



Effect of Particle Size on the Dielectric and Piezoelectric Properties of $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.05\text{BaTiO}_3$ Lead-free Piezoelectric Ceramics

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The particle sizes of $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.05\text{BaTiO}_3$ powder were controlled by secondary milling time after calcination. The average particle sizes, D_{mean} , of $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.05\text{BaTiO}_3$ powders were critically changed from $14.31\ \mu\text{m}$ to $0.91\ \mu\text{m}$ by secondary milling time. The dielectric and piezoelectric properties of $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.05\text{BaTiO}_3$ ceramics depended on the particle sizes of powders after calcination and the secondary milling process. As secondary milling times after calcination were increased to more than 48 hr, the dielectric and piezoelectric properties of $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.05\text{BaTiO}_3$ ceramics were deteriorated.

Keywords: $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-BaTiO}_3$, Particle sizes, Secondary milling time, Dielectric, Lead-free piezoelectric

1. INTRODUCTION

Due to its excellent piezoelectric properties, perovskite $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) based ceramics are widely used in sensors and actuators [1]. However, it is well known that PZT ceramics have disadvantages, which generate toxic PbO in the sintering process and compositional fluctuation through PbO evaporation. To overcome these problems, extensive research has been

conducted on Pb-free piezoelectric ceramics, such as the Bi layer-type [2], Tungsten-bronze type [3], BaTiO_3 based piezoelectric ceramics [4] and alkaline niobate-based perovskite ceramics [5-6]. Among them, potassium-sodium niobate ($(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, KNN) ceramics have attracted much attention because they are eco-friendly and have good electrical properties [7]. However, it is difficult to obtain KNN ceramics, having dense and good electrical properties, when sintered under an atmospheric condition. It was found that K and Na ions can be evaporated easily in the high temperature sintering process and cause deviation of compositional stoichiometry. Therefore, a lot of research has been conducted to improve electrical properties of KNN ceramics by additions of aids and changes of the sintering process [8,9]. The BaTiO_3 (BT) ceramic has been used widely as capacitors, sensors,

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and actuators, due to its excellent dielectric and piezoelectric properties, with the exception of its low Curie temperature and high sintering temperature. The combination of KNN ceramics with BT composition showed new possibilities to extend applications of lead-free piezoelectric ceramics. However, there are few studies about the effects of the KNN-BT powder condition, such as particle size, on dielectric and piezoelectric properties.

In this study, we fabricated $0.95(K_{0.5}Na_{0.5})NbO_3-0.05BaTiO_3$ ceramics that were different particle sizes by changing the secondary milling time after calcination. We then, investigated the effects of particle size on the dielectric and piezoelectric properties.

2. EXPERIMENTS

K_2CO_3 (Junsei Chemical, Japan, 99.0%), Na_2CO_3 (Kanto Chemical, Japan, 99.5%), Nb_2O_5 (Junsei Chemical, Japan, 99.9%), $BaCO_3$ (Kanto Chemical, Japan, 99.0%), and TiO_2 (Hanawa Chemical, Japan, 99.0%) were used as raw materials to prepare $0.95(K_{0.5}Na_{0.5})NbO_3-0.05BaTiO_3$ (KNN-BT) ceramics using the conventional mixed oxide method. The powders were mixed by ball-milling in ethanol for 24 hr and dried in an oven at $100^\circ C$ for 24 hr. The dried powders were calcined at $900^\circ C$ for 24 hr and the calcined powders were underwent secondary milling for 0 hr, 24 hr, 48 hr and 72 hr to investigate the effects of particle size on the dielectric and piezoelectric properties of KNN-BT ceramics. The calcined and secondary milled powders were mixed with a 3 wt% polyvinyl alcohol (PVA) solution, and then compacted at a 1.5 ton pressure to form the pellets with a size of 15.8 mm in diameter and 2mm in thickness. The disks were sintered at $1,200^\circ C$ for 2 hr with a rising rate of $3^\circ C/min$ at atmospheric pressure. In addition, silver pastes were fired on both surfaces of the sintered specimens at $600^\circ C$ for 30 min for the electrodes. Subsequently, the specimens were poled in a silicon oil bath at $100^\circ C$ by applying a DC field of $3 kV/mm$ for 30 min.

