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Textured $(K_{0.5}Na_{0.5})NbO_3$ ceramics prepared by screen-printing multilayer grain growth technique

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Abstract

The screen-printing multilayer grain growth (MLGG) technique is successfully applied to alkaline niobate lead-free piezoelectric ceramics. Highly textured $(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramics with $\langle 0\ 0\ 1\rangle$ orientation ($f = 93\%$) were fabricated by MLGG technique with plate-like $NaNbO_3$ templates. The influence of sintering temperature on grain orientation and microstructure was studied. The textured KNN ceramics showed very high piezoelectric constant $d_{33} = 133$ pC/N, and high electromechanical coupling factor $k_p = 0.54$. These properties were superior to those of conventional randomly oriented ceramics, and reach the level of those of textured KNN ceramic prepared by tape-casting technique. Compared with other grain orientation techniques, screen-printing is a simple, inexpensive and effective method to fabricate grain oriented lead-free piezoelectric ceramics.

Keywords: A. Grain growth; C. Piezoelectric property; Screen-printing; Orientation degree

1. Introduction

Recently, KNN ceramics have drawn considerable attention and been described as most promising candidates for lead-free piezoelectric materials to reduce environmental damages. However, it is difficult to obtain dense KNN ceramics through ordinary sintering, and the piezoelectric properties of ceramics are inferior to those of PZT ceramic [1–3]. Thus, microstructure control as well as composition design is required to develop ceramics with excellent piezoelectric properties. It have been reported that an appropriate amount of CuO added in KNN ceramic can improve density and the piezoelectric properties [4]. Texture control of ceramics is an important approach to enhance the piezoelectric properties of lead-free materials. Saito et al. [5] have improved the piezoelectric constant d_{33} value of KNN-based ceramics from 300 pC/N to 416 pC/N through texture technique.

Screen-printing is another high volume technique employed for fabricating thick-film electronic materials, yet, has remained relatively neglected for processing textured ceramics. Screen-printing has numerous advantages over tape-casting or extrusion, which include the realization of polymorphism and streamline production [6]. The use of screen-printing multilayer grain growth of texturing ceramics was proposed by Zeng et al. for textured BLSFs $CaBi_4Ti_4O_{15}$ (CBT) in 2005 [7], and later on used successfully for the perovskite structure $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ (NBBT) lead-free piezoelectric ceramics with a grain orientation of 92% [8].

In this paper, textured $(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramics with (0 0 1) orientation were prepared by screen-printing method using plate-like $NaNbO_3$ as templates. As a sintering aid, 0.5 mol% CuO was added to help sintering process. The electric properties of textured KNN ceramics were investigated.

2. Experimental

Plate-like $NaNbO_3$ templates were synthesized from $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ particles by topochemical microcrystal conversion method. $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ precursor particles were synthesized from a mixture of Bi_2O_3 (99.7%), Nb_2O_5 (99.9%), and Na_2CO_3 (99.95%) at 1100 °C for 3 h using molten NaCl salt as a flux. Plate-like $NaNbO_3$ templates were then synthesized from a mixture of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ and Na_2CO_3

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at 950 °C in a NaCl flux. The $NaNbO_3$ templates obtained were with an average thickness of 0.5 μm and length of 15 μm.

$(K_{0.5}Na_{0.45})Nb_{0.95}O_{2.85}$ matrix powders were synthesized by milling Na_2CO_3, K_2CO_3, and Nb_2O_5 raw material powders and then calcining at 820 °C for 3 h. The obtained powders were milled with 0.5 mol% CuO again. The resulting milled powders were mixed with ethyl-cellulose and α-terpineol organic solution for 2 h, and then the $NaNbO_3$ templates were added. The matrix powders, templates and organic solution were well mixed in a ball mill to obtain aiming slurry. The matrix and templates were mixed at a ratio of 20:1. The obtained slurry was composed of 30 wt% of the inorganic powders and 70 wt% of the organic solution.

The screen-printing process was described as below: the slurry was forced by a blade through the open pattern in a stencil screen and deposited onto a glass substrate and then dried at 80 °C. Repeat the above steps until the multilayered thick film to 150 μm. The films were cut into 12 mm × 12 mm, removed from the substrate, stacked, and then laminated to fabricate green compacts. After binder burned out at 650 °C, the samples were applied to cold-isostatic pressing (CIP) at 250 MPa. The samples were sintered at temperatures between 1100 °C and 1130 °C for 2 h in air. The samples used for microstructure observation were thermal etched at 1060 °C for 30 min.

