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Piezoelectric and Dielectric Properties of $(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ Ceramics with Sintering Temperature

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Lead-free $(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ (NKN-LST) ceramics were fabricated by the conventional mixed oxide method at various sintering temperatures. The results indicate that the sintering temperature significantly influences the sinterbility, microstructure, phase transition, and electrical properties of the NKN-LST ceramics. For the NKN-LST ceramics sintered at 1060°C to 1100°C, the bulk density increased with increasing sintering temperature and showed a maximum value at a sintering temperature of 1080°C. The Curie temperature of the NKN-LST ceramics slightly decreased with increasing sintering temperature. The dielectric constant, piezoelectric constant, and electromechanical coupling factor increased with increasing sintering temperature, which might be due to the increase in density. However, a high d_{33} of 175 ρC/N, k_p of 39.3%, and ε of 4614 were obtained for the NKN-LST ceramics sintered at 1080°C for 4 h.

Keywords: piezoelectric properties, dielectric properties, lead-free, sintering temperature

1. INTRODUCTION

Lead-based piezoelectric materials, represented by $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), and PZT-based materials are presently the most widely used materials in transducers, sensors, and actuators, as well as microelectronic devices, because of their superior electrical properties close to the morphotropic phase boundary (MPB). However, the use of lead-based materials causes serious environmental problems, because of the high toxicity of lead oxide.[1-3] Extensive research has accordingly been conducted into lead-free piezoelectric materials with piezoelectric properties comparable to those of PZT ceramics. Generally, two types of lead-free ceramic materials have been extensively investigated: $(Bi_{0.5}Na_{0.5})TiO3$ (BNT) based and $(Na_{0.5}K_{0.5})NbO_3$ (NKN) based materials. BNT-based ceramics have a perovskite structure with a rhombohedral symmetry at room temperature.[4-6] They are considered to be a promising candidate material, because BNT shows a fairly satisfactory remanent polarization ($P_r = 38.0\ \mu C/cm^2$). However, the high coercive field ($E_c = 7.30$ kV/mm) of pure BNT makes the poling of the ceramic difficult and, as a result, BNT usually has relatively poor piezoelectric properties ($d_{33} = 58$ ρC/N). By comparison, NKN-based ceramics have superior piezoelectric properties ($d_{33} =$ 80-110 ρC/N, $k_p =$ 36-40%) and a high Curie temperature (T_c) of 420°C. However, difficulties in the sintering process of pure NKN ceramics have led to deterioration of their otherwise excellent properties, for example, relatively low electrical properties ($d_{33} = 70$ ρC/N, $k_p = 25\%$).[7-9]

In efforts improve the densification and piezoelectric properties of NKN-based ceramics, a number of studies have been performed to improve their sinterbility and electrical properties; these include the formation of solid solutions of NKN ceramics with other ABO_3 perovskite structures, such as NKN-$BaTiO_3$, NKN-$LiNbO_3$, NKN-$Bi_{0.5}Na_{0.5}TiO_3$, NKN-Bi_2O_3, etc..[10-12] These NKN-based ceramics exhibit enhanced piezoelectric properties owing to the formation of an MPB. It is well known that the piezoelectric and dielectric properties show a maximum around the MPB. Alternatively, to obtain piezoelectric ceramics with high density, hot pressing, cold-isostatic pressing, and spark plasma sintering have been used. However, these techniques are not easily used in many fields due to their high cost. Therefore, it is necessary to develop advanced ceramics with different compositions.[13]

This paper reports on experimental results for an NKN-LST ceramic, which deviates largely from the well-known essential compositional condition of a nearly equal molar ratio of K/Na and also is K-rich in contrast with previously investigated Na-rich compositions that show high piezoelectric properties.[14-16] The sintering temperature significantly influences the microstructure, density, and electrical properties of NKN-LST ceramics. The purpose of the present study is to clarify the effects of the sintering temperature on the structural and electrical properties of NKN-LST ceramics.