The particle size of the powders after calcination and the secondary milling (0 hr, 24 hr, 48 hr, and 72 hr) process was analyzed by using a particle size analyzer (Cilas 1190, France). The bulk density of the sintered KNN-BT ceramics was measured and calculated using an Archimedes method. The crystal structures of all KNN-BT ceramics were examined by X-ray diffraction (XRD, Rigaku, Japan) with $Cu K\alpha$ radiation (step: 0.01°) to analyze the phases of the KNN-BT ceramics. A JSM-7001F scanning electron microscope (SEM, JEOL, Japan) was used for the microstructural analysis of the KNN-BT ceramics. The temperature dependence of the dielectric constant of the KNN-BT ceramics was examined using an LCR meter (Ando, AG-4303) in an electric furnace by measuring the capacitance in the range from room temperature to $500^\circ C$ and 1 kHz. The electromechanical coupling factor (k_p) and piezoelectric properties of the KNN-BT ceramics were measured by the resonance-antiresonance method using an impedance analyzer (Agilent, 4294A). Furthermore, the piezoelectric constant d_{33} was measured using a piezo- d_{33} meter (PM 100, APC, USA).

3. RESULTS AND DISCUSSION

Figure 1 shows particle size distributions of the KNN-BT powders after calcination and secondary milling times of: a) 0 hr, b) 24 hr, c) 48 hr and d) 72 hr. Average particle sizes, D_{mean} of the KNN-BT powders after calcination and secondary milling were $14.31 \mu m$, $1.27 \mu m$, $0.96 \mu m$ and $0.91 \mu m$, respectively. The particle size distribution of the powder without the secondary milling process (0 hr) showed double peak distribution and, con-

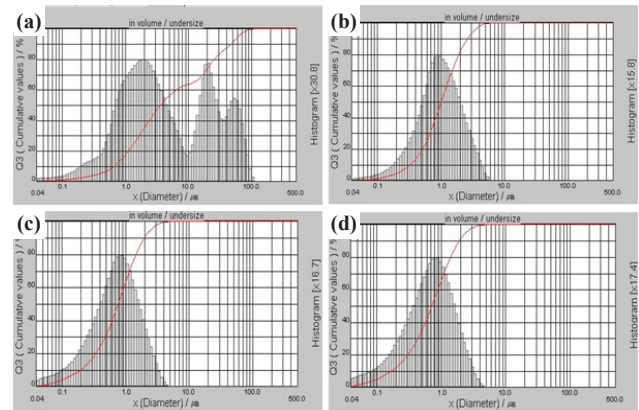


Fig. 1. Particle size distributions of KNN-BT powders according to secondary milling time after calcination: (a) 0 hr, (b) 24 hr, (c) 48 hr, and (d) 72 hr.

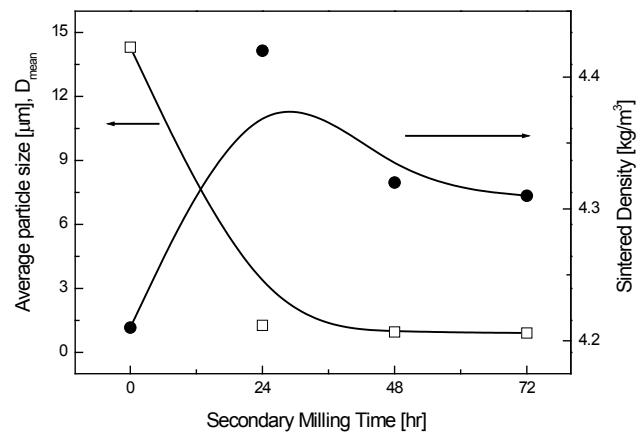


Fig. 2. The variations of the average particle size of the powders after calcination and the secondary milling process (a) 0 hr, (b) 24 hr, (c) 48 hr, and (d) 72 hr and sintered density of the KNN-BT ceramics fabricated with the powders.

sequentially, had a high value of D_{mean} . In addition, we can see that the amount of submicrometer particle powders increased at conditions when the secondary milling time was more than 48 hr. From the above results, we can estimate that the excess secondary milling process after calcination increased the amount of submicrometer particle powders. Subsequently, the submicrometer particle powders may easily be lost or agglomerated with each other during the process.

Figure 2 shows the relationship between the variations in the average particle size and sintered density of the KNN-BT ceramics, and secondary milling time. As secondary milling time increases and particle sizes decrease, the sintered density increased and then dropped. We can interpret this as follows: the powder that is a larger size has a lower packing density of particles in lattices and, consequently, low sintered density. On the other hand, the lowered sintered density by submicrometer particle powders that are smaller than $1 \mu m$ could be due to the formation of the liquid phases.

