Microstructural control of (Li, Na, K)NbO₃ ceramics using additives

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The microstructure of Li₀.₈₆Na₀.₃₂K₀.₈₄NbO₅ piezoceramics was designed and controlled by the use of additives such as Li₂CO₃, SiO₂, MnCO₃, and SrZrO₃. The electric and piezoelectric properties, microstructures, and compositional distribution of the additive elements are investigated in this paper. The average grain diameters decreased from 5.8 to 3.0 µm when the following additives were incorporated: 0.65 mol % Li₂CO₃, 1.3 mol % SiO₂, 0.2 mol % MnCO₃, and 0.5 mol % SrZrO₃. In addition, the maximum grain diameters decreased from 15 to 7.7 µm. The compositional distributions were analyzed by energy dispersive X-ray spectrometry using a transmission electron microscope. Grains of SiO₂ glass and the MnO compound were evaluated as diverse grains on the ceramic matrix. Because of the homogenization of the microstructure and the increased relative density, the resistivities were increased over the whole measuring temperature range. For example, the resistivities increased from 5.2 to 74 Ω·cm at 160°C. The piezoelectric properties remained about the same: ε₃₃/ε₀ = 880, tan δ = 1.9%, kₙ = 41.8%, d₃₃ = −74 pC/N, and Tₑ = 470°C. These results indicate an improvement in the reliability of structural refinement techniques for ceramics.

Key-words : Lead-free, Piezoceramics, Microstructure, Additives, Piezoelectricity

1. Introduction

About a decade ago, it was found that (Li, Na, K)NbO₃ exhibits high piezoelectricity, as well as a high Curie temperature, making it one of the most attractive lead-free piezoceramics. Y. Guo et al. demonstrated that the radial-mode electromechanical coupling factor (kₙ), the longitudinal-mode piezoelectric coefficient (d₃₃), and the Curie temperature (Tₑ) for Li₀.₈₆Na₀.₃₂K₀.₈₄NbO₅ are 42%, 235 pC/N, and 470°C, respectively. Y. Saito et al. reported the Tₑ and d₃₃ of the Li-, Ta-, and Nb-modified complex compound Li₀.₀₆Na₀.₃₂K₀.₄₈Nb₀.₈₆Ta₀.₁₀Sb₀.₀₄O₅ as 253°C and 235 pC/N, and 470°C, respectively. In addition, textured ceramics of this compound have excellent piezoelectric properties (e.g., d₃₃ = 416 pC/N), rendering it comparable to Pb(Zr, Ti)O₃-based piezoceramics.

(Li, Na, K)NbO₃ ceramics present low sinterability due to alkaline vaporization that occurs during sintering. Consequently, various sintering methods have been applied to (Li, Na, K)NbO₃ ceramics—for example, the hot-pressing method, and the spark-plasma sintering method. However, these methods are difficult to apply in a manufacturing setting because of low mass productivity. In order not to prevent alkaline vaporization, but also to improve the electric and piezoelectric properties, additives are often used in (Li, Na, K)NbO₃ ceramics. In our previous study, the Si-glass phase was able to alter the microstructure of Na₀.₉₅K₀.₅NbO₃. According to this technique, the median grain diameter decreased from 2.2 to 1.3 µm, and maximum grain diameters decreased from 12.3 to 5.3 µm, respectively. Moreover, the breakdown electric field rose to 11 kV/mm in silicon oil at 150°C.

This study aims to evaluate the additive effects on (Li, Na, K)NbO₃ ceramics in terms of fine homogeneus microstructures,

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with energy-dispersive X-ray spectroscopy (STEM-EDS). The analysis was carried out under an accelerating voltage of 300 kV.

The dense sintered ceramics were cut and polished to about 30 μm thickness and then underwent an Ar-ion milling procedure (PIPS, Gatan) to produce electron-transparent sections for STEM-EDS.

2.3 Electric and piezoelectric properties

The dense sintered ceramics were polished to 8.5 mm diameter × 0.5 mm thickness samples and coated with silver paste on both surfaces. The samples were poled in silicone oil under a 3 kV/mm for 15 min at 150°C. The resistivity was measured under a 2 kV/mm electric field on a 15 min delay from 200°C down to 100°C using a resistance meter (R8340, Advantest) and a thermostatic chamber (STH-120; Espec). The radial-mode electromechanical coupling factor ($k_r$), Young’s modulus ($Y_{11}$), and the piezoelectric coefficient ($d_{31}$) for the samples were evaluated by the resonance-antiresonance method using an impedance analyzer (4294A; Agilent Technologies). The relative permittivities ($\varepsilon_r$) were measured at 1 kHz and 25°C with an inductance-capacitance-resistance (LCR) meter (E4980A, Agilent Technologies). The Curie temperature ($T_c$) was observed the maximum relative permittivities corresponding to the phase transitions of cubic-tetragonal for depending on temperature.