The relative densities of the specimen were measured by the Archimedean method. The crystalline phases of textured ceramics were determined by X-ray diffraction analysis. The microstructure was observed using the electron microprobe microscopy analysis. The temperature dependence of dielectric constant and dielectric loss was examined with an HP 4284A (Agilent Technology Co., Ltd.) precision LCR meter. The *P–E* hysteresis loops were observed using a TF Analyzer 2000 FE-Module (aixACCT) ferroelectric tester. The piezoelectric constant d_{33} was measured by a quasi-static d_{33} meter (Model ZJ-3A). The electromechanical coupling factor, k_p was determined by the resonance and anti-resonance method with an HP 4294A (Toyo Corp.) precision impedance analyzer.

The grain orientation degree of textured ceramics was examined by X-ray diffraction analysis. The degree of grain orientation was calculated by the Lotgering factor *f*, which was defined as [9]:

$$f = \frac{P - P_0}{1 - P_0} \quad (1)$$

where $P_0 = \sum_i I(0\,0\,l)/\sum_i I(h\,k\,l)$, $P = \sum_i I^*(0\,0\,l)/\sum_i I^*(h\,k\,l)$, and $\sum I^*$ is the sum of the XRD peak intensities on the parallel plane of the textured sample and $\sum I$ is the sum of peak intensities in the powder diffraction pattern. The diffraction peaks between $2\theta = 10°$ and $60°$ were used for the calculation.

3. Results and discussion

Fig. 1 shows the effect of sintering temperature on the degree of grain orientation. It can be seen that the orientation degree was very low at 1110 °C. With sintering temperature increasing, the orientation degree sharply increased starting from 1120 °C and reached up to the maximum of 93% at 1130 °C when the relative

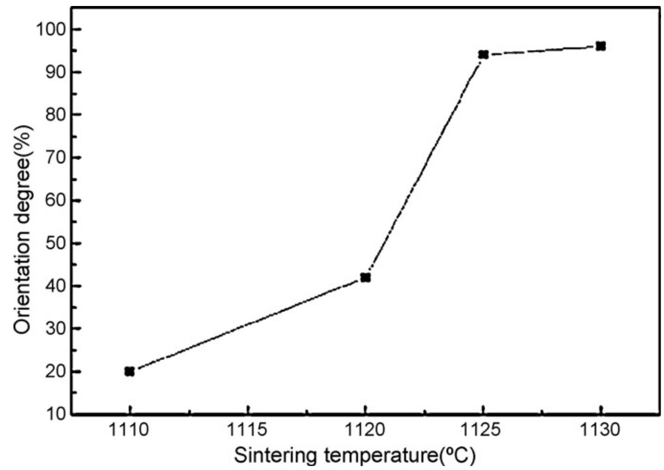

Fig. 1. The degree of grain orientation as a function of sintering temperature for KNN–0.5 mol%CuO ceramics.

density of the samples is 92%. The samples began to melt partly at 1135 °C. It is generally believed that in the texturing process, only when the density of the ceramic body reaches up to 90% of the theoretical density, the growth of templates could effectively develop [10,11]. The added CuO exists as liquid phase above its melting point (1050 °C), which promotes the densification of KNN ceramics. Hence the contact area between templates and matrix powders is needed to be large enough to allow for oriented grains growth [12].

Fig. 2 shows the cross-sectional surface of a textured KNN–0.5 mol% CuO specimen sintered at 1100 °C for 2 h in air.

