

## Electrical properties of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-BiTiO}_3$ ceramics with the variation of sintering temperature

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Piezoelectric  $0.93(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}0.07\text{BiTiO}_3$  (NKN-BTO) ceramics were fabricated by the mixed-oxide method and their structural and dielectric properties was investigated with the variation of sintering temperature. All specimens were crystallized in the perovskite single phase without any formation of a second phase such as pyrochlore. The average grain size of the NKN-BTO specimen sintered at  $1130^\circ\text{C}$  is  $0.32\text{ }\mu\text{m}$ . The specimen sintered at  $1100^\circ\text{C}$  showed the highest relative density of 98%. Electromechanical coupling factor, relative dielectric constant and dielectric loss of the NKN-BTO specimens sintered at  $1110^\circ\text{C}$  were 0.31, 1222 and 0.02, respectively. Curie temperature of the specimen sintered at  $1110^\circ\text{C}$  was  $445^\circ\text{C}$ .

**Key words:** NKN, BTO, Piezoelectric, Dielectric constant.

### Introduction

Lead-based ferroelectric materials such as  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT),  $\text{Pb}(\text{Mg,Nb})\text{O}_3\text{-PbTiO}_3\text{-PbZrO}_3$  are the most widely used materials for the electronic devices such as actuators, sensors and transducers, because of their excellent piezoelectric properties [1, 2]. Especially, lead-based piezoelectric materials are widely used due to their excellent piezoelectric properties near the morphotropic phase boundary (MPB), showing a good temperature stability of electrical properties. However, lead-based piezoelectric materials fatally contain large quantities of the toxic element, alternative lead-free piezoelectric materials have attracted much attention for environmental issues recently.

Among the several lead-free ferroelectric materials,  $(\text{Na,K})\text{NbO}_3$  (NKN)-based ferroelectric material is a promising candidate material because it has a high Curie temperature and good piezoelectric properties [3, 4]. NKN composition is a solid solution of ferroelectric  $\text{KNbO}_3$  and antiferroelectric  $\text{NaNbO}_3$  [5]. Recently, ferroelectric  $\text{NaNbO}_3\text{-BaTiO}_3$  (NN-BT) solid solution has been investigated as a candidate material, and has shown good ferroelectric and piezoelectric properties [6]. In general, for the preparation or fabrication of alkali niobate ceramics, it is difficult to control the chemical composition because the volatilization of the alkali metal element easily occurs during heat treatment at sintering temperature. Therefore, alkali niobate-base ceramics have a serious problem of their low electrical resistivity or high leakage current

characteristic. In order to solve these problems, alkali niobate ceramics have been fabricated by the dopant addition or various sintering methods such as hot-pressing, spark plasma sintering, and hydrothermal synthesis. To realize lead-free piezoelectric NKN-base ceramics, the  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  specimens doped with 0.07 mol%  $\text{BiTiO}_3$  [ $(\text{Na}_{0.465}\text{K}_{0.465}\text{Bi}_{0.07})(\text{Nb}_{0.93}\text{Ti}_{0.07})\text{O}_3$ ] were prepared for the basic composition [7] and their structural and electrical properties were investigated with the variation of sintering temperature.

### Experimental

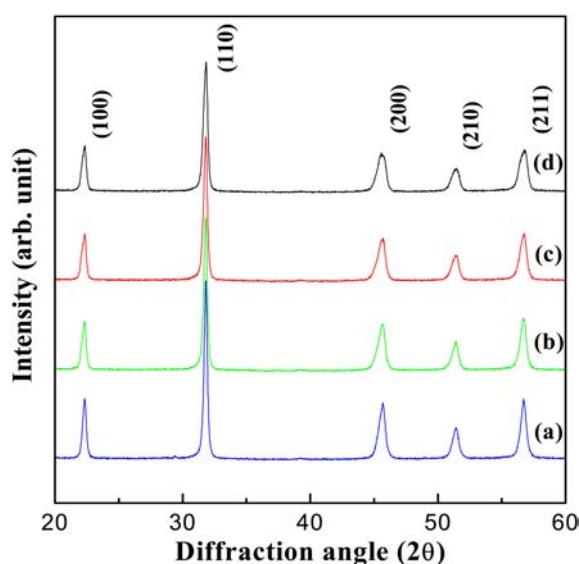
$0.93(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}0.07\text{BiTiO}_3$  ceramics were fabricated the conventional mixed-oxide method. Reagent-grade  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  were weighed in accordance with the formula, and mixed together with zirconia media and ethanol by ball milling for 24 hrs, followed by drying. After drying, the mixture was calcined at  $950^\circ\text{C}$  for 2 hrs. The calcined powders were crushed well with alumina mortar, and the powder granulated with polyvinyl alcohol. Finally, the granulated powder was pressed into the pellet shape with  $1000\text{ kg/cm}^2$  pressure and then cold isostatic press (CIP) process was performed with 30 MPa. The specimens were sintered in air at a temperature range of  $1070\sim1130^\circ\text{C}$  with heating rate of  $2^\circ\text{C/min}$ . Ag paste was put into the both side of the specimens as electrodes and all specimens were electrical poled in silicon oil at  $120^\circ\text{C}$  under a dc field of  $4\text{ kV/mm}$  for 30 minutes. According to the variation of sintering temperature, structural properties were investigated by field emission scanning electron microscopy (FE-SEM) and X-ray diffractometer (XRD). The dielectric properties were measured using LCR meter (HP 4284) and impedance analyzer (HP 4192A).

