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Lead-free $KNbO_3$ piezoceramics synthesized by pressure-less sintering

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Abstract

Dense $KNbO_3$ ceramics have been successfully synthesized by pressure-less sintering under optimized heat-treatment conditions using a small amount of La_2O_3 and Fe_2O_3 additives. X-ray diffraction (XRD) analysis revealed that $KNbO_3$ forms $(K_{1-x}La_x)(Nb_{1-x}Fe_x)O_3$ solid solutions and changes in the crystal system, depending on the additive content, from orthorhombic to tetragonal at x of 0.020, and from tetragonal to cubic at x of 0.200 or higher. The $x = 0.002$ specimen showed orthorhombic symmetry and demonstrated the best saturated ferroelectric hysteresis loop with largest remanent polarization (P_r) of 18 $\mu C/cm^2$, which is comparable to the value reported for pure $KNbO_3$ ceramics fabricated by hot pressing. This specimen also showed a planar electromechanical coupling ratio (k_p) of 0.17 and thickness mode (k_t) of 0.48. The piezoelectric d_{33} constant was 98 pC/N.

Keywords: Sintering; Ferroelectric properties; Piezoelectric properties; Niobates; Actuators

1. Introduction

Much attention has been paid to environmental preservation worldwide in recent years. In the research field of piezoelectric ceramics, there is an increasing strong demand to develop alternative lead-free piezoelectric materials against PZT based compounds. $KNbO_3$ is receiving considerable interest as a candidate of lead-free piezoelectrics, since the single crystal shows a large electromechanical coupling coefficient ($k^2 = 0.53$) of the surface acoustic wave (SAW) on the *Y*-cut plane,[1] compared to k^2 of only 0.05 for lithium niobate ($LiNbO_3$) crystal. It has also reported that *X*-cut $KNbO_3$ single crystals rotated by 49.5° along the *Y*-axis demonstrated the electromechanical coupling coefficient (k_t) as high as 0.69 for the thickness mode.[2] This value of k_t is the highest among all known piezoelectrics including even lead-oxide based crystals. In most case, however, the interest and success in $KNbO_3$ have been almost limited to bulk single crystal, since the synthesis of dense and stoichiometric $KNbO_3$ ceramics has been difficult by pressure-less sintering because of the massive vaporization of K_2O during sintering process and low liquidus temperature near 1000 °C.

Despite of such difficulties in the sintering of $KNbO_3$ ceramics, the authors have succeeded in the synthesis of dense $KNbO_3$ ceramics by pressure-less sintering.[3] This success resulted from several key points including (1) the careful control of processing conditions to prevent potassium loss and (2) addition of a slight amount of La_2O_3 and Fe_2O_3 to enhance the sintering temperature for densification. In the present report, further findings with the compositional dependences of crystal structure, ferroelectric and piezoelectric properties for the new class of dense $KNbO_3$ ceramics are described, together with some remarks about the engineering of the stoichiometric $KNbO_3$ ceramics.

2. Experimental

High-purity (99.9%) powders of K_2CO_3, Nb_2O_5, La_2O_3 and Fe_2O_3 were used as the starting materials. These powders were weighed to obtain the compositions according to the formula of $(1-x)KNbO_3$–$xLaFeO_3$, where x is varied from 0 to 0.500. In the case of $x = 0$, K/Nb = 1.03 was also prepared to examine the effect of extra potassium content on the calcined

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powder. The weighed powders were mixed with zirconia ball milling in acetone. The dried mixture was calcined at 820 °C, then peletized disk was calcined again at 850 °C. The calcined disk was pulverized, sieved and formed to a disk with 12 mm in diameter. The disk was further cold-isostatic-pressed under 200 MPa, then sintered at selected temperatures, depending x value, in the range between 1020 and 1280 °C.

Powder X-ray diffraction (XRD) technique was used for phase identification and investigation of the crystal system. Electric-field induced polarization (P–E) and strain (S–E) loops were measured by an aixACT TF2000FE-HV ferroelectric test unit equipped with a laser Doppler interferometer. Specimens for the piezoelectric measurements were poled at 100 °C in a silicon oil bath with a dc field strength of 5 kV/mm for 60 min. Electromechanical coupling factors for planar (k_p) and thickness (k_t) modes were determined from the resonance-antiresonance method on the basis of IEEE standards using an impedance analyzer (Agilent 4294A). Piezoelectric d_{33} constants were directly measured at room temperature using the quasi-static method by a d_{33} meter (Academia Sinica ZJ-4B).

