Journal of Ceramic Processing Research. Vol. 15, No. 1, pp. 26~29 (2014)

J O U R N A L O F
Ceramic Processing Research

Effect of sintering temperatures on electrical properties of $0.95(Na_{0.5}K_{0.5})NbO_3$-$0.05(Ba_{0.5}Sr_{0.5})(Ti_{0.95}Sn_{0.05})O_3$ lead-free ceramics

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In this study, we fabricated the $0.95(Na_{0.5}K_{0.5})NbO_3$-$0.05(Ba_{0.5}Sr_{0.5})(Ti_{0.95}Sn_{0.05})O_3$(here after NKN-BSTS) lead free ceramics by conventional solid state reaction method. The effects of sintering temperatures on electrical properties were investigated in detail. The NKN-BSTS ceramics sintered at 1080 °C ~ 1120 °C. The poling temperature and electric field cause superior piezoelectric properties of NKN-BSTS ceramics and the piezoelectric properties were shown the highest value at optimum sintering temperature. The NKN-BSTS ceramics sintered at 1100 °C show an optimal performance with dielectric constant was 4485, electromechanical coupling constant was 0.37 and the piezoelectric constant was 213 ρC/N. Therefore, it is believed that the NKN-BSTS ceramics is a candidate material with good prospect to make lead-free piezoelectric ceramics.

Key words: NKN-BSTS, Lead-free, Poling, Piezoelectric constant, Sintering temperature.

Introduction

The lead-based ceramics has been used to various ferroelectric and piezoelectric devices for example actuators, sensors and transducers etc. due to their superior piezoelectric properties than lead-free ceramics. However, the PbO affects human health and environmental issue owing to toxicity of PbO during their preparation. Therefore it is essential to find lead-free ceramics which have compatible electrical properties with lead-based ceramics. $(Na_{0.5}K_{0.5})NbO_3$ (NKN) ceramics has been known to alternative materials for lead-free ceramics because NKN have excellent piezoelectric properties, ferroelectric properties (d_{33} ~ 100 ρC/N, k_p ~ 0.34, Q_m ~ 130) and high Curie temperature (T_c) ~ 420 °C. However, pure NKN ceramics were volatilized during ordinary sintering process. It causes inferior piezoelectric and ferroelectric properties due to its porous structural properties. Therefore hot pressing, spark plasma sintering, cold-isotataic pressing have been used to suppress volatilization [1, 2]. Recently, various $BaTiO_3$(BT)-based ceramics such as $(Ba,Ca)TiO_3$ (BCT), $Ba(Zr,Ti)O_3$(BZT), $(Ba,Sr)TiO_3$(BST) etc. were studied. Among them, BST consists of $BaTiO_3$ and $SrTiO_3$. $BaTiO_3$ is a ferroelectric material which has high piezoelectric and ferroelectric properties. $SrTiO_3$ is a paraelectric material which has low dielectric loss. Also attempts to obtain improved piezoelectric properties BT-based ceramics by codoping Sn and Ca ions have been performed so far [2, 3]. This study mains focsed on the effects of sintering temperatureson the microstructure, pie-zoelectric, dielectric, fer-roelectric properties of $0.95(Na_{0.5}K_{0.5})NbO_3$-0.05 $(Ba_{0.5}Sr_{0.5})$ $(Ti_{0.95}Sn_{0.05})O_3$ lead free ceramics. Through optimizing the sintering temperatures, the NKN-BSTS ceramics showed the maximum electrical properties such as dielectric constant was 4642, electromechanical coupling constant was 0.37 and piezoelectric constant was 213 ρC/N. These results suggest that NKN-BSTS ceramics were possible to be promising alternative lead-free piezoelectric materials.

