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Electrical properties of $(Na_{0.5}K_{0.5})NbO_3$-$(Sr_{0.5}Ca_{0.5})TiO_3$ ceramics with the variation of sintering temperature

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Piezoelectric $0.94(Na_{0.5}K_{0.5})NbO_3$-$0.06(Sr_{0.5}Ca_{0.5})TiO_3$ ceramics were fabricated by the mixed-oxide method and the structural and dielectric properties was investigated with the variation of the sintering temperature. All specimens were crystallized in the perovskite single phase without any formation of a second phase such as pyrochlore. The specimen sintered at 1200 °C showed the highest relative density of 98%. Electromechanical coupling factor, relative dielectric constant and dielectric loss of NKN-SCT specimens sintered at 1200 °C were 0.25, 2028 and 0.03, respectively. Curie temperature increased with increasing the sintering temperature, and the value of the specimen sintered at 1200 °C was 345 °C.

Key words: NKN, SCT, Piezoelectric, Dielectric constant.

Introduction

Lead-based piezoelectric materials such as Pb $(Zr,Ti)O_3$ (PZT), $Pb(Mg,Nb)O_3$-$PbTiO_3$-$PbZrO_3$ are the most widely used materials for 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 electrical 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 (Pb), alternative lead-free piezoelectric materials have attracted much attention for environmental issues recently.

Among the several lead-free ferroelectric materials, $(Na,K)NbO_3$ (NKN) - based piezoelectric material is a promising candidate material because it has a high Curie temperature and good electrical properties [3, 4]. NKN composition is a solid solution of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$ [5]. Recently, ferroelectric $NaNbO_3$-$BaTiO_3$ (NN-BT) solid solution has been investigated as a candidate material, and has shown good ferroelectric and piezoelectric properties [6]. In generally, 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. However, the above methods are not suitable for mass production. Recently, much attention has been paid to $(Na,K)NbO_3$ (NKN) with a perovskite structure due to their excellent ferroelectric properties using the conventional sintering method [7]. To realize lead-free piezoelectric NKN-base ceramics, in this study, $(Na_{0.5}K_{0.5})NbO_3$ specimens doped with 0.06 mol% $(Sr_{0.5}Ca_{0.5})TiO_3$ [0.94NKN-0.06SCT], from the previous experiments, were chosen for the basic composition. And, we investigated the structural and electrical properties with variation of sintering temperature.

Experimental

$0.94(Na_{0.5}K_{0.5})NbO_3$-$0.06(Sr_{0.5}Ca_{0.5})TiO_3$ ceramics were fabricated the conventional mixed-oxide method. Reagent-grade Na_2CO_3, K_2CO_3, Nb_2O_5,$SrCO_3$, $CaCO_3$ and 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 850 for 2 hrs. The calcined powder was crushed well with alumina mortar, and the powder granulated with polyvinyl alcohol. Finally, the granulated powder was pressed into pellet shape with 1000 kg/cm^2 pressure and then cold isostatic press (CIP) process was performed with 30 MPa. Generally, CIP can be applied pressure uniformly to all parts. So we obtained the specimens with uniform density. The specimens were sintered in air at a temperature range of 1150 ~ 1225 °C with heating rate of 5 °C/min. Ag paste was put into the both side of the specimens as electrodes and all

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specimens were electrical poled in silicon oil at 120 °C under a dc field of 3 kV/mm for 30 min. 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).

Results and Discussion

Fig. 1 shows the XRD patterns of 0.94NKN-0.06SCT specimens with variation of sintering temperature, and the dependence on sintering temperature was not observed. The diffraction pattern was similar to that of randomly oriented pseudo- cubic perovskite dielectric, 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 0.94NKN-0.06SCT specimens with variation of the sintering temperatures. Ceramic texture is denser with an increase the sintering temperature up to 1200 °C and then decreased. Thus, the 0.94NKN-0.06SCT specimens sintered at 1200 °C exhibited well crystallized phase based on XRD and SEM measurements. The average grain size of the NKN-BTO specimen sintered at 1200 °C is 0.40 μm.