3. Results and discussions

3.1 Microstructural control using additives

In our previous report, we showed that the addition of Si-glass (K$_2$Nb$_2$O$_7$Si$_2$O$_5$) phase could cause the microstructure of Na$_{0.5}$K$_{0.5}$NbO$_3$ ceramics to become fine and homogeneous. However, the addition of the Si-glass phase could not precisely control the grain diameter on LNKN ceramics because the sintering temperature was over 1100°C. After some experiments, we found that the microstructure can be manipulated by adding both Li$_2$CO$_3$ and SiO$_2$ compounds with an atomic ratio (Li/Si) equal to one. It should be noted that this ratio produced Lithium disilicate (Li$_2$Si$_2$O$_5$), which is a eutectic crystal. Figure 1(a) shows the microstructure of the ceramic surface of LNKN without any additives. Figure 1(b) shows the microstructure of the surface of LNKN with 0.65 mol % Li$_2$CO$_3$ and 1.3 mol % SiO$_2$ added (LNKN+LiSi is omitted). The additives Li$_2$CO$_3$ and SiO$_2$ clearly improved the microstructure of the LNKN, with the exception of a few large grains.

The large grain on LNKN+LiSi ceramics should be eliminated from the viewpoint of homogeneity. It is presumed that the formation behavior of this large grain was controlled by the diffusion of alkaline ions. Accordingly, SrZrO$_3$ compounds were further added to LNKN+LiSi ceramics, because the diffusion of Sr$^{2+}$ ion was slower than the alkaline ions, and Zr$^{4+}$ ions prevented Nb$^{5+}$ ions from being reduced to Nb$^{4+}$. Additionally, MnCO$_3$ was used as a sintering additive. Figure 1(c) shows the microstructure of the ceramic surface for LNKN with 0.65 mol % Li$_2$CO$_3$, 1.3 mol % SiO$_2$, 0.2 mol % MnCO$_3$, and 0.5 mol % SrZrO$_3$ added (LNKN+SZLiSiM2) sintered at 1000°C.

3.2 Composition analysis of several grains

The XRD profiles in Fig. 3 show that LNKN and LNKN+SZLiSiM2 exhibited a typical perovskite structure, in which the crystal system is tetragonal. The full width at half maximum of each profile is different as a result of the diverse grain diameters.
Figure 4 shows STEM images of the bright field for LNKN+SZLiSiM2 ceramics. The points (i), (ii), and (iii) are different grains that were evaluated by STEM-EDS. The results of STEM-EDS are shown in Fig. 5. From the spectrum of point (i) it can be determined that the sample contained Na, K, and Nb. Thus, the grain of point (i) was an LNKN ceramic. The grain of point (ii) consisted primarily of the SiO2 glass components. (b) Point (iii) consisted primarily of the MnO component. The evaluation results according to STEM energy-dispersive X-ray spectroscopy (STEM-EDS) are shown in Fig. 5.

EDS because do not observed an electron transition. Point (iii) in the grain consisted primarily of the MnO component. These observations were confirmed from the low intensity of the K-Kα spectrum, and imply the diffusion of K+ ions during the sintering. Moreover, Li+ ions probably diffused on these grains. The Mn-Kα spectrum did not confirm the other grains, regardless of which many previous reports discussed for solid solution of Mn ions in this composition. It would be difficult for the MnO compound to react with LNKN because LNKN+SZLiSiM2 was sintered at 1000°C. If Mn2+ ions were substituted at the Nb sites, one might expect the sintering temperature of LNKN+SZLiSiM2 to be higher than 1000°C. Lastly, STEM-EDS of our analysis was not able to detect the spectra of Sr and Zr elements. The SrZrO3 component was suggested as a homogeneous diffusion agent on the ceramic matrix.