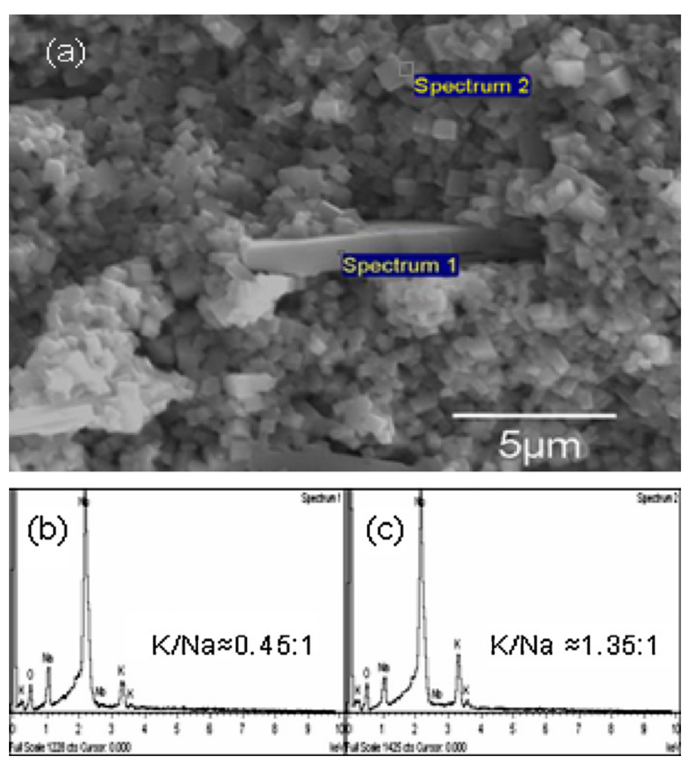

Fig. 2. Electron probe image of cross-section of textured specimen sintered at 1100 °C for 2 h in air. (a) Electron probe image, EDX profile of (b) the template and (c) the matrix powders.

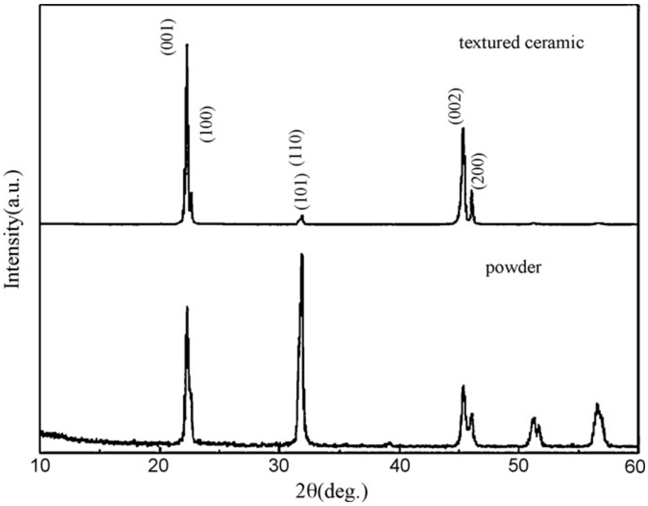

Fig. 3. The XRD patterns of KNN–0.5 mol% CuO textured ceramics and the KNN–0.5 mol% CuO powders prepared by solid state reaction.

From the results of EDX, as shown in Fig. 2(b), it is found that K atoms have diffused into the $NaNbO_3$ templates, and the ratio of K/Na in templates is obviously lower than that in matrix KNN powders shown in Fig. 2(c). The reason is that the atomic radius of K is larger than that of Na, and the sintering temperature is not high enough to allow K atom to diffuse into the $NaNbO_3$ template. Therefore, the sintering temperature needed to be increased, which is favor to provide thermal power to K atom and accelerate the oriented grain growth.

Fig. 3 shows the XRD patterns of grain oriented KNN–0.5 mol% CuO ceramics prepared by MLGG technique and the KNN powders prepared by solid state reaction. The sample was sintered at 1130 °C for 2 h. It can be seen that all the (0 0 *l*) reflections increased significantly. The (1 0 1) peak was the most intense peak of KNN–0.5 mol% CuO powders, while it remarkably decreased for the textured sample. The orientation degree of textured ceramics was calculated from the Lotgering method to be 93%.

Fig. 4 shows the microstructure of textured KNN–0.5 mol% CuO ceramic sintered at 1130 °C for 2 h. It can be seen that the

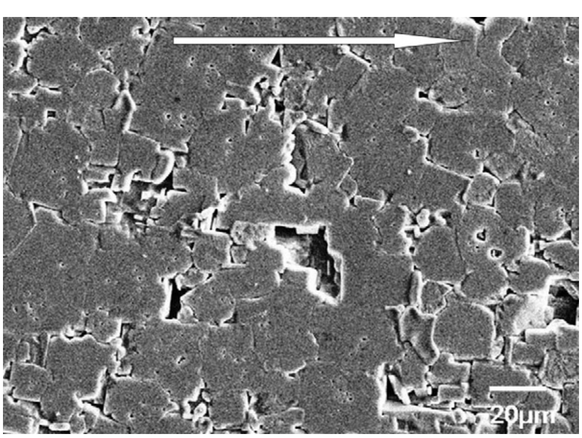

Fig. 4. The microstructure of textured specimen sintered. The arrow shows the screen-printing direction.

Table 1
Piezoelectric and dielectric properties of KNN ceramics.