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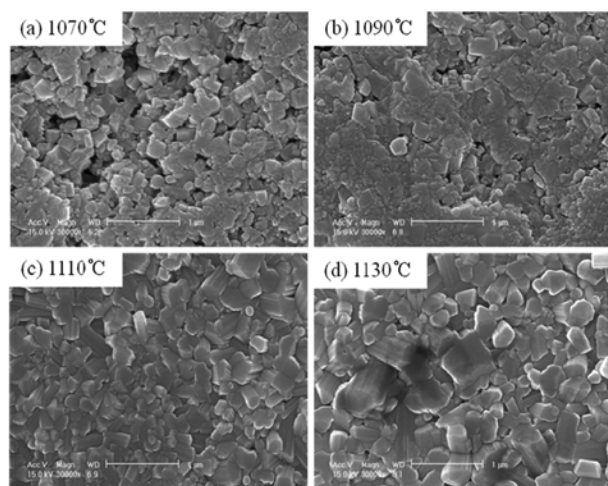
## Results and discussion

Fig. 1 shows the XRD patterns of NKN-BTO specimens with the variation of sintering temperature. There was not any dependence on sintering temperature observed and the diffraction pattern was similar to that of randomly oriented pseudo cubic perovskite dielectrics. All specimens were crystallized in the perovskite single phase without any formation of a second phase such as pyrochlore.

Fig. 2 shows the surface micrographs of NKN-BTO specimens with the variation of the sintering temperatures. Average grain size increased and ceramic texture is denser with increasing the sintering temperature. The average grain size of the NKN-BTO specimen sintered at 1130 °C is 0.32  $\mu\text{m}$ . The XRD and SEM results



**Fig. 1.** XRD patterns of NKN-BTO specimens with as a function of sintering temperature: (a) 1070 °C, (b) 1090 °C, (c) 1110 °C, and (d) 1130 °C.

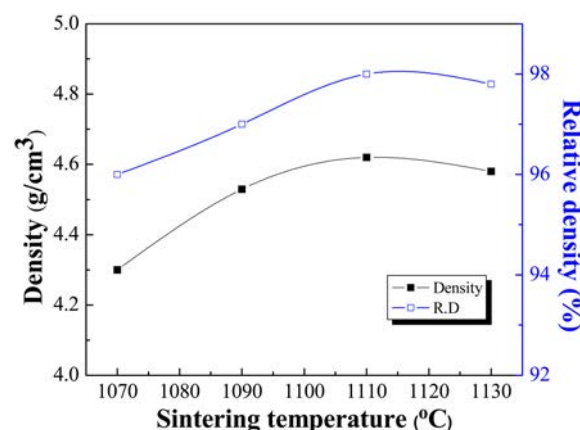


**Fig. 2.** SEM micrographs of NKN-BTO specimens with the variation of the sintering temperature.

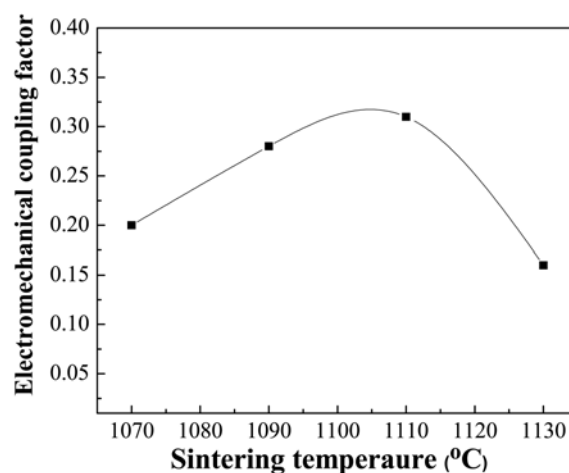
indicated that the KNK-BTO specimens sintered at 1110 °C and 1130 °C exhibited well crystallized phase.

Fig. 3 shows the sintering temperature dependence of the sintered density and the relative density of NKN-BTO specimens. The sintered density of the specimens increased with increasing the sintering temperature up to 1110 °C and then decreased. This result indicates that specimens which were sintered at 1130 °C or more, showed the grain growth with the rod shape, and the sintered density was decreased due to the formation of pores. As shown in Fig. 2(d), the NKN-BT specimen sintered at 1130 °C showed the highest surface roughness. The specimen sintered at 1100 °C showed the highest relative density of 98%.