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2. EXPERIMENTAL PROCEDURE

The NKN-LST ceramics were prepared by the conventional mixed-oxide method using high-purity starting materials: Na_2CO_3, K_2CO_3, Nb_2O_5, Li_2CO_3, Sb_2O_3, and Ta_2O_5. These powders were separately dried in an oven at 100°C for 4 h. They were ball-milled for 24 h using ZrO_2 balls in alcohol. After being dried at 110°C for 24 h, the powders were calcined at 850°C for 3h. The calcined powders were pressed into a disk sample of 12 mm. The samples were sintered at 1060°C to 1100°C for 4h. After the samples were polished to a thickness of 1.0 mm, silver paste was screen-printed on their surfaces as electrodes and then fired at 400°C for 10 min. We used X-ray diffraction (XRD) to analyze the crystallinity and microstructures of the samples. Their dielectric properties were measured using an LCR meter (PM6306, Pluke) and the hysteresis loops of the samples were measured using a Sawyer-Tower circuit. The samples were poled under a DC field of 4 kV/mm for 20 min. The piezoelectric strain constant d_{33} was measured by a d_{33} meter (Channel Product DT-3300). The electromechanical coupling factor k_p was calculated by measuring the anti-resonance and resonance frequencies. The relative density of the sintered samples was measured by the Archimedes method.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of the NKN-LST ceramics sintered at various temperatures are shown in Fig. 1. All of the samples show a single perovskite structure and no evidence of any secondary phases was found. The sintering temperature of the NKN-LST ceramics influenced the phase formation and the XRD patterns were characterized by (002)/(200) peaks splitting at a 2θ angle of around 46.5°. It can be inferred that an orthorhombic-tetragonal morphotropic phase boundary exists in the NKN-LST ceramics synthesized at 1080°C. The NKN-LST ceramics sintered at 1070°C have orthorhombic symmetry, while those sintered at temperatures above 1090°C have tetragonal symmetry. The structural transitions from orthorhombic to tetragonal are similar to the MPB behavior generally found by changing the composition of ceramics. For the ceramics with the same composition but sintered at different temperatures, the differences in their XRD patterns indicate that the real compositions are different from the nominal compositions and depend on the sintering temperature. Such a compositional change can be attributed to volatilization of the alkali metal oxides during the sintering process. The diffraction peaks of the NKN-LST ceramics shift slightly to a lower angle with increasing sintering temperature below 1090°C, as calculated by the Bragg equation, 2dsinè = në. It can be inferred that both Na^+ (0.97Å) and K^+ (1.33Å) are volatilized in the sintering process, but that Na is more volatile than K. The greater volatilization of Na indicates that there is a relatively higher K content in the A-sites and, since the radius of Na is smaller than that of K, this leads to an increase in the crystal parameter. Figure 2 shows SEM images of the NKN-LST ceramics sintered at different temperatures. A porous microstructure with a small grain size was observed in the specimen sintered at 1060°C. The grain size is distinctly promoted at sintering temperatures ranging from 1060°C to 1100°C. The cavities are smaller in the NKN-LST ceramics sintered in this temperature range and those sintered at temperatures below 1080°C have a dense structure. However, further increase of the sintering temperature of the NKN-LST ceramics above 1090°C caused the microstructure of the NKN-LST ceramics to melt in homogeneously, in which case we could not distinguish the individual grains over a wide area. This is likely related to restriction of grain growth in the sintering process. These results verified that it is possible not only to artificially control the grain size of the NKN-

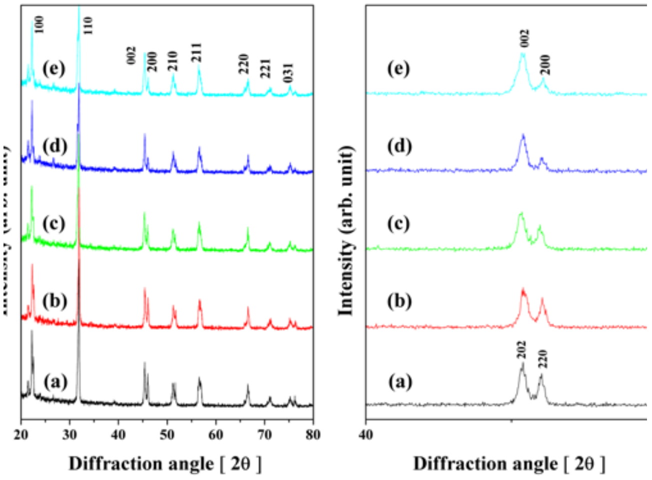

Fig. 1. XRD patterns of NKN-LST ceramics: (a) 1060°C (b) 1070°C (c) 1080°C (d) 1090°C (e) 1100°C.

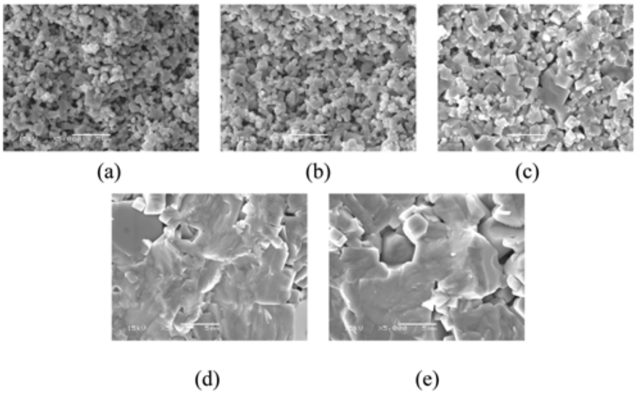
(a) (b) (c)
(d) (e)

Fig. 2. SEM images of NKN-LST ceramics: (a) 1060°C, (b) 1070°C, (c) 1080°C, (d) 1090°C, and (e) 1100°C.

LST ceramics, but also to regulate the electrical properties.

