Recent study progresses of $(K,Na)NbO_3$-based lead-free piezoelectric ceramics

J. L. ZHANG[a,b*], X. J. ZONG[a], Y. GAO[a], Y. L. QING[a], M. L. ZHAO[a], C. L. WANG[a,b]
[a]School of physics, Shandong University, Jinan 250100, P. R. China
[b]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P. R. China

This paper outlines our recent study progresses on $(K,Na)NbO_3$-based lead-free piezoelectric ceramics. It has been found in $(K_xNa_{1-x})NbO_3$ ceramics that piezoelectric properties are almost irrelevant to the K/Na ratio within x=0.40 ~ 0.60 and orthorhombic phase possesses the much better piezoelectric temperature stability than tetragonal phase. Similar phenomena are also observed in some $(K,Na,Li)(Nb,Ta)O_3$ ceramics, of which $(K_{0.55}Na_{0.45})_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramic shows particularly an outstanding piezoelectric performance with the piezoelectric properties of d_{33} =262 pC/N, k_p=0.53 and k_{33}=0.63 at room temperature and the weak temperature dependence of electromechanical coupling coefficients in the common usage temperature range. Furthermore, we have successfully obtained a remarkably high d_{33} value of 413 pC/N in $(K_{0.45}Na_{0.55})_{0.98}Li_{0.02}(Nb_{0.77}Ta_{0.18}Sb_{0.05})O_3$ ceramic through the conventional solid state reaction process.

1. Introduction

Piezoelectric ceramics are a type of functional materials that can realize the mutual conversion between mechanical energy and electric energy, thereby being widely applied for fabricating the electronic devices such as sensors, transducers, actuators, resonators and filters. $Pb(Zr,Ti)O_3$-based piezoelectric ceramics are currently the most popularly utilized ones because of their superior performances with both high piezoelectric properties and good temperature stabilities. However, due to the toxicity of lead oxide, there has been an increasing demand worldwide to replace them with lead-free alternatives from the perspective of environmental concerns and sustainable development. Correspondingly, $(K,Na)NbO_3$-based ceramics (abbreviated below as KNN-based ceramics) have attracted much attention in recent years since they might become the promising candidates as lead-free piezoelectric materials [1].

On the other hand, much fundamental work is still essential from both technological and scientific viewpoints in order to further realize the possibility that KNN-based ceramics are practically used as the popular lead-free piezoelectric materials in future. The following issues are considered to be especially important in our study. First, by checking the literature, we find that most of the previous investigations on KNN-based ceramics were carried out on the basis of equal molar ratio of K/Na or nearly so. Chemical compositions of such K/Na ratios had been widely believed to be essential for obtaining the good

piezoelectric properties in KNN-based ceramics. To a great extent, the situation could be explained to arise from the early study results. It was reported that $(K_xNa_{1-x})NbO_3$ ceramics show a k_p peak at x=0.50 [2-4] and there exists a slight discontinuity in lattice parameters at x=0.475, which separates two orthorhombic phases and acts like morphotropic phase boundary (MPB) [5]. However, considering the large compositional intervals adopted experimentally in the early studies [2-4] and the importance of this issue to the further materials' composition designs, it is appropriate to treat the previously obtained results with care and to reinvestigate systematically the influence of K/Na ratio. Secondly, it has been gradually recognized by many researchers that enhanced piezoelectric properties of KNN-based ceramics always appear with the occurrence of an orthorhombic-tetragonal polymorphic phase transition around room temperature and strong piezoelectric temperature dependence is usually observed in those KNN-based ceramics that show the enhanced piezoelectric properties [6-11]. Nevertheless, for a piezoelectric material, the good piezoelectric temperature stability is usually very important in practical applications. Therefore, it is necessary to find out some chemical compositions that could show a high piezoelectric performance with both excellent piezoelectric properties and good piezoelectric temperature stability even when being prepared by the conventional solid-state reaction technique and elucidate the underlying mechanisms.

