STRUCTURE AND DIELECTRIC PROPERTIES OF LEAD-FREE SODIUM POTASSIUM NIOBATES PIEZOELECTRIC CERAMICS

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Lead-free, potassium sodium niobate piezoelectric ceramics substituted with lithium $K_{0.5}Na_{0.5}NbO_3$ have been synthesized by traditional solid state sintering. The compositions chosen are among those recently reported to show high dielectric properties. We show that high densities and dielectric properties can be obtained for all compositions by pressureless sintering in air. Lead-free piezoelectric ceramics $K_{0.5}Na_{0.5}NbO_3$ with the relative density of 94.5% have been synthesized by solid state process. In addition, the pure KNN ceramics sintered at 1100^{o}C showed optimized densification and piezoelectric properties (ρ = 4.4 g/cm^3 and Tc = 415 ^{o}C).

Lead-free piezoelectric ceramics have attracted considerable attention as new piezoelectric materials in place of $PbZrO_3$–$PbTiO_3$ (PZT) based ceramics because of environmental protection reasons [1–4]. Recently, much attention for lead-free piezoelectric ceramics has been paid to $K_{0.5}Na_{0.5}NbO_3$ (abbreviated as KNN)-based ceramics because Saito et al. [6] had developed KNN-based textured ceramics with properties comparable to those of a basic, unmodified PZT ceramics [5–8]. However, pure KNN ceramics are known to be difficult to densify fully by ordinary sintering method [9]. There are two reasons for this problem. First, the phase stability of pure KNN ceramics is limited to 1140^{o}C according to the phase diagram for $KNbO_3$–$NaNbO_3$ [5]. Therefore, high sintering temperature is not possible. In addition, Na_2O and K_2O easily evaporate at high temperature, which slight change stoichiometry of KNN ceramics and lead to the formation of extra phase [1]. KNN is one of the important lead-free piezoelectric materials with perovskite structure. Jaeger and Egerton reported that the hot pressed KNN ceramics had high Curie temperature (Tc) of 420^{o}C. Perovskite $K_{0.5}Na_{0.5}NbO_3$ ceramics are conventional piezoelectric materials widely used in sensor and actuator. Therefore, it is important to develop lead-free ceramics with good piezoelectric properties.

$K_{0.5}Na_{0.5}NbO_3$ ceramics in this study were fabricated by traditional ceramics process. Reagent-grade oxide and carbonate powers of K_2CO_3 (>99.5%), Na_2CO_3 (>99.9%) and Nb_2O_5 (>99.99%) were used as starting raw materials. All of the starting materials were weighed according to the chemical formula and ball milled with a planetary mill in anhydrous ethanol for 48 h. After drying, the mixed powder was calcined in an alumina crucible at 850 ^{o}C for 4 h, and pressed into disks of 10 mm in diameter and 1.2~1.5 mm in thickness using PVA as a binder. After burning off PVA, the pellets were sintered at 1060-1140^{o}C for 3 h soaking period in air with different sintering temperature. The bulk densities of sintered sample were measured by Archimedes method. The crystal structures were det- ermined by X-ray powder diffraction analysis obtained using a Co Kα radiation (Japan;Rigaku PC-2000) in the 2θ range of 20^o-60^o. The microstructure evolution was observed using a scanning electron microscopy (SEM; Model JSM-6360, Japan). The Dielectric constant by an impedance analyzer (Mode: HP 4292A) on the basis of IEEE standards.

Fig. 1 shows the XRD patterns of KNN power calcined at 865 ^{o}C and the ceramics sintered at 1060 ^{o}C~1140 ^{o}C with the different sintering temperature. The phase structure in all samples is pure perovskite phase with typical orthorhombic symmetry and no any secondary impurity could be certified. Among 22~23 degrees, and discovered that increase as the sintering temperature of $K_{0.5}Na_{0.5}NbO_3$ ceramics increases gradually. In addition (110) among,discoveryed that increasing with the sintering temperature of $K_{0.5}Na_{0.5}NbO_3$ to the right skew gradually. It have reported that the unstable phase was $K_4Nb_6O_{17}$ resulted from slight changes in stoichiometric ratio because of highly volatile activity of K_2O during sintering process, $K_4Nb_6O_{17}$showed deliquescence when exposed to humidity[10]. Fig. 2. shows the SEM micrograph of the KNN ceramics with the sintering temperature of 1140^{o}C. In all specimens, the micrographs of specimens had orthorh- ombic crystal feature. The sintering temperature signif- icantly affected microstructure of pure KNN ceramics as shown Fig. 2. It can be seen from Fig. 2 that many distinct pores exist in the grain boundary of pure KNN ceramics sintered at 1060~1140 ^{o}C and the average grain size is about 10 μm. With sintering temperature increased, the grain sizes were increased simultaneously as seen in Fig. 2. However, above 1120 ^{o}C, the $K_{0.5}Na_{0.5}NbO_3$ ceramics reduce gradually. There are two reasons for pure KNN ceramics with loose structure and high porosity. First, the phase stability of pure KNN ceramics is limited to 1140 ^{o}C according to the phase diagram for $KNbO_3$–$NaNbO_3$. Therefore, the high sintering temperature is not possible and the grains could not growsufficiently. Second, the grain growth cannot eliminate the pores because the morphology of the grain for pure KNN ceramics is quadrate [11].

