The Dielectric Characteristics of Lead-Free Piezoelectric Ceramics $K_{0.5}Na_{0.5}NbO_3$

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1. Introduction

Lead-free piezoelectric ceramics have been attracted attention as new piezoelectric materials in place of $PbZrO_3$–$PbTiO_3$ (PZT) based ceramics because of environmental protection reasons [1–4]. Recently, $K_{0.5}Na_{0.5}NbO_3$ (abbreviated as KNN) based ceramics has been paid much attention for lead-free piezoelectric ceramics since Saito et al. [6] had developed KNN-based textured ceramics with properties comparable to those of a basic, unmodified PZT ceramics [5–8]. However, it was difficult to dense pure KNN ceramics by ordinary solid-state method [9], the reasons were that the phase stability of pure KNN ceramics is limited to 1140ºC 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 change stoichiometry of KNN ceramics slightly and lead to the formation of extra phase [1].

2. Experimental

In this letter, $(K_{0.5}Na_{0.5})NbO_3$ ceramics were fabricated by traditional solid-state method. Reagent-grade powers of K_2CO_3, Na_2CO_3, and Nb_2O_5 (>99.9%) were weighted and mixed according to the stoichiometry and ball-milled in the anhydrous ethanol for 48 h. After drying, the mixed powder was calcined at 850ºC for 4 h, and then pressed into disks (diameter 10 mm and thickness 1.2~1.5 mm) using PVA as a binder. After debindering, the pellets were sintered at 1060-1140ºC in air for 3 h, respectively.

The bulk densities of the sintered specimens were measured by the Archimedes method. The crystal structures were determined by X-ray diffraction (XRD) (CuK_α radiation, 2θ=20º~60º). The microstructures were observed by a scanning electron microscopy (SEM), and the dielectric constants were measured by an impedance analyzer.

3. Results and Discussion

Fig. 1 shows the XRD patterns of KNN power calcined at 865ºC and the specimen sintered at 1060~1140ºC. It is found that all of the phase structures are pure perovskite with typical orthorhombic symmetry and no other secondary phases could be found. In addition, the intensity of (110) peak increases as the sintering temperature increases, it have been reported that the unstable phase was $K_4Nb_6O_{17}$, which resulted from the slight changes in stoichiometric ratio owing to highly volatile activity of K_2O during the sintering process [10].

The SEM micrographs of the KNN ceramics with the different sintering temperature are shown in Fig. 2, and for all of the specimens, the KNN ceramics reveal orthorhombic structures. The sintering temperature affected the grains growth significantly for pure KNN ceramics, as Fig. 2(a)–(e) shown. It also could be found that distinct pores exist and the average grain size is about 10 μm. Comparing Fig. 2(a) and 2(c), as the sintering temperature increased, the grain sizes were increased gradually. However, above 1120ºC, the grain size of KNN ceramics reduce gradually. There are two reasons for pure KNN ceramics that reveal loose structure and high porosity. First, the phase stability of pure KNN ceramics is limited to 1140ºC according to the phase diagram for $KNbO_3$–$NaNbO_3$. Therefore, higher sintering temperature is impossible. Second, the grain growth cannot eliminate the pores because the morphology of the grain for pure KNN ceramics is quadrate [11, 12].

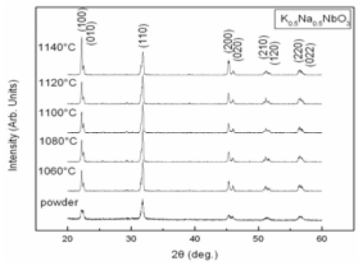
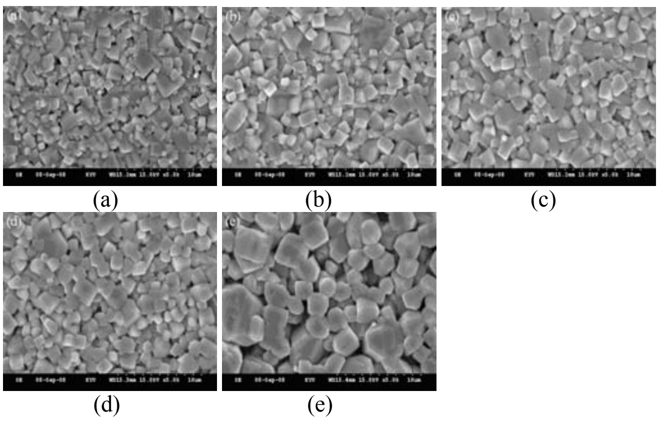


Fig. 1 The XRD patterns of KNN ceramics and the 850ºC-sintered calcined powder.



