperature due to the Li and Ta doping as in other KNN-based ceramics. It is generally acknowledged that the temperature shifting correspondingly results in a strong temperature dependence of the piezoelectric properties, being limited further by domain instability, during thermal cycling between the two ferroelectric phases. However, KNLNT ceramics in the work also present good temperature stability, which can be still explained by the existence of the polymorphic phase transition.

Fig.6 displays the varying of dielectric constants with different temperatures that is observed during the successive heating and cooling processes around T_{O-T} at 100 kHz. As shown in the figure, the KNLNT ceramics display a quite large thermal hysteresis, which indicates that the two different phases could coexist quite stably over a considerably wide temperature region around T_{O-T} and phase change from one to the other occurs gradually. Consequently, the piezoelectric properties exhibit the weak temperature dependence. Moreover, the good temperature stability of piezoelectric properties also might be ascribed to that they lie more closed to the tetragonal phase side seen from Fig.2, and the closing to the tetragonal side exhibit much less temperature dependence. The stable thermal aging characteristic of the KNLNT ceramics implies that the intrinsic contribution from crystalline structural lattice should be the dominant part in its observed high piezoelectric properties or the reproducible domain configuration in the polymorphic phase transition, and a further study is urgently needed to provide a deeper understanding.

3 Conclusions

1) $(K_xNa_{1-x})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ (KNLNT, x=0.4~0.6; y=0.03, 0.035, 0.04) ceramics are prepared by the conventional solid-state reaction technique. The ceramics present perovskite structure, and no obvious secondary phase is detected; the average grain size is between 1.0 and 2.0 μm for the ceramic.

2) Li/Ta addition to pure KNN ceramics can strongly enhance their piezoelectric properties. The KNLNT ceramics present high piezoelectric constants: d_{33}=250 pC/N and k_p=50%; are very stable in the severe thermal aging test, and the d_{33} and k_p remain nearly unchanged within −150 °C to T_C (325 °C).

3) The k_p exhibits the weak temperature dependence over a wide measured temperature range from −50 ℃ to 120 ℃.

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$(K_xNa_{1-x})NbO_3$ 基陶瓷的热稳定性研究

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摘　要：采用传统固溶反应法制备了$(K_xNa_{1-x})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ (x=0.40~0.60; y=0.03, 0.035, 0.04) 系列无铅压电陶瓷，研究了其压电性能的温度稳定性。实验得出在研究的组分范围内，陶瓷的压电常数d_{33}可达到250 pC/N，k_p到达50%。在高达约325 ℃的老化试验中发现，尽管在室温下存在多型相变的影响，但陶瓷的d_{33}和k_p值几乎一直保持不变。而且，陶瓷的k_p值在−50 ℃到120 ℃的宽温度范围内几乎不受温度影响，显示了很好的温度稳定性。另外还从两相共存的温度范围对陶瓷的热稳定性能进行了讨论。

关键词：无铅陶瓷；压电性能；K/Na 比例；温度稳定性

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