Figure 3 shows the temperature dependence of the dielectric constant and dielectric loss of the NKN-LST ceramics sintered at 1060°C to 1100°C, measured at 1 kHz. All of the samples show transitional peaks both from orthorhombic to tetragonal phase ($T_{O\text{-}T}$) and from tetragonal to cubic phase (T_c). The $T_{O\text{-}T}$ and T_c values for all of the samples are about 175°C and 450°C, respectively. One possible reason for this is the significantly increased K content. The continuously increasing trend of T_c is similar to that observed in the NKN system with increasing K content. The highest T_c is 470°C, which was obtained in the sample sintered at 1100°C. The dielectric constant shows a maximum value at the MPB, due to the transition from a ferroelectric to anti-ferroelectric state. The maximum dielectric constant and dielectric loss of the NKN-LST ceramics are 4614 and 0.42, respectively, when the sintering process was conducted at 1080°C.

The compositional dependence of the poled piezoelectric properties and the relative density were measured for the NKN-LST ceramics, as shown in Fig. 5. It is well known that the electrical properties of NKN-LST ceramics rapidly increase near the MPB, as in the case of PZT. For the NKN-LST ceramics, the electromechanical coupling factor k_p varied from 31% to 40% and the piezoelectric constant d_{33} was in a range of 142 ρC/N-175 ρC/N, which represents an improvement compared with the pure NKN ceramics. The poled NKN-LST ceramics sintered at 1080°C showed the highest values of the electromechanical coupling factor (k_p = 39.3%) and piezoelectric constant (d_{33} = 175 ρC/N). The improvement of the piezoelectric properties could be explained by the increase in the bulk density. However, at sintering temperatures above 1090°C, the piezoelectric properties decreased due to deformation of the NKN structure.

4. CONCLUSION

Lead-free NKN-LST piezoelectric ceramics sintered at different temperatures were prepared by the conventional mixed oxide method. These results indicate that the sintering temperature significantly influences the sintering, microstructure, and electrical properties of the NKN-LST ceramics. It is not only possible to artificially control the structural properties of the NKN-LST ceramics, but also to regulate their electrical properties. The NKN-LST ceramics sintered at 1080°C have a high dielectric constant of 4614, an electromechanical coupling factor k_p of 39.3%, and a piezoelectric constant d_{33} of 175 ρC/N. On the basis of these superior piezoelectric and dielectric properties, NKN-LST ceramics are promising lead-free piezoelectric materials.

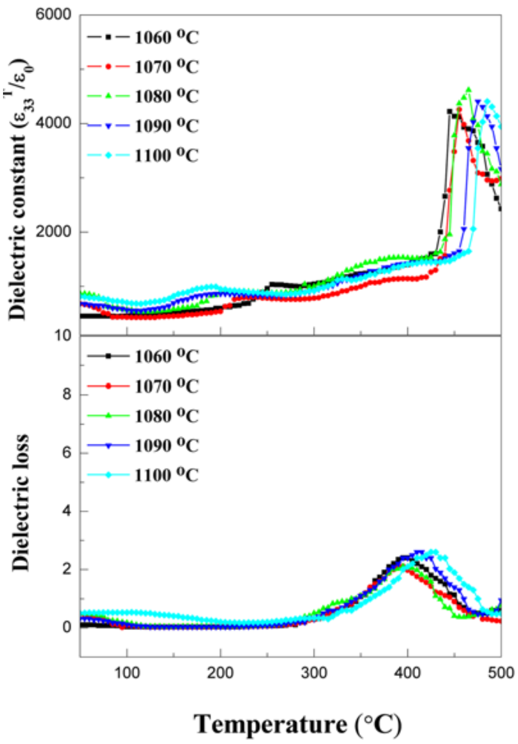

Fig. 3. Temperature-dependent dielectric properties of the NKN-LST ceramics.

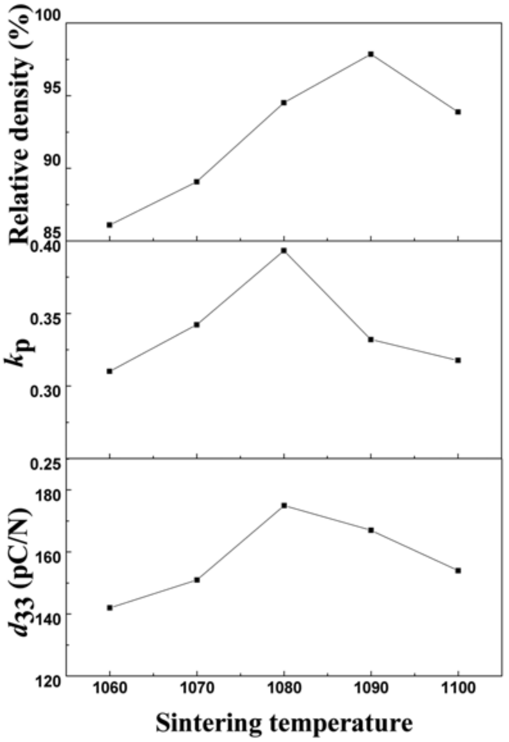

Fig. 4. Piezoelectric properties and relative density of NKN-LST ceramics.

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