Under the abovementioned circumstances, our efforts

in the study of KNN-based ceramics have been mainly focused on the following three aspects: (1) examining whether the widely-believed MPB nearby the compositional ratio of K/Na=1:1 really exits or not, (2) searching for some chemical compositions with excellent piezoelectric properties, and (3) improving the piezoelectric temperature stability.

2. Experimental

Various ceramics with the nominal chemical compositions of $(K_xNa_{1-x})NbO_3$, $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$, $(K_{1-x}Na_x)_{0.965}Li_{0.965}Nb_{0.80}Ta_{0.20}O_3$ and $(K_xNa_{1-x})_{0.98}Li_{0.035}Nb_{0.82-z}Ta_{0.18}Sb_zO_3$ were prepared by the conventional solid-state reaction technique using the raw materials of K_2CO_3, Na_2CO_3, Li_2CO_3, Ta_2O_5, Nb_2O_5 and Sb_2O_5. The raw materials were weighed according to the stoichiometric ratio, ball-mixed in alcohol for 12 h and calcined at about 900ºC for 2 ~ 3 h. After the calcination, the mixtures were again ball-milled and pressed into pellet disks. Sintering was carried out in ambience at 1080 ~ 1200ºC for 2 ~ 4 h. For electrical characterization, specimens were coated with silver paint on both surfaces and fired. Poling was accomplished in silicon oil under a DC electric field at about 130ºC for 30 min. Piezoelectric measurement was performed 24 h after poling procedure. k_p and k_t were calculated from the resonance-antiresonance frequencies measured with an Agilent 4294A precision impedance analyzer, and d_{33} was measured using a Berlincourt-type d_{33}-meter (YE 2730A). The major part of evaluation work about piezoelectric temperature stability was carried out in an Espec SU-261 chamber. Further detailed experimental information can be referred to the previous papers [7,12-15].

3. Results and discussion

Fig. 1 shows the variations of d_{33} and k_p with respect to x in $(K_xNa_{1-x})NbO_3$ ceramics at room temperature. Both d_{33} and k_p exhibit broad peaks, and are almost independent of the K/Na ratio within x=0.40 ~ 0.60. For the ceramic with x=0.50, its d_{33} value is 124 pC/N, which is much higher than the reported result of 80 pC/N [2]. The k_p curve differs from the previous one of the conventionally sintered $(K_xNa_{1-x})NbO_3$ ceramics [2], but are quite similar to that of hot-pressed $(K_xNa_{1-x})NbO_3$ ceramics [3,4]. Meanwhile, no lattice discontinuity near x=0.475 is confirmed in our detailed XRD analysis [13], which contradicts with the result reported in Ref. 5 but in agreement with the one reported in Ref. 16. By the systematic examination of other factors such as theoretical density, phase transitions and microstructure and the comparison with the MPB characteristic of $Pb(Zr,Ti)O_3$ ceramics, we conclude that the microstructure of well-faceted and uniformly distributed large grains in $(K_xNa_{1-x})NbO_3$ ceramics rather than the well-believed

MPB plays the important role in the observed piezoelectric properties [13]. Figure 2 describes the piezoelectric temperature dependence of $(K_{0.50}Na_{0.50})NbO_3$ ceramic in terms of k_p. Similarly to that found in $(K_{0.48}Na_{0.52})NbO_3$ ceramic [15], the piezoelectric properties of $(K_{0.50}Na_{0.50})NbO_3$ ceramic are extremely temperature-stable in orthorhombic phase. k_p is nearly temperature-independent over a considerably wide temperature interval in orthorhombic phase from the experimentally low limit temperature of -150°C to about 175°C, and shows a peak corresponding to the orthorhombic-tetragonal phase transition around 205°C and a rapid decrease in tetragonal phase.
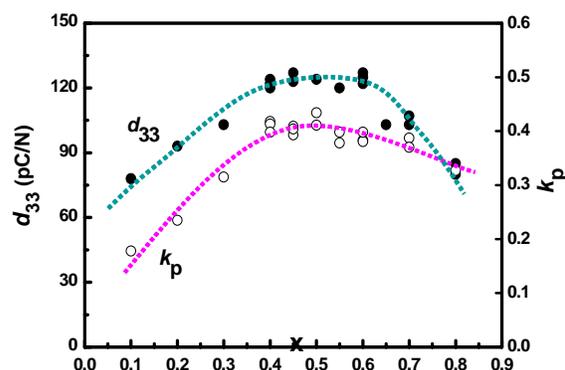