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Experimental

Solid solutions of $0.95(Na_{0.5}K_{0.5})NbO_3$-$0.05(Ba_{0.5}Sr_{0.5})(Ti_{0.95}Sn_{0.05})O_3$(NKN-BSTS) ceramics were prepared using the conventional mixed oxide process. The starting materials used in this study were Na_2CO_3, K_2CO_3, Nb_2O_5, $BaCO_3$, $SrCO_3$ and TiO_2 SnO_2 of 99.9% purity. They were ball-milled in alcohol with zirconia balls for 24 h and dried at 100 °C for 12 h and then calcined at 900 °C for 3 h in air. After calcination, the calcined powders were pressed into disk samples with a diameter of 12.8 φ. The disk samples were sintered from 1080 °C to 1120 °C for 2 h in air. After the sintered samples were polished to a thickness of 1.0 mm, Ag electrodes were fired on their top and bottom surfaces. The crystalline structure and microstructure of NKN-BSTS ceramics were observed X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. The dielectric constant was measured as a function of temperature using an LCR meter (HP 4284). A conventional sawyer-tower circuit was used to measure the polarization hysteresis (P-E) loop. The specimens were immersed in silicon oil and poled at 4 kV/mm for 20 min. and piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (Channel Product DT-3300). The electromechanical coupling factor k_p was calculated by the resonance method according to IEEE standards using an impedance analyzer (4294A, Agilent).

Result and Discussion

Figure 1 shows the XRD patterns of NKN-BSTS ceramics sintered at various sintering temperature from 1080 °C to 1120 °C. All samples exhibited 002, 200 peaks which indicate that crystal structure of NKN-BSTS ceramics show orthorhombic structure. The shape of XRD peaks was shown sharp. It is inferred that all samples have homogeneity and crystallization. The XRD peaks of NKN-BSTS ceramics shift slightly to a lower angle according to lowering sintering temperatures. This phenomenon was caused by Ba^{2+} and Sr^{2+} (ion radius of 1.35Å and 1.13 Å, respectively) substitutes to Na^+ and K^+ (0.95 Å and 1.33 Å, respectively) according to Bragg's law, $n\lambda = 2d\sin\theta$. The peaks of NKN-BSTS ceramics increase when sintering temperatures below 1100 °C. However, sintering temperatures reached 1110 °C, peak intensity declined reversely. We can infer that NKN-BSTS ceramics show optimal piezoelectric properties and dielectric properties of sintered at 1100 °C. The Microstructure of NKN-BSTS ceramics sintered at various sintering temperatures was shown in Figure 2. The grain size of NKN-BSTS ceramics was grew with increasing sintering temperatures. The average grain size of NKN-BSTS ceramics sintered at 1080 °C and 1120 °C were observed approximately 1.0 μm and 4.0 μm, respectively. The NKN-BSTS ceramics sintered at 1080 °C shows small grain size with pores. It is indicated that sintering temperature of 1080 °C is too low to sinter. As increasing sintering temperature, dense structure with grown grain was shown in NKN-BSTS ceramics. This microstructure

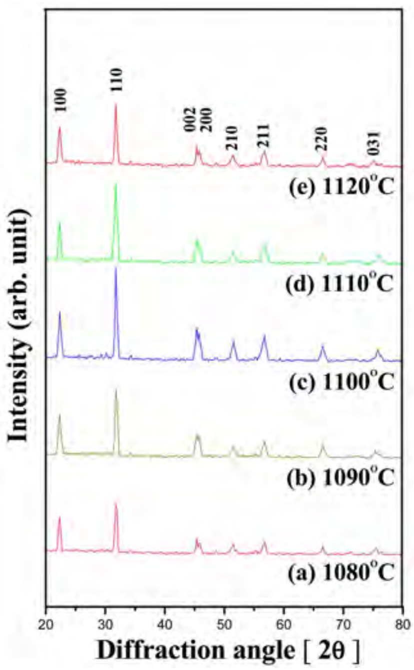


Fig. 1. XRD patterns of the NKN-BSTS ceramics with sintering temperature (a) 1080 °C, (b) 1090 °C, (c) 1100 °C, (d) 1110 °C, (e) 1120 °C.