Figure 3 shows the XRD patterns of the sintered KNN-BT ceramics. All the sintered KNN-BT ceramics had a single phase with tetragonal structures and a homogeneous phase without any second phases. Furthermore, we can see that the (200) peak weakened and the space distance between the (002) and (200)

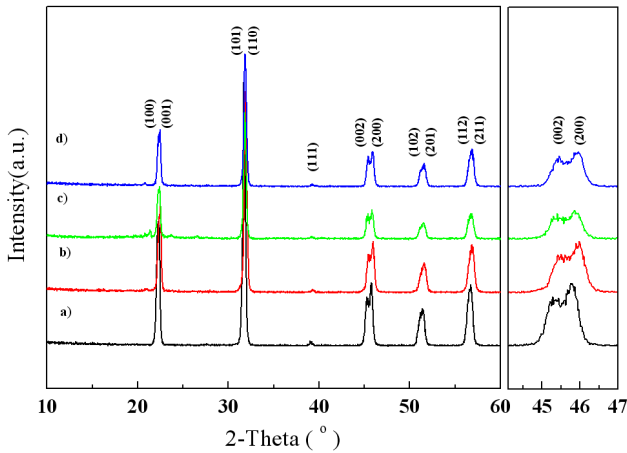


Fig. 3. XRD patterns of KNN-BT ceramics fabricated by powders calcined with different particle sizes: (a) 14.31 μm, (b) 1.27 μm, (c) 0.96 μm, and (d) 0.91 μm.

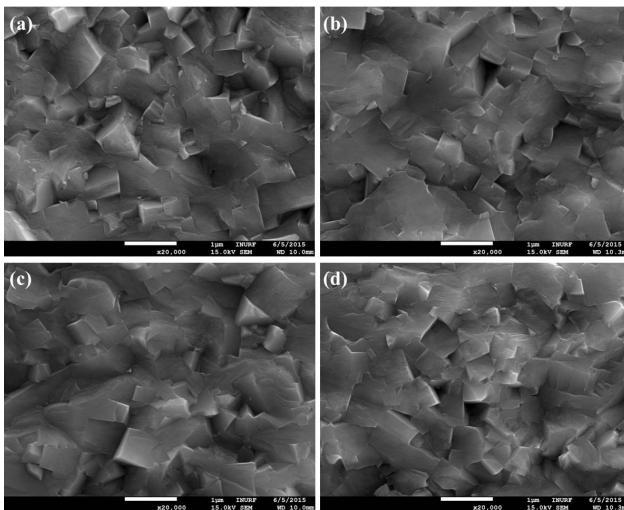


Fig. 4. SEM images of the fractured KNN-BT ceramics fabricated by powders with different particle sizes after calcination and then the secondary milling process.

peaks increased gradually. As the secondary milling time increased, the Na and K ions may have undergone much loss, but the amount of K ions might be smaller. Therefore, this might cause the higher content of K ions in all KNN-BT ceramics. Therefore, the increased space distance between the (002) and (200) peaks of KNN-BT ceramics can be explained as occupying more of the K ion (1.33 Å) than that of the Na ion (0.97 Å) in the A-site as secondary milling time increases [10].

Figure 4 shows the SEM images of the KNN-BT ceramics that were fabricated by powders with different particle sizes after calcination and then the secondary milling process. The grain size slightly decreased and then increased as the secondary milling time increased after calcination. When the specimen with an average powder particle size of 14.31 μm, was sintered under the same sintering conditions, non-uniform grains were developed as we expected above. On the contrary, for the specimens sintered with an average particle size of 1.27 μm, uniform grain sizes were developed. It is interesting to notice that the grain sizes were slightly increased for the specimens when the secondary milling time exceeded 48 hr after calcination. This can be in-

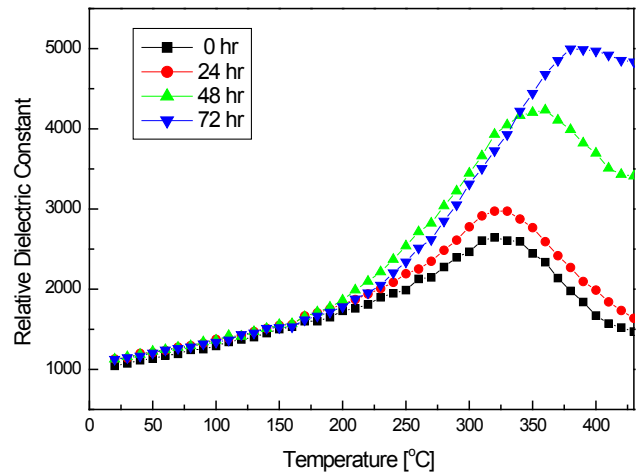


Fig. 5. The temperature dependence of dielectric constants of the KNN-BT ceramics fabricated by powders with different particle sizes after calcination and secondary milling process.