Fig. 1. Variations of d_{33} and k_p with x in $(K_xNa_{1-x})NbO_3$ ceramics. Dashed lines are given for eyes' guide.
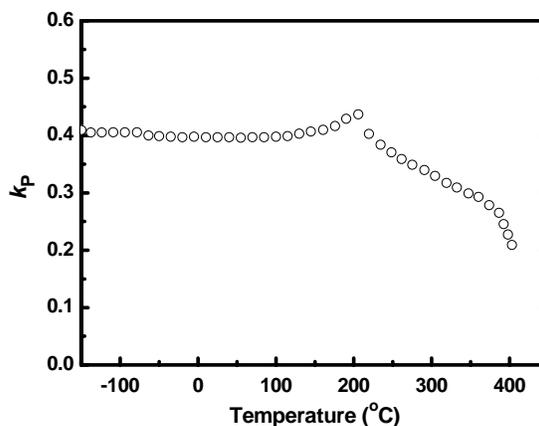

Fig. 2. Piezoelectric temperature dependence of $(K_{0.50}Na_{0.50})NbO_3$ ceramic in terms of k_p.

Table 1 tabulates the piezoelectric parameters of d_{33}, k_p and k_{33}, mass density ρ, dielectric permittivity ε' and dielectric loss $tan\delta$ for $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics at room temperature. d_{33}, k_p and k_{33} increase first, reach maxima around y=0.03~0.035 and then decrease with the increase of y. For the composition with y=0.035,

d_{33}, k_p and k_{33} are 250 pC/N, 0.51 and 0.64, respectively. Figure 3 displays the hysteresis curves of ε' vs. temperature around the orthorhombic-tetragonal phase transition. The phase transition peaks are considerably broad, and the hysteresis is quite large. The existence of hysteresis indicates that the orthorhombic-tetragonal phase transition is a first-order one. The phase transition temperature T_{O-T} decreases monotonically with the increase of y. Furthermore, compared to $(K_xNa_{1-x})NbO_3$ ceramics, $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics exhibit the much lower values of T_{O-T} due to the addition of Li and Ta. It is considered that the enhanced piezoelectric properties observed in the $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics with y=0.03~0.035 associate closely with the phase coexistence due to the polymorphic phase transition, as in other KNN-based ceramics [1,6,8-11]. This is clear from Fig. 3 that the $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics with y=0.03 or 0.035 show their T_{O-T} values particularly close to room temperature.

Table 1. Physical properties of $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics at room temperature.

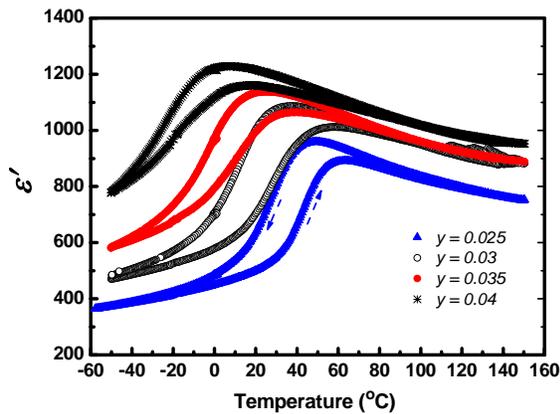|	y=0.015	y=0.02	y=0.025	y=0.03	y=0.035	x=0.04	x=0.05	x=0.06
ρ (g/cm³)	4.79	4.84	4.73	4.76	4.72	4.86	4.79	4.82
ε' at 1kHz	729	670	1086	1170	1278	1374	1215	1031
tan δ (%)	2.4	2.3	2.3	2.2	2.2	1.5	1.5	1.32
d_{33} (pC/N)	162	170	196	253	250	235	178	148
k_p	0.44	0.46	0.50	0.53	0.51	0.53	0.42	0.38
k_{33}	0.56	0.59	0.55	0.66	0.64	0.63	0.52	0.54

Fig. 3. Thermal hysteresis curves of $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics, which were measured during the successive heating and cooling processes around T_{O-T}.