3. Results and discussion

Highly volatile activity of K_2O limited stoichiometric control of $KNbO_3$ ceramics during sintering process. This serious problem prevented $KNbO_3$ ceramics fully densifining and resulted in the formation of an unstable secondary phase, $K_4Nb_6O_{17}$, which showed deliquescence when exposed to humidity. Fig. 1(a) presents the top external view of a $KNbO_3$ ceramic specimen (~90% of theoretical density) sintered by a standard ceramic processing used for oxide ferroelectrics. When the specimen was immersed in water, it immediately demonstrated a highly hygroscopic behavior; i.e., the sintered body showed a quick disintegration and dissolved into water. A large straight crack was observed at the center of the specimen, and the surrounding water got muddy at the same time. In contrast, the specimen shown in Fig. 1(b) demonstrated no reaction under water. This ceramics was prepared by careful handling at each processing step to avoid the reaction with moisture, and the heat treatments were carried out under K_2O-riched atmosphere produced by a combination of powder bed and double crucible techniques. These techniques effectively suppressed potassium loss during sintering process, which resulted in the synthesis of "water-proof" $KNbO_3$ ceramics with approximately 97% of theoretical density even by pressure-less sintering. Especially in the present study, it was also found that a controlled dry atmosphere for preventing moisture deposition from the starting and calcined powders was another key factor for the densification of $KNbO_3$ ceramics.

In general, extra amounts of chemicals are often added to the starting powder mixture to compensate the vapor loss of constituents at elevated temperature. However, the starting powder mixture with K/Nb of 1.03 showed poor

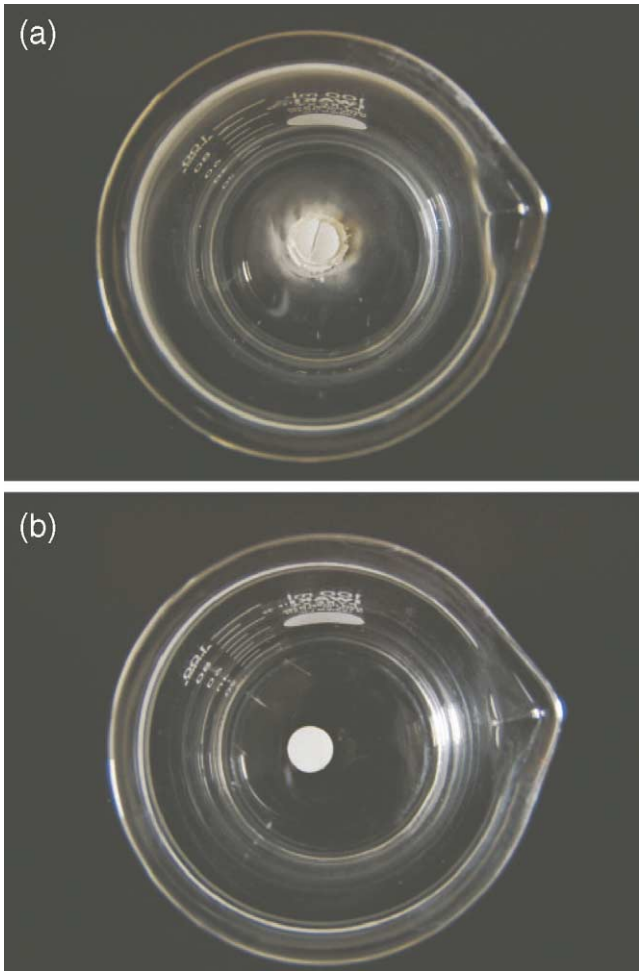

Fig. 1. Top external view of $KNbO_3$ ceramic specimens just after immersion into water. The specimens were sintered (a) by ordinary ceramic processing and (b) under carefully controlled conditions.

densification. Fig. 2 compares the morphology between the calcined powders with the starting mixing ratios of K/Nb = 1.00 and 1.03. Relatively uniform and fine distribution with a mean particle size of approximately 500 nm was observed for the calcined powder derived from K/Nb = 1.00. These fine powders were suitable for densification during the next sintering step. On the other hand, the calcined powder derived from K/Nb = 1.03 demonstrated a wide size distribution consisting of quasi-cubic particles with maximum 3 μm in size and spherical particles with minimum 500 nm in size. According to the powder XRD analysis, both of K_3NbO_4 and Nb_2O_5 phases were detected as secondary phases beside $KNbO_3$ in the specimen. Large quasi-cubic particles shown in the micrograph were $KNbO_3$; therefore, extra amounts of potassium in the starting mixture seem to have worked as a flux for abnormal grain growth. Similar size distributions with secondary phases were also observed at different calcination temperatures. As a result, uniform and fine size distributions of calcined powders were not obtained at any condition for the case of K/Nb = 1.03.