Fig. 4 shows the electromechanical coupling factor of NKN-BT specimens with the variation of the sintering temperature. Electromechanical coupling factor of NKN-BT specimens increased with increasing the sintering temperature up to 1110 °C and then decreased, and the value of the specimen sintered at 1110 °C was 0.31. In general, the piezoelectric properties of NKN-



**Fig. 3.** Sintered density and relative density of the NKN-BTO specimens with the variation of the sintering temperature.



**Fig. 4.** Electromechanical coupling factor of the NKN-BTO specimens as a function of the sintering temperature.

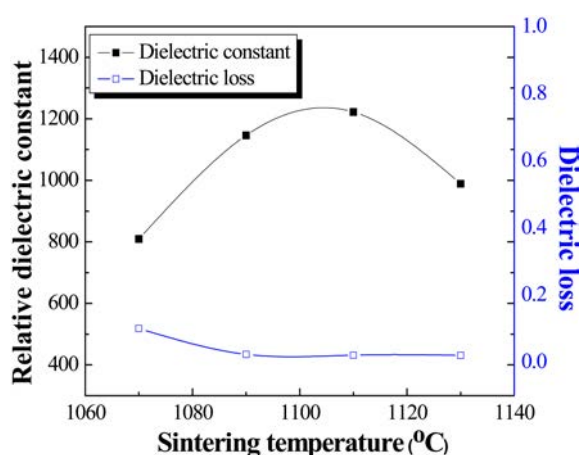


Fig. 5. Relative dielectric constant and dielectric loss of the NKN-BTO specimens as a function of the sintering temperature.

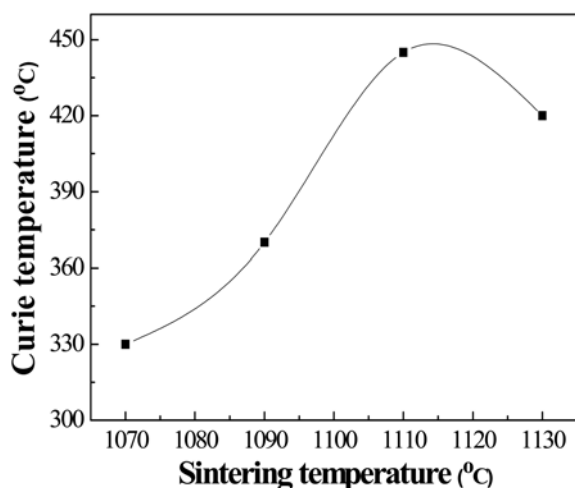


Fig. 6. Curie temperature of the NKN-BTO specimens as a function of the sintering temperature.

based specimens increased with an increase the average grain size. However, in this work, the NKN-BT specimen sintered at 1110 °C with smaller grain size showed the largest electromechanical coupling factor. It is suggested that the electrical properties of the piezoelectric ceramics is affected by the sintered density or densification rather than the grain size.

Fig. 5 shows the relative dielectric constant and dielectric loss of NKN-BT specimens with variation of the sintering temperature. Relative dielectric constant increased with increasing the sintering temperature up to 1110 °C and dielectric loss slightly decreased with increasing the sintering temperature. As shown in Figs. 2 and 3, the specimen sintered at 1100 °C with the most favorable structural characteristics showed the highest dielectric constant value. Relative dielectric

constant and dielectric loss of the specimen sintered at 1100 °C were 1222 and 0.02, respectively.

Fig. 6 shows Curie temperature of NKN-BT specimens with variation of sintering temperature. Curie temperature increased with increasing the sintering temperature up to 1110 °C and the value of the specimen sintered at 1110 °C was 445 °C. NKN specimens doped with  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ( $T_c = 675$  °C [8]) showed the high Curie temperature property. In general, the Curie temperature is heavily influenced by the porosity or second phase which form a depolarizing field in the specimen. Therefore, the specimen, having a lot of pores, showed low Curie temperature characteristics.

## Conclusions

The  $0.93(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}0.07\text{BiTiO}_3$  (NKN-BTO) ceramics were prepared using the mixed-oxide method and their structural and dielectric properties was investigated with the variation of the sintering temperature. The NKN-BTO specimens exhibit the high sintered density and electrical properties compared with the single NKN specimens [7]. It is considered that the volatilization of Na and K ions is suppressed because the sintering temperature decreased due to the addition of Bi ion with low melting point. All specimens were crystallized in the perovskite single phase without any formation of a second phase such as pyrochlore. Average grain size is increased and ceramic texture is denser with increasing the sintering temperature. Sintered density, dielectric constant and electromechanical coupling factor properties of the NKN-BTO specimens increased with increasing the sintering temperature up to 1110 °C and then decreased.

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