Fig. 4 presents the k_p vs. temperature curves of $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics with y=0.025 ~ 0.04, which were measured in the temperature range between -60°C and 150°C. These curves reveal broad peaks, and the temperature values that correspond to the k_p maxima decrease with y, which is in consistency with the result given in Fig. 3. The inset in Fig. 4 shows representatively the data measured for $(K_{0.50}Na_{0.50})_{0.975}Li_{0.025}Nb_{0.80}Ta_{0.20}O_3$ ceramic over an extended temperature range. It is clear that this ceramics is quite like $(K_xNa_{1-x})NbO_3$ ceramics and possesses the extremely temperature-stable characteristic of orthorhombic phase.
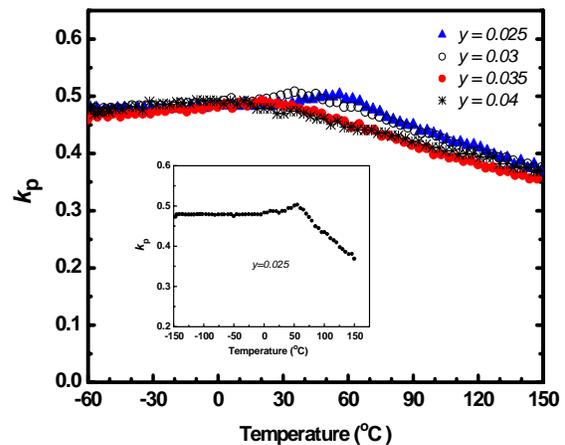

Fig. 4. Temperature dependence of k_p for $(K_{0.50}Na_{0.50})_{1-y}Li_yNb_{0.80}Ta_{0.20}O_3$ ceramics. The inset shows representatively the data of the ceramic with x=0.025 that were measured over an extended temperature range.

Table 2 lists the physical properties of $(K_{1-x}Na_x)_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramics with various K/Na ratios. Clearly, those ceramics with x=0.40~0.55 show high piezoelectric properties of d_{33} larger than 240 pC/N , and k_p and k_{33} of about 0.50 and 0.60, respectively. The further investigation indicates that $(K_{0.55}Na0_{.45})_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramic shows particularly an outstanding piezoelectric performance among these ceramics, despite having the orthorhombic-tetragonal polymorphic phase transition near

room temperature. It holds the piezoelectric properties of d_{33} =262 pC/N, k_p=0.53 and k_{33}=0.63 with ε'=1290 and tan δ =0.019 at room temperature. As shown in Fig. 5, its electromechanical coupling coefficients have little temperature dependence in the common usage temperature range between -30 and 85°C. We ascribe the outstanding piezoelectric performance of this ceramic to the phase coexistence in a wide temperature range and the Ta-rich composition [7,14].

Table 2. Physical properties of $(K_{1-x}Na_x)_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramics at room temperature.

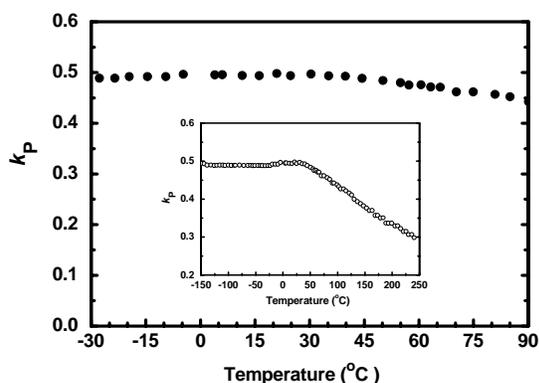|	x=0.30	x=0.35	x=0.40	x=0.45	x=0.50	x=0.55	x=0.60	x=0.65	x=0.70
ρ (g/cm^3)	4.80	4.68	4.80	4.84	4.76	4.72	4.91	4.52	4.42
ε' at 1kHz	893	913	1124	1110	1200	1290	1080	975	735
tan δ (%)	3.5	3.9	2.3	1.9	2.2	1.9	2.1	3.0	4.2
d_{33} (pC/N)	197	193	242	248	250	262	211	124	111
k_p	0.42	0.47	0.49	0.50	0.51	0.53	0.42	0.40	0.36
k_{33}	0.54	0.57	0.58	0.60	0.62	0.63	0.53	0.52	0.49