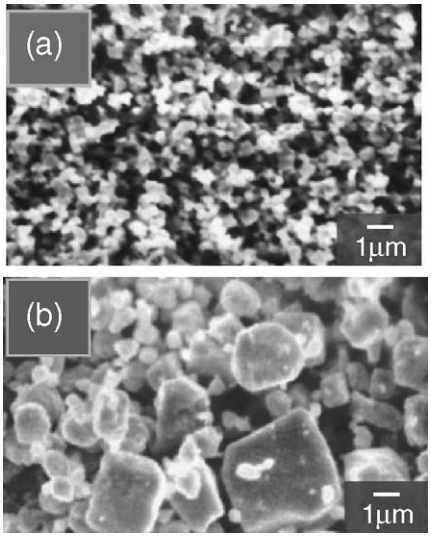

Fig. 2. SEM micrographs of the calcined $KNbO_3$ powders derived from the starting mixtures with K/Nb of (a) 1.00 and (b) 1.03.

Based on the above results, further trial was performed in order to obtain dense de $KNbO_3$ ceramics with showing better ferroelectric and piezoelectric properties. Fig. 3 shows powder XRD patterns of $(1-x)KNbO_3$–$xLaFeO_3$ sintered ceramics. The $x = 0$ specimen shows an orthorhombic symmetry of pure $KNbO_3$ (JCPDS 32-0822). When La_2O_3 and Fe_2O_3 were added to the starting composition, the sintered materials seems to have formed a $KNbO_3$-based solid solution whose diffraction peaks shift toward a higher angle with increasing x. It is also shown that the crystal system changes from orthorhombic (*Amm*2) to tetragonal (*P*4*mm*) at x of 0.020, and from tetragonal to cubic at x of 0.200 or more, which correlates with lowering of the Curie temperature (T_c) with increasing x.[3] Rietveld refinement revealed that $KNbO_3$ certainly formed a solid solution represented by $(K_{1-x}La_x)(Nb_{1-x}Fe_x)O_3$; i.e., in which La^{3+} (1.36 Å) substituted for larger K^+ (1.64 Å), while Fe^{3+} (0.64 Å) did for Nb^{5+} (0.64 Å).[4]

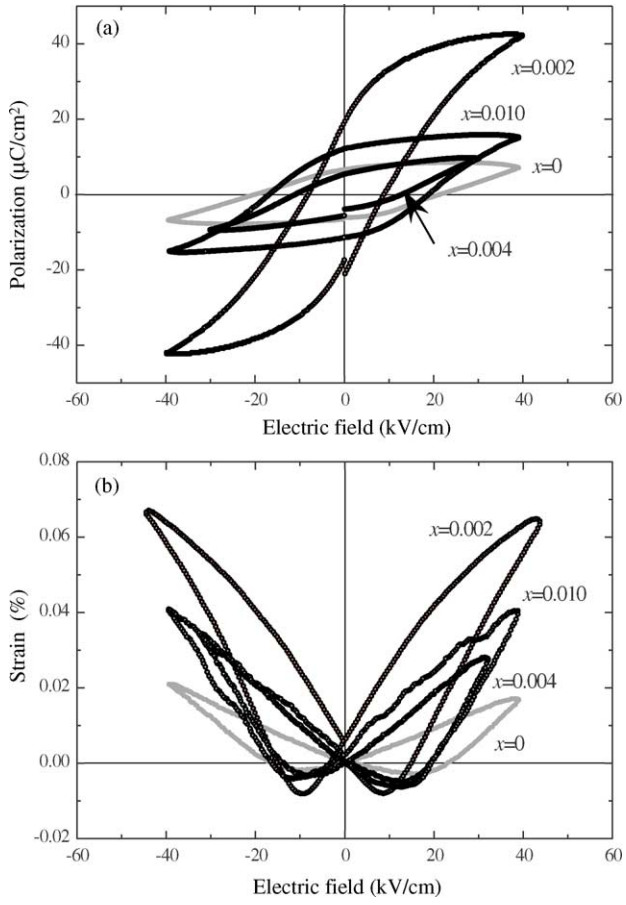

Fig. 4. Electric-field induced (a) polarization and (b) strain hysteresis curves of the La and Fe co-doped (x mol) $KNbO_3$ ceramics.