Property	KNN in this work	Conventional [4]	Conventional [13]
CuO aids (mol%)	0.5	0.5	1
Sintering in air	1130 °C	960 °C	1120 °C
Orientation degree	93%	0	0
d_{33} (pC/N)	133	102	82
k_p	0.54	0.30	0.39
Q_m	150	500	2500
tan δ at 1 kHz	0.034	0.005	–

specimen had brick-layer-like grains with diameter of about 20 μm. Some pores can be observed, which is compatible with the final relative density of 92%. Although residual porosity would reduce the relative density and affected the electrical properties in a certain extent, optimization of the amounts of sintering aids and processing parameters would help fabricate a better body. A detailed investigation will be carried out in future studies.

From Table 1, it can be seen that the textured KNN–0.5 mol% CuO ceramics exhibited much higher room temperature piezoelectric properties (d_{33} = 133 pC/N, and k_p = 0.54) compared to conventional randomly oriented ceramics with the same composition (d_{33} = 102 pC/N, and k_p = 0.30), which was attributed to the high $\langle 0\,0\,1 \rangle$ orientation degree. Compared to the d_{33} (123 pC/N) of textured KNN ceramics by tape-casting technology reported previously [12], the d_{33} values of textured ceramics by screen-printing technology have been increased by about 9%. Meanwhile, the dielectric loss of textured KNN–0.5 mol% CuO ceramics was relatively larger at room temperature, and the Q_m value was also very low. All these owed to the lower relative density of 92%. As sintered in air, a large number of positively charged oxygen vacancies were produced to form the defect dipoles that affected the electrical properties of the specimens [4,13]. Some impurities could run into the green laminates during the screen-printing process, besides the volatility of the potassium and sodium component during high temperature sintering process. All these are the reasons for the lower density of textured KNN ceramics prepared by screen-printing technique. For reducing the sintering temperature and improving the density of the ceramics, adding more sintering aids is an effective way, while which will reduce the d_{33} value [4].

Fig. 5 shows the temperature dependence of dielectric permittivity and the *P*–*E* loops of the textured KNN–0.5 mol% CuO ceramic. The textured ceramics showed two phase transitions at 168 °C and 405 °C respectively, corresponding to orthorhombic to tetragonal and tetragonal to cubic phase transitions. The Curie temperature of textured KNN–0.5 mol% CuO ceramics was similar to that of conventional randomly oriented KNN–0.5 mol% CuO ceramics ($T_c \approx 403$ °C) [13]. The remnant polarization P_r and the coercive field E_c were 20 μC/cm^2 and 9.1 kV/cm respectively. The *P*–*E* loop was well saturated, and is inflated slightly due to finite electrical loss.

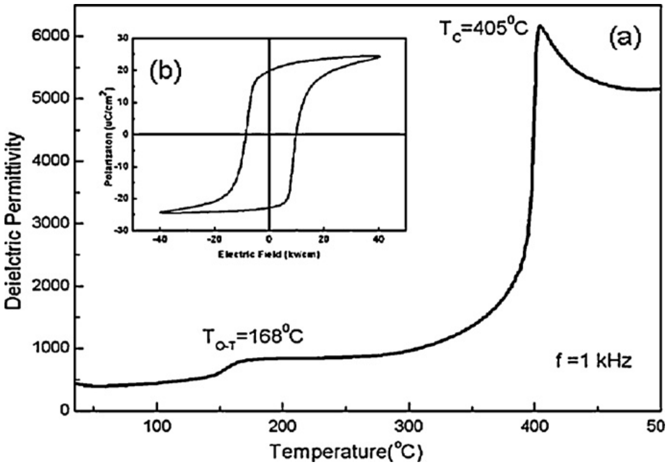

Fig. 5. (a) Temperature dependence of dielectric permittivity and (b) *P–E* hysteresis loops for textured KNN ceramic.

The shape of the *P–E* loop is close to square, which resulted from the high degree of ⟨0 0 1⟩ orientation of textured KNN ceramics [14].

4. Conclusions

The screen-printing technique was used to prepare textured KNN–0.5 mol% CuO piezoelectric ceramics with high grain orientation of 93%. Compared to conventional randomly oriented KNN ceramics, the obtained textured ceramics showed good electrical properties: $d_{33} = 133$ pC/N, $k_p = 0.54$, $P_r = 20$ μC/cm^2, $E_c = 9.1$ kV/cm and $T_c = 405$ °C. The screen-printing technique is a simple and effective method to fabricate high quality textured piezoelectric ceramics. Further exploration of texture development through screen-printing is of great significance.

Acknowledgments

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