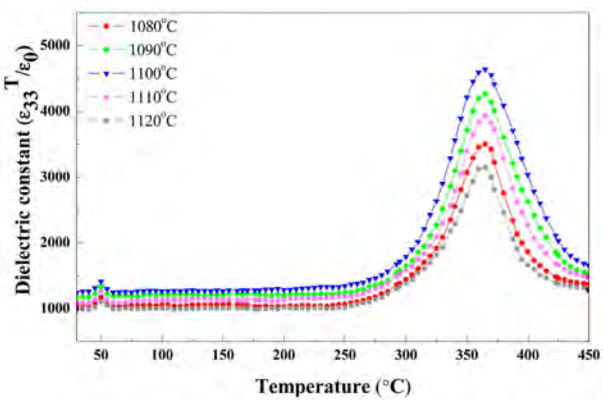
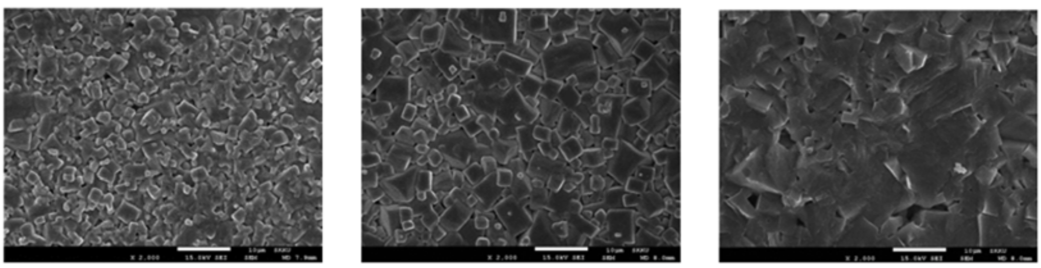


Fig. 3. Dielectric constant of the NKN-BSTS ceramics with sintering temperature (a) 1080 °C, (b) 1090 °C, (c) 1100 °C, (d) 1110 °C, (e) 1120 °C.



(a) 1080°C (b) 1100°C (c) 1120°C

Fig. 2. The SEM images of the NKN- BSTS ceramics with sintering temperature (a) 1080 °C, (b) 1100 °C, (c) 1120 °C.

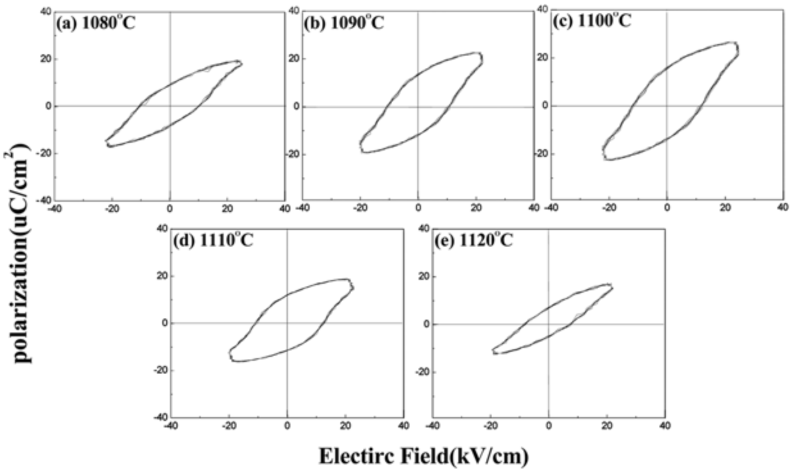


Fig. 4. Hysteresis loops of the NKN-BSTS with sintering temperature (a) 1080 °C, (b) 1090 °C, (c) 1100 °C, (d) 1110 °C, (e) 1120 °C.