3.3 Results of the measurement for electric and piezoelectric properties

The dielectric and piezoelectric properties of LNKN and LNKN+SZLiSiMx (x = 0, 2, 4), which were sintered at 1000°C for 2 h, are collected in Table 1 (x represents the additive amount of 0.0 mol % MnCO3). The density of LNKN+SZLiSiM0, the relative density of which was 92.6%, was not sufficient. It was problematic that LNKN+SZLiSiM0 presented lower resistivity -6.6 x 10^4 Ω·cm at 160°C, as shown in Fig. 6. In contrast, LNKN+SZLiSiM2 and LNKN+SZLiSiM4 obtained high densities (95.3 and 95.2%, respectively) almost same as LNKN due to the sintering additive MnCO3. The STEM-EDS analysis indicated that several grains of different compositions, such as SiO2 glass and the MnO compound, exist in LNKN+SZLiSiM2 ceramics. The increase of relative density for LNKN+SZLiSiM2 was probably the result of filling the void of SiO2 glass and MnO compound by comparison with LNKN+SZLiSiM0 ceramics. Concerning the piezoelectric properties of LNKN and LNKN+SZLiSiMx ceramics, the k33 of LNKN+SZLiSiM0 increased from 40.1 to 44.8%. However, the k33 of LNKN+SZLiSiM2 and LNKN+SZLiSiM4 slightly decreased to 41.8 and 39.0%, respectively, which corresponds to the additive amount of 0.0 mol % MnCO3. LNKN+SZLiSiM4 ceramics contained excessive amounts of MnCO3. Moreover, LNKN+SZLiSiM0 ceramics displayed low densities, as mentioned above. Therefore, the best choice in terms of reliability and piezoelectric properties is LNKN+SZLiSiM2.
In general, when the crystallite diameter became smaller, the full width at half maximum of the XRD profile became larger, as shown in Fig. 3. The small crystallite diameter suggests the small domain regions on the grain. Thus, it can be inferred that the LNKN+SZLiSiMx ceramics are easier to polarize than the LNKN ceramics. The MnO compound that filled the pores on the ceramics occurred when \( Y^{21} \) was increased, because the MnO compound was non-ferroelectric materials. As a result, the piezoelectric constant \( d_{31} \) remained at about the same value compared between LNKN and LNKN+SZLiSiM2 ceramics.

Figure 6 shows the temperature dependence of the resistivity for LNKN and LNKN+SZLiSiMx. Because of the homogenization of the microstructure and the increased relative density, the resistivity increased over the whole measuring temperature range. For example, the resistivity of LNKN ceramics and LNKN+SZLiSiM2 ceramics increased from 1.2 \( \times 10^{10} \) to 2.6 \( \times 10^{11} \) \( \Omega \) cm at 120°C; from 5.2 \( \times 10^{10} \) to 2.7 \( \times 10^{11} \) \( \Omega \) cm at 160°C; and from 1.1 \( \times 10^{9} \) to 6.0 \( \times 10^{9} \) \( \Omega \) cm at 200°C. This result indicated an improvement in the reliability of the ceramics for structural refinement.

In this study, the additives (0.65 mol % \( \text{Li}_2\text{CO}_3 \), 1.3 mol % \( \text{SiO}_2 \), 0.2 mol % \( \text{MnCO}_3 \), and 0.5 mol % \( \text{SrZrO}_3 \)) provided the fine, homogeneous microstructure of LNKN ceramics. Moreover, the resistivity increased over the whole measuring temperature range without decreased piezoelectricity. We are currently testing the experimental production of these ceramics, the results of which will be reported in the near future.

4. Conclusion

Several additives were incorporated into LNKN compounds for the purpose of microstructural alteration. We showed the best choice of the additives that were 0.65 mol % \( \text{Li}_2\text{CO}_3 \), 1.3 mol % \( \text{SiO}_2 \), 0.2 mol % \( \text{MnCO}_3 \), and 0.5 mol % \( \text{SrZrO}_3 \) after some experiments. The average grain diameter and maximum grain diameter of LNKN+SZLiSiM2 ceramics sintered at 1000°C were 3.0 and 7.4 \( \mu \)m, respectively. In addition, we succeeded in avoiding large grains (i.e., over 10 \( \mu \)m). The grains of \( \text{SiO}_2 \) glass and MnO compounds of the additives were evaluated as diverse grains on the ceramic matrix, which was analyzed via STEM-EDS. As a result of the homogenization of the microstructure and the increased relative density, the resistivity of LNKN+SZLiSiM2 ceramics increased over the whole measuring temperature range, e.g., from 5.2 \( \times 10^{10} \) to 2.7 \( \times 10^{11} \) \( \Omega \) cm at 160°C. The piezoelectric properties were \( \varepsilon^{31} / \varepsilon_{0} = 880 \), \( \tan \delta = 1.9\% \), \( k_r = 41.8\% \), \( Y^{21} = 7.9 \), \( d_{31} = -74 \text{ pC/N} \), and \( T_r = 470°C \).

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