Sintering Temperature Effect on Ferroelectric and Piezoelectric Properties of Lead-Free Piezoelectric (K$_{0.5}$Na$_{0.5}$)NbO$_3$ Ceramics

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Abstract. Lead-free potassium sodium niobate ceramic, with the nominal composition of K$_{0.5}$Na$_{0.5}$NbO$_3$, were synthesized by conventional solid state sintering, and its dielectric, ferroelectric, and piezoelectric properties were characterized as a function of sintering temperature. The orthorhombic to tetragonal phase transition (T$_{O-T}$) temperature of K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic sample was about 220°C, and its Curie temperature was about 420°C. The high bulk density was obtained for all compositions by solid state sintering in air. Bulk density was increased with temperature and it reached to 4.4 g/cm$^3$. The K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic sample sintered at 1100°C was optimized densification properties. In addition, the ferroelectric loop and dielectric characteristics dependence of different sintering temperature for K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic sample was obtained. Finally, we found that the piezoelectric constant (d$_{33}$) was 160 pC/N, high remanent polarization (Pr) was 33 μC/cm$^2$, and high electromechanical coupling coefficients (k$^p$) was about of 45%.

Introduction

Currently, piezoelectric materials were found to be the most promising candidates for electrical devices such as actuators, ultrasonic generators, accelerators, filters, piezoelectric transducers, and microwave applications. The PbTiO$_3$ system piezoelectric ceramics materials were widely used in piezoelectric devices because of their excellent piezoelectric properties, high Curie temperature (Tc), high dielectric constant, low dielectric loss, and low anisotropy [1-2]. However, the environmental friendly, non-toxic, and lead-free properties were the dominant material in piezoelectric device to date. Recent works have focused mainly on barium strontium titanate (BST) and barium zirconium titanate (BZT) application because of their interesting compromise in terms of tenability and dielectric loss [3-4]. Besides, the pervoskite type compound such as, potassium tantalite niobate K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) was well known for excellent dielectric permittivity and low loss tangent. It was a promising alternative candidate for tunable microwave devices. The KNN system material was first fabricated in the 1960s by Jaeger et al. [5-7]. They reported that the hot pressed KNN ceramics had high Curie temperature (Tc) of 420°C, large piezoelectric constant (d$_{33}$) of 160 pC/N, high remanent polarization (Pr) of 33μC/cm$^2$, and high electromechanical coupling coefficients (k$^p$) of 45%. Saito et al. also developed KNN-based textured ceramics with excellent properties comparable to those of modified PZT ceramics [8]. However, the phase stability of pure K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramics was limited to sintering temperature according to the phase diagram for KNbO$_3$–NaNbO$_3$ system [9].
The sodium and potassium elements were easily evaporated at high temperature. The stoichiometry of K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramics were slight change. The aim of this study was to investigate the influence on the different sintering temperature electrical and piezoelectric properties of K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) system. The effect of sintering temperature on the structure, phase transition, dielectric behavior, and ferroelectric properties were been studied.

**Experimental Detail**

In this study, K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramics samples were fabricated by conventional solid state sintering process. Reagent-grade oxide and carbonate powers of K$_2$CO$_3$ (>99.5%), Na$_2$CO$_3$ (>99.9%) and Nb$_2$O$_5$ (>99.99%) were used as starting raw materials. All of the starting materials were weighed according to the chemical formula and ball milled with a planetary mill in anhydrous ethanol for 12 h. After drying, the mixed powder was calcined in an alumina crucible at 865°C for 4 h, and pressed into disks of 10 mm in diameter and 1.2~1.5 mm in thickness using PVA as a binder. After burning off PVA, the pellets were sintered at 1060-1140°C for 3 h soaking period in air with different sintering temperature. The crystal structures were determined by X-ray diffraction analysis obtained using a Cu K$_\alpha$ radiation in the 2$\theta$ range of 20°-60°. The surface micro structure was observed using a scanning electron microscopy. The bulk densities of sintered ceramic sample were measured by Archimedes method. The dielectric constant and loss (tan$\delta$) of ceramic samples was obtained using an LCR analyzer at 1, 10, 100 kHz at room temperature.