Fig. 3 shows the sintered density and the relative density of 0.94NKN-0.06SCT specimens with variation of the sintering temperature. The sintered density of the specimens increased with increasing the sintering temperature up to 1200 °C and then decreased. As shown in Fig. 2, the specimen sintered at 1225 °C show the low sintered density due to the formation of pores and nevertheless had the largest average grain size. As shown in Fig. 2(d), the NKN-SCT specimen sintered at 1225 °C showed the many surface pores. The specimen sintered at 1200 °C showed the highest relative density of 98%. Fig. 4 shows the electromechanical coupling factor of 0.94NKN-0.06SCT specimens with variation of the sintering temperature. Electromechanical coupling factor of 0.94NKN-0.06SCT specimens increased with increasing the sintering temperature up to 1200 °C and

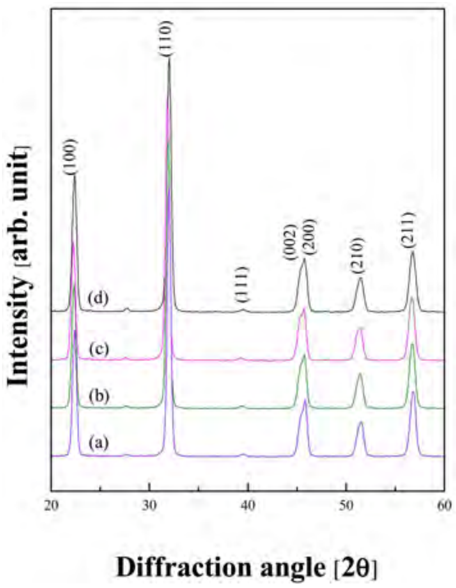

Fig. 1. XRD patterns of 0.94NKN-0.06SCT specimens with as a function of sintering temperature; (a) 1150 °C, (b) 1175 °C, (c) 1200 °C and (d) 1225 °C.

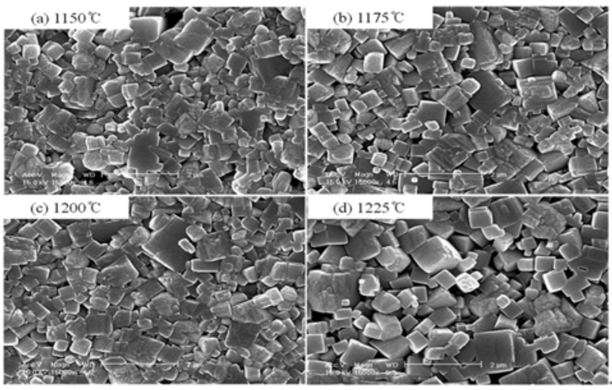

Fig. 2. Surface SEM micrographs of 0.94NKN-0.06SCT specimens with the variation of the sintering temperature.

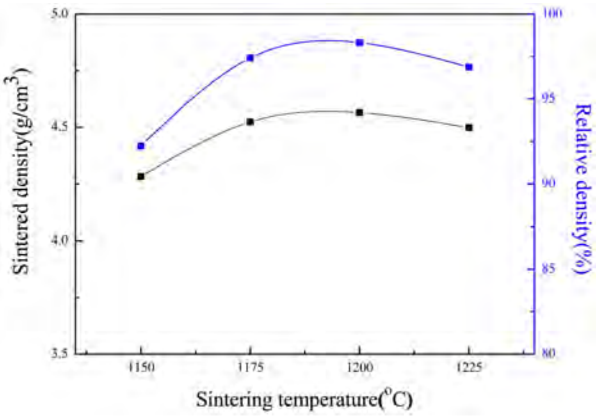

Fig. 3. Sintered density and relative density of 0.94NKN-0.06SCT specimens with the variation of the sintering temperature.

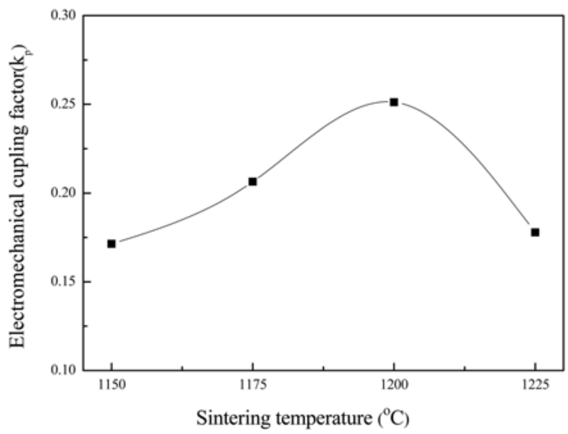

Fig. 4. Electromechanical coupling factor of 0.94NKN-0.06SCT specimens as a function of the sintering temperature.

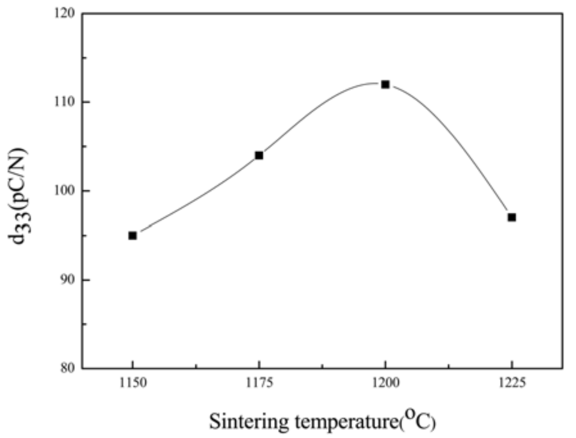

Fig. 5. Piezoelectric properties of 0.94NKN-0.06SCT specimens as a function of the sintering temperature.