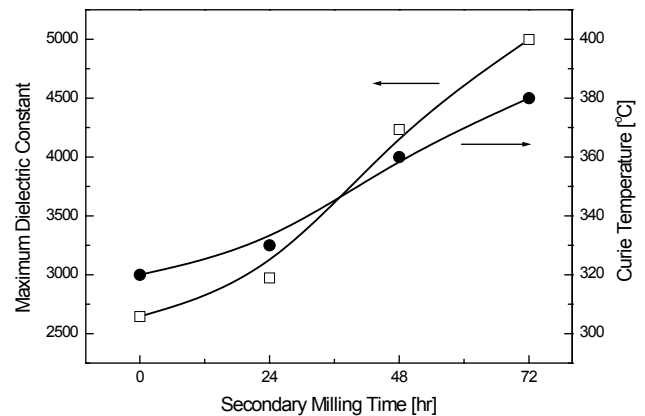


Fig. 6. The maximum dielectric constant and Curie temperature of the KNN-BT ceramics fabricated by powders with different particle sizes after calcination and the secondary milling process.

terpreted as follows: the submicrometer particle powders easily made a large amount of the liquid phase and a nuclei during the sintering process for grain growth at the early stage of sintering, as shown in Fig. 4 (c) and (d) [11].

Figure 5 shows the temperature dependence of the dielectric constant of the KNN-BT ceramics that were fabricated by powders with different particle sizes after calcination and the secondary milling process, which were measured at 1 kHz. The maximum dielectric constant increases as the particle size decreased. The specimen sintered with a submicrometer particle size showed a larger dielectric constant than those that had a micrometer particle size. This might be due to the increase of grain size despite the low sintered densities.

Figure 6 shows the variations of the maximum dielectric constant and Curie temperature of the KNN-BT ceramics that were fabricated by powders of different particle sizes after calcination and the secondary milling process. As seen in Fig. 6, Curie temperatures (T_c) were gradually increased from 320°C to 380°C as the grain size of the KNN-BT ceramics decreased. This is the result of the nonuniform grain size in Fig. 3, (c) and (d) as we mentioned above. It is well known that nonuniform grain size generates internal stress, resulting in an easier domain wall motion. The result is in agreement with the study by Samara who

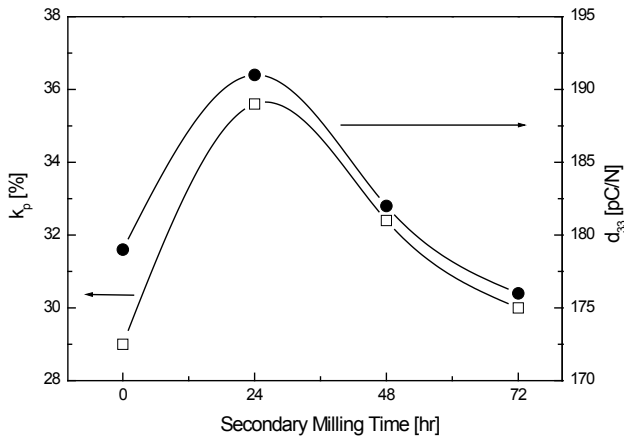


Fig. 7. The variations of the electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) of the KNN-BT ceramics that had different particle sizes after calcination and the secondary milling process.

had systematically reported the change of the paraelectric-ferroelectric phase transition of BaTiO₃ ceramics in the 1960s [12].

Figure 7 shows the variations of electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) of the KNN-BT ceramics that were fabricated by powders with different particle sizes after calcination and then the secondary milling process. The electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) of the KNN-BT ceramics showed the maximum values at the specimen with a particle size of 1.27 μm after calcination and then the secondary milling process. At the specimens fabricated with submicron powders, the piezoelectric properties got worse due to the formation of the liquid phase. The result is in agreement with the result of the sintered density of the KNN-BT ceramics.

4. CONCLUSIONS

We investigated the effects of the different particle sizes of the powder on the dielectric and piezoelectric properties of KNN-BT lead-free ceramics.

The particle sizes of the powder with increasing secondary milling time after calcination for the KNN-BT ceramics were decreased from 14.31 μm to 0.91 μm . As the particle size of the powder decreased, the sintered density of KNN-BT ceramics increased. It, subsequently, decreased due to the formation of the liquid phase. The Curie temperature (T_c) of the KNN-BT ceramics was gradually increased and the maximum dielectric constants of KNN-BT ceramics were abruptly increased as the particle size

of powder was decreased.

The electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) of the KNN-BT ceramics showed the maximum values at the specimen with a particle size of 1.27 μm after calcination and then the secondary milling process. Excess milling process after calcination cause an unnecessary loss of powders and make submicrometer particle powders. In addition, this would be responsible for the decreased piezoelectric properties.

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