**Result and Discussion**

Figure 1 hows the X-ray diffraction (XRD) patterns of the K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramics calcined at 865°C and sintering in different temperature. The (100), (110), (002), and (200) peaks were found in fig. 1 All the ceramic samples were single perovskite phase. The ceramic samples were orthorhombic symmetry (a=4.03 Å, b=4.11 Å, and c=4.07 Å) and no any secondary impurity were certified. The (100) peaks of K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples increased gradually as the sintering temperature increased. The stronger (100) peak of K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples for 1100°C sintering temperature was observed. All ceramic samples showed no deliquescence properties in fig. 1. The unstable secondary phase was K$_4$Nb$_6$O$_{17}$ resulted from highly volatile activity of K$_2$O during the sintering process [10-11]. Figure 2 shows the change in sintered density of the K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples as a function of sintering temperature. When the sintering temperature was increased to 1100°C, the bulk density of ceramic samples increased and reached to 4.3 g/cm$^3$. They were relative density of 96% (near 97.6% of the theoretical density of 4.51 g/cm$^3$). The bulk density of ceramic samples was decreased above sintering temperature of 1100°C, and they begin to drop. These results caused by many distinct pores existed in grain boundary. In addition, the bulk density of ceramic samples increases with increase of sintering temperature in the range between 1060 and 1100°C. In the following experimental results, the micro structure of K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples was found in the fig. 3. Figure 3 shows the surface morphology of the K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples with the different sintering temperature. All of K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples sinter different sintering temperature was orthorhombic structure. The sintering temperature significantly affected microstructure of pure K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramic samples were shown in fig. 1. The microstructure of ceramic samples sintered temperature of 1100°C was dense and fine. The average grain size was about 10 μm, and no fracture surface was found. The grain sizes of ceramic samples were increased while the sintering temperature increased to 1100°C. The phase stability of pure K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramics is limited to 1140°C according to the phase diagram for KNbO$_3$–NaNbO$_3$[9]. In addition, many distinct pores existed in grain boundary was also found while the sintering temperature of 1100°C. The high sintering temperature was not appropriate and the grains could not grow sufficiently because of the pure K$_{0.5}$Na$_{0.5}$NbO$_3$ ceramics was quadrat.
temperature dependence of dielectric constant of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples with different sintering temperature. The dielectric constant increased rapidly from 200°C and reached a peak at the temperature corresponding to the Curie temperature of 400°C. Two dielectric peaks of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples were 220 and 420°C, respectively. We found that two phase transitions from orthorhombic to tetragonal phrase and from tetragonal to cubic phrase, respectively. According to above experimental results, we reveal that the ferroelectric to paraelectric occurred caused by phase transition. The maximum dielectric constant of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples for sintering temperature of 1100°C was found, and it was about 5800. Figure 5 shows the temperature dependence of dielectric constant and loss parameters of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples with different sintering temperature. The dielectric loss factor decreased as the sintering temperature was increased. The sintering temperature increased to 1100°C, and the dielectric loss was about 0.04. The dielectric loss was continuous decreasing while the sintering temperature increased. The dielectric constant decreases and loss increases were attributed by the high sintering temperature and many pores for \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples. The sintering temperature dependence of orthorhombic to tetragonal transition temperature and cubic transition temperature for \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples were found. The \( T_{O-T} \) transition temperature was a shift to high sintering temperature and it was increased form 200 to 220°C. In addition, the cubic transition temperature also shift to high sintering temperature was observed. From the experimental results obtained, we found the \( T_{O-T} \) and \( T_C \) temperature were affected by different sintering temperature. The \( T_{O-T} \) and \( T_C \) transition temperature was increased and this result was attributed to less sodium and potassium volatilization of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic in the high sintering temperature. According to the phase diagram and \( KNbO_3-KNaO_3 \) system obtained, we found that the ratio of potassium to sodium was about 0.4 [9].

The different sintering temperature dependence of ferroelectric hysteresis loops for \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples measured by ferroelectric tester. All of the \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples show clearly ferroelectricity. The maximum remanent polarization of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples for sintering temperature of 1100°C was observed. We found that the remanent polarization and coercive field were 22 \( \mu \)C/cm\(^2\) and 100 kV/cm, respectively. The ferroelectric hysteresis loops of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples with different sintering temperature were different. For high sintering temperature, we suggested that the remanent polarization for \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples decreased because of its high leakage current and dielectric loss of electrical properties. According to above the statement, high dielectric loss was contributed to many distinct pores existed in grain boundary of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples. Figure 6 shows \( d_{33} \) and \( k_p \) parameters as a function of sintering temperature. The change of \( d_{33} \) parameters with different sintering temperature was similar to those of the bulk density for \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples. From the experimental results, we found that \( d_{33} \) parameter was about 120 pC×N\(^{-1}\). The increasing sintering temperature was responsible for the enhancement of \( d_{33} \) and \( k_p \) parameters of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples. The dense and no-pore microstructure of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples were found under the sintering temperature of 1120°C. Therefore, we suggested that the sintering temperature was sensitive to the piezoelectric properties of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples form these experimental results. Moreover, the \( d_{33} \) and \( k_p \) parameter increases with increase of sintering temperature because of increase in grain size of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples.

**Conclusion**

In conclusion, sodium potassium niobate ceramic samples with the nominal composition of \( K_{0.5}Na_{0.5}NbO_3 \) for different sintering temperature were fabricated using conventional solid state sintering technology. All of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic samples show typical ferroelectric loop and piezoelectric properties. The remnant polarization (Pr) and the coercive field (Ec) of \( K_{0.5}Na_{0.5}NbO_3 \) samples decreased while the sintering temperature increased, and remnant polarization decreased with the sintering temperature of 1100°C. The optimal dielectric constant and loss of \( K_{0.5}Na_{0.5}NbO_3 \) ceramic sample were found to be 5800 and 0.04, respectively. The \( d_{33} \) and \( k_p \) piezoelectric parameters
was about 120 pC/N and 0.4. In addition, the sintering temperature significantly affected microstructure of pure K0.5Na0.5NbO3 ceramic samples was found. The microstructure of K0.5Na0.5NbO3 ceramic samples sintered temperature of 1100°C was dense and fine. The average grain size was about 10 μm, and no fracture surface was found. The measured bulk density of K0.5Na0.5NbO3 ceramic sample reaches 4.4 g/cm³, which is approximately 94% of the theoretical density. These experimental results provided that K0.5Na0.5NbO3 ceramic sample was an excellent candidate for lead-free ferroelectric and piezoelectric ceramic.

References


Fig. 1 The XRD patterns of K0.5Na0.5NbO3 ceramics calcined at 865°C and sintering in different temperature.

Fig. 2 Change in bulk and relative density as a function of sintering temperature.

Fig. 3 Scanning electron microscopy morphology of K0.5Na0.5NbO3 ceramic samples with different sintering temperature (a) 1080°C (b) 1100°C (c) 1120°C.

Fig. 4 The relative dielectric constant of K0.5Na0.5NbO3 ceramic samples as function of sintering temperature.

Fig. 5 The dielectric constant and loss parameters of K0.5Na0.5NbO3 ceramic samples as function of sintering temperature.

Fig. 6 The d33 and kp piezoelectric parameters of K0.5Na0.5NbO3 ceramic samples as function of sintering temperature.