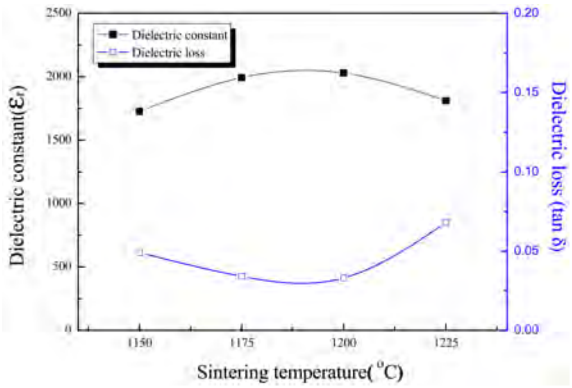

Fig. 6. Relative dielectric constant and dielectric loss of 0.94NKN-0.06SCT specimens as a function of the sintering temperature.

then decreased, and the value of the specimen sintered at 1200 °C was 0.25. In general, the piezoelectric properties of NKN-based specimens increased with an increase the average grain size. However, in this study, 0.94NKN-0.06SCT specimen sintered at 1200 °C with similar 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 piezoelectric properties of 0.94NKN-0.06SCT specimens with variation of the sintering temperature. The piezoelectric properties of d_{33} increased with increasing the sintering temperature up to 1200 °C and then decreased, and the value of the specimen sintered at 1200 °C was 112pC/N. It is suggested that as shown in Figs. 2 and 3, the specimen sintered at 1200 °C showed the highest sintered density. Fig. 6 shows the relative dielectric constant and dielectric loss of 0.94NKN-0.06SCT specimens with variation of the sintering temperature. Relative dielectric constant increased with increasing the sintering temperature up to 1200 °C and dielectric loss

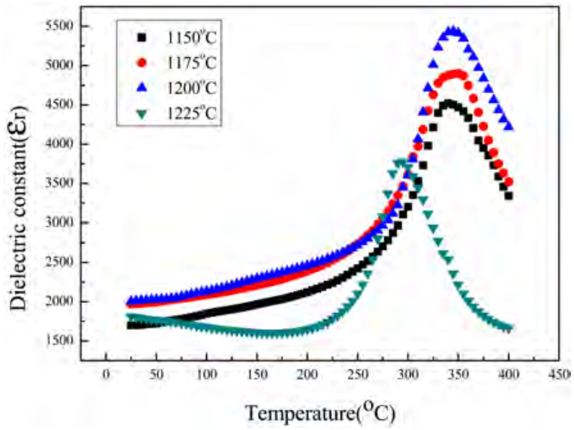

Fig. 7. Curie temperature of 0.94NKN-0.06SCT specimens as a function of the sintering temperature.

slightly decreased with increasing the sintering temperature. As shown in Figs. 2 and 3, the specimen sintered at 1200 °C with the most favorable structural characteristics showed the highest dielectric constant value. Generally, the relative dielectric constant increased with increasing the grain size. However, in the specimen sintered at 1225 °C , the relative dielectric constant decreased and dielectric loss increased for the increasing pores with low dielectric constant. Relative dielectric constant and dielectric loss of the specimen sintered at 1200 °C were 1222 and 0.02, respectively.

Fig. 7 shows Curie temperature of 0.94NKN-0.06SCT specimens with variation of sintering temperature. Curie temperature of the specimen sintered at 1200 °C was 345 °C. In generally, the Curie temperature is heavily influenced by the porosity or second phase which form a depolarizing field in the specimen. Therefore, the specimen sintered at 1225 °C, having a lot of pores, showed low Curie temperature characteristics.

Conclusions

In this work, we fabricated $0.94(Na_{0.5}K_{0.5})NbO_3$-$0.06(Sr_{0.5}Ca_{0.5})TiO_3$ ceramics using the mixed-oxide method, and the structural and dielectric properties was investigated with variation of the sintering temperature. 0.94NKN-0.06SCT specimens exhibit the high sintered density and electrical properties compared with the single NKN specimens. We consider 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. Sintered density, dielectric constant and electromechanical coupling factor properties of 0.94NKN-0.06SCT specimens increased with increasing the sintering temperature up to 1200 °C and then decreased.

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