Fig. 3 shows the variation of bulk density of KNN ceramics with sintering temperature. It can be seen that the bulk density of specimens increases with increase of sintering temperature over the range between 1060 ^{o}C and 1100 ^{o}C. The bulk density reaches its maximum value of 4.26 g/cm^3, However, above sintering temperature of 1100 ^{o}C, the bulk density begins to drop, which may be because many distinct pore existed in grain boundary. Fig. 4. shows the temperature dependence of relative dielectric constant of KNN ceramics with the sintering temperature of 1100^{o}C. It can evidently be seen that two dielectric peaks exist at 230 and 415^{o}C, which corresponding to two-phase transitions from orthorhombic to tetragonal and from tetragonal to cubic, respectively. This result is in agreement with the previously research reported.

Lead-free piezoelectric ceramics $K_{0.5}Na_{0.5}NbO_3$ with the relative density of 94.5% have been synthesized by solid state process owing to the careful control of processing conditions. Therefore, the grain growth cannot eliminate the pores because the morphology of the grain for pure KNN ceramics is quadrate. Pure KNN ceramics sintered at 1100^{o}C showed optimized densification and piezoelectric properties (ρ = 4.4 g/cm^3 and Tc = 415 ^{o}C).The results showed KNN is a promising candidate for lead-free piezoelectric ceramics.

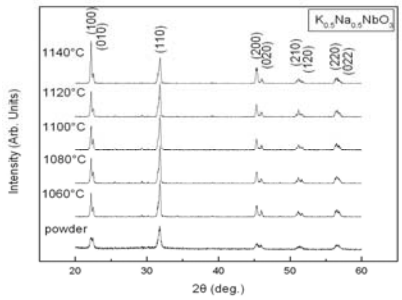

Fig. 1.

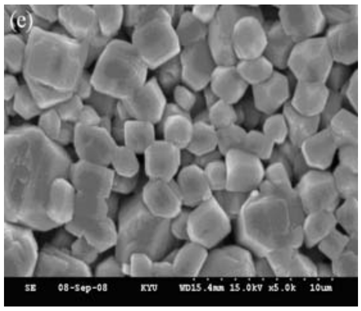

Fig. 2.

Fig. 1 XRD patterns of KNN ceramics calcined at 850 ^{o}C with the different sintering temperature.

Fig. 2. Scanning electron microscopy micrographs of the KNN ceramics with sintering temperature of 1100 ^{o}C.

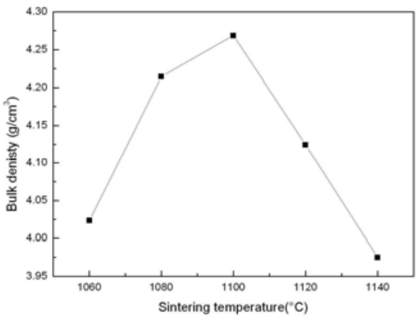

Fig. 3.

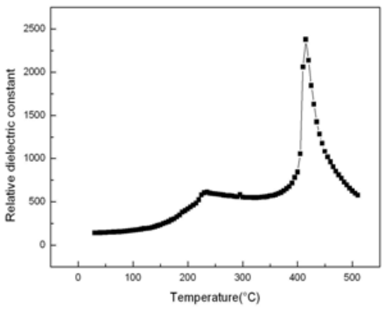

Fig. 4.

Fig. 3. The bulk density of KNN ceramics with the different sintering temperature.

Fig. 4. The temperature dependence of relative dielectric constant of KNN ceramics with the sintering temperature of 1100 ^{o}C.

Reference

[1] W.W. Wolny, Ceram. Inter. 30 (2004) 1079–1083.
[2] M.D. Maeder, D. Damjanovic, N. Setter, J. Electroceram. 13 (2004)385–392.
[3] T. Takenaka, H. Nagata, J. Eur. Ceram. Soc. 25 (2005) 2693–2700.
[4] M. Kosec, V. Bobnar, M. Hrovat, et al., J. Mater. Res. 19 (2004)1849–1854.
[5] E. Ringgaard, T. Wurlitzer, J. Eur. Ceram. Soc. 25 (2005) 2701–2706.
[6] Y. Saito, H. Takao, T. Tani, et al., Nature 432 (2004) 84–87.
[7] E. Cross, Nature 432 (2004) 24–25.
[8] E. Hollenstein, M. Davis, D. Damjanovic, et al., Appl. Phys. Lett. 87 (2005) 182905.
[9] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic, New York, 1971.
[10]H. Du, Z. Li, F. Tang, Z. Pei , W. Zhou, S. Qu,Materials Science and Engineering B 131 (2006) 83–87
[11] M.D. Maeder, D. Damjanovic, N. Setter, J. Electroceram. 13 (2004) 385–392.