Fig. 4 presents the *P*–*E* and *S*–*E* hysteresis loops observed for the $x = 0$, 0.002, 0.004 and 0.010 specimens. The $x = 0.002$ specimen demonstrates the best saturated hysteresis loop with remanent polarization (P_r) of 18 μC/cm^2 and coercive field of 9 kV/cm. This P_r value is three times larger than that obtained in the $x = 0$ specimen and is comparable to the value of 18 μC/cm^2 reported for pure $KNbO_3$ ceramics

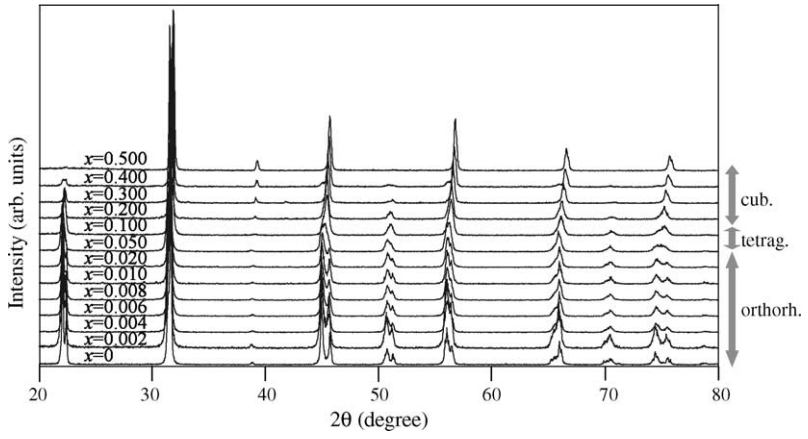

Fig. 3. Powder XRD patterns of the La and Fe co-doped (x mol) $KNbO_3$ ceramics.

Table 1
Piezoelectric properties of the La and Fe co-doped (x mol) $KNbO_3$ ceramics

x	k_p	k_t	d_{33} (pC/N)
0	0.15	–	57
0.002	0.17	0.48	98
0.004	0.15	0.22	77
0.006	0.12	–	50

fabricated by hot pressing.[5,6] Moreover, typically butterfly loops were obtained in the electro-field induced strain curve for all the specimens, and the $x = 0.002$ specimen demonstrates the largest strain of 0.067% under a bipolar driving field of 40 kV/cm. On the other hand, less saturated curve shape and reduced loop area were observed in the *P–E* and *S–E* hysteresis loops, respectively, for the $x = 0.004$ and 0.010 specimens. This degradation was caused by the decrease of dielectric constant and increase of dielectric loss. Ionic radius of Fe^{3+} (0.64 Å) equals to that of Nb^{5+} (0.64 Å), but Fe^{2+} is 0.78 Å that is approximately 20% larger than Nb^{5+}; therefore, a distorted solid solution structure is also considered to have affected the ferroelectric property with increasing x value.

Table 1 lists the piezoelectric property of the $(1-x)KNbO_3$–$xLaFeO_3$ ceramics. Although k_p value was hardly affected by x value, both of k_t and d_{33} values depended on the doping content of La and Fe. Of all the specimens investigated, the $x = 0.002$ specimen demonstrated a best k_p of 0.17, k_t of 0.48 and d_{33} of 98 pC/N.

4. Conclusions

The compositional dependences of crystal structure, ferroelectric and piezoelectric properties for the new class of dense $KNbO_3$ ceramics were investigated. It was found that the synthesis of stoichiometric $KNbO_3$ ceramics with high density needed careful control of atmosphere against vaporization of K_2O and moisture deposition at all the processes. Furthermore, it was revealed that excellent ferroelectric and piezoelectric properties appeared in $KNbO_3$ ceramics with addition of only a 0.002 mol of La_2O_3 and Fe_2O_3. In particular, relatively large k_t value (0.48) is much attractive in the category of lead-free piezoelectric ceramics.

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