resulted in partially presence of a liquid phase. However, further increasing sintering temperatures induce abnormally growth of grain. This result indicated that piezoelectric and dielectric properties of NKN-BSTS ceramics decline. Figure 3 shows the temperature-dependent dielectric constants of NKN-BSTS ceramics sintered at 1080 °C ~ 1120 °C. As increasing sintering tem-perature, T_c of NKN-BSTS ceramics shift far lower temperature. The T_c and dielectric constant of NKN-BSTS ceramics sintered at 1100 °C are 365 °C, 4642 respectively. Also, NKN-BSTS ceramics show phase transition temperature (from orthorhombic to tetragonal (T_{O-T})) near 50 °C. Figure 4 shows the hysteresis loops of NKN-BSTS ceramics sintered from 1080 °C to 1120 °C. The values of remnant polarization (P_r) are increased as increasing sintering temperature. When the sintering temperature was increased up to 1100 °C, P_r shows the highest value of 26.5 μC/cm^2 due to the increase of the bulk density within original structure of NKN-BSTS ceramics. The results reveal that bulk density affects not only piezoelectric properties but also ferroelectric properties. However, NKN-BSTS ceramics sintered above 1100 °C, remnant polarization (P_r) value decreased rapidly. These values resulted in deformation of original structure of NKN-BSTS ceramics despite increase of bulk density. In order words, NKN-BSTS ceramics lost their well-crystallized structure. Figure 5 shows the piezoelectric constants (d_{33}) and electromechanical coupling factor (k_p) of NKN-BSTS ceramics sintered from 1080 °C to 1120 °C. These piezoelectric properties of NKN-BSTS ceramics were increased with increasing sintering tem-perature. The NKN-BSTS ceramics sintered at 1100 °C shows the highest electromechanical coupling factor and piezoelectric constants of 0.37, 213 ρC/N, re-spectively. However, increasing sintering temperature above 1110 °C decreased piezoelectric properties like other dielectric and ferroelectric properties. These similar results mean that electrical

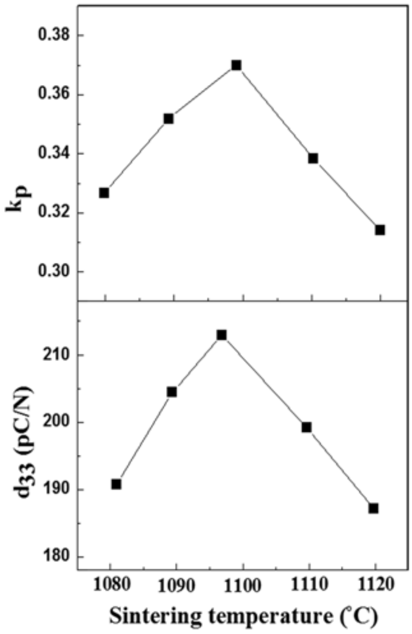


Fig. 5. Electrical properties of the NKN-BSTS with sintering temperature.

properties of NKN-BSTS ceramics were affected by bulk density.

Conclusions

The lead-free $0.95(Na_{0.5}K_{0.5})NbO_3$-$0.05(Ba_{0.5}Sr_{0.5})(Ti_{0.95}Sn_{0.05})O_3$ ceramics is prepared by using a conventional mixed-oxide method. In order to investigate properties of NKN-BSTS ceramics, the range of sintering temperature is from 1080 °C to 1120 °C. Especially, the highest piezoelectric and dielectric properties showed at 1100 °C. For XRD analysis, all samples exhibited perovskite structure. The NKN-BSTS ceramics sintered at 1100 °C exhibited dielectric constant = 4485, electromechanical coupling factor = 0.37, piezoelectric constant = 213 ρC/N, remnant polarization = 26.5 μC/cm^2.

These excellent piezoelectric, dielectric properties mean that NKN-BSTS ceramics might be one of the promising lead free piezoelectric materials.

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