(a) (b) (c)
(d) (e)

Fig. 2. The SEM micrographs of the KNN ceramics. (a) 1060ºC; (b) 1080ºC; (c) 1100ºC; (d) 1120ºC; (e) 1140ºC

Fig. 3 shows the variation of bulk density for KNN ceramics with different sintering temperatures. It can be found that the bulk density increases as the sintering temperature increases from 1060ºC to 1100ºC, and reaches to a maximum value of 4.26 g/cm^3, and then decreases as the sintering temperature over than 1100ºC.

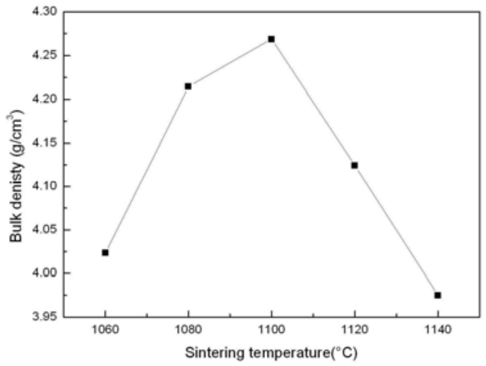


Fig. 3. The bulk density of KNN ceramics.

The relationship between the tested temperature and relative dielectric constant for 1100ºC-sintered KNN ceramics is shown in Fig. 4. It can be evidently found that there are two peaks exist at 230 and 415ºC, which corresponding to two phase transitions that transit from orthorhombic to tetragonal and transit from tetragonal to cubic, respectively. This result is in agreement with the previously research reported by Guo et al. [13].

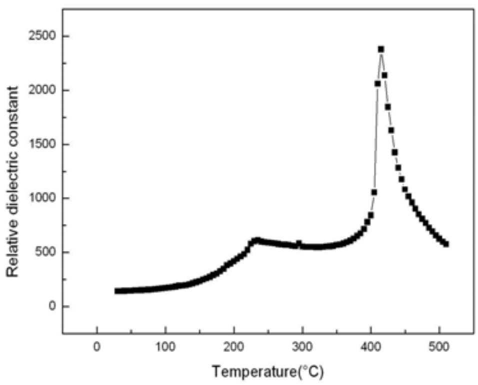


Fig. 4. The relationship between the tested temperature and relative dielectric constant for 1100ºC-sintered KNN ceramics.

4. Conclusions

Lead-free piezoelectric ceramics $(K_{0.5}Na_{0.5})NbO_3$ with the relative density of 94.5% have been synthesized and investigated by solid state method in this letter. The pores cannot be eliminated easily because the shapes of the grains for pure KNN ceramics are quadrate. Pure KNN ceramics sintered at 1100ºC reveal optimized densification (4.4 g/cm^3) and Curie temperature (415ºC).

References

[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 and H. Jaffe, Piezoelectric Ceramics, Academic, New York, 1971.
[10] H. Du, Z. Li, F. Tang, Z. Pei , W. Zhou and S. Qu, Materials Science and Engineering B **131** (2006) 83–87.
[11] M.D. Maeder, D. Damjanovic and N. Setter, J. Electroceram. **13** (2004) 385–392.
[12] H. Du, F. Tang, D. Liu, D. Zhu,W. Zhou and S. Qu, Materials Science and Engineering B **136** (2007) 165–169.
[13] Y. Guo, K. Kakimoto and H. Ohsato, Appl. Phys. Lett. **85** (2004) 4121–4123.