Fig. 5. Piezoelectric temperature dependence of $(K_{0.55}Na_{0.45})_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramic in terms of k_p in the common usage temperature. The inset shows the data measured over an extented temperature interval.

On the basis of the above results, we have recently designed and prepared a series of $(K_xNa_{1-x})_{0.98}Li_{0.02}Nb_{0.82-z}Ta_{0.18}Sb_zO_3$ ceramics, aiming to obtain a type of KNN-based lead-free materials with very high d_{33} values. It is found that the one with the composition of $(K_{0.45}Na_{0.55})_{0.98}Li_{0.02}Nb_{0.77}Ta_{0.18}Sb_{0.05}O_3$ show particularly high piezoelectric properties of d_{33} =413 pC/N, d_{31} =153 pC/N, k_p =0.50, k_t =0.41, k_{33} =0.62 with ε' =2385 and $tan\delta$ =0.027 at room temperature. We note that this d_{33} value is the highest one ever reported so far for all

the KNN-based ceramics that were prepared under the conventional solid-state reaction technique and is higher than 374 pC/N of the well-known soft piezoelectric material PZT-5A, being comparable to the record value of 416 pC/N for the textured $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ ceramic (labeled as LF4T in literature and prepared by the complicated technique of reactive-templated grain growth) [1,17]. The fact that our $(K_{0.45}Na_{0.55})_{0.98}Li_{0.02}Nb_{0.77}Ta_{0.18}Sb_{0.05}O_3$ ceramic shows the considerably large d_{33} value seems to relate with the phase coexistence due to the occurrence of an orthorhombic-tetragonal polymorphic phase transition in the vicinity of room temperature and the larger electronegativity and smaller radius of Sb^{5+} ion than those of Nb^{5+} and Ta^{5+} ions.

4. Conclusion

The study progresses of $(K,Na)NbO_3$-based lead-free piezoelectric ceramics achieved in our group over the past few years have been reviewed. For $(K_xNa_{1-x})NbO_3$ ceramics, d_{33} and k_p show broad peaks and are nearly independent of the K/Na ratio within x=0.40 ~ 0.60, and the existence of lattice parameter discontinuity at x=0.475 is not confirmed in contrast to the early literature result. Much better piezoelectric temperature stability is observed in the orthorhombic phase than in the tetragonal phase. The irrelevance of piezoelectric properties with the K/Na ratio within x= 0.40 ~ 0.60 and the highly stable characteristic of piezoelectric coupling coefficients in the

orthorhombic phase is also seen in some (K,Na,Li)(Nb,Ta)O$_3$ ceramics. In spite of the orthorhombic-tetragonal polymorphic phase transition near room temperature, $(K_{0.55}Na0_{.45})_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ ceramic shows a good piezoelectric performance with the high piezoelectric properties of d_{33} =262 pC/N, k_p=0.53 and k_{33}=0.63 at room temperature and the weak piezoelectric temperature dependence over the common usage temperature range. Furthermore, $(K_{0.45}Na_{0.55})_{0.98}Li_{0.02}(Nb_{0.77}Ta_{0.18}Sb_{0.05})O_3$ ceramic with d_{33} as high as 413 pC/N has been successfully obtained by the conventional solid-state reaction technique.

Acknowledgment

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[*]Corresponding author: zhangjialiang@sdu.edu.cn