

Strain characteristics and electrical properties of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ceramics

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$[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) ceramics were prepared by the partial sol-gel (PSG) method to improve the microstructure homogeneity of Ta^{5+} ion and were compared to those prepared by the conventional mixed oxide (CMO) method. For the PSG method, $\text{Ta}(\text{OC}_2\text{H}_5)_5$ was directly reacted with calcined $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}]\text{NbO}_3$ powders and the specimens sintered at 1100°C for 5 hrs showed a single phase with a perovskite structure. Compared to the specimens prepared by conventional mixed oxide powders, the relative ratio of tetragonal phase to orthorhombic phase of the sintered specimens prepared by $\text{Ta}(\text{OC}_2\text{H}_5)_5$ was larger than that of the sintered specimens prepared by Ta_2O_5 . The electromechanical coupling factor (k_p), piezoelectric constant (d_{33}) and dielectric constant (ϵ_r) of the sintered specimens were increased with Ta^{5+} content. These results could be attributed to the decrease of the orthorhombic-tetragonal polymorphic phase transition temperature (T_{o-t}), which could be evaluated by oxygen octahedral distortion. Strain of the sintered specimens prepared by the PSG method was higher than that of specimens prepared by the CMO method due to the increase of relative density. The effects of crystal structure on the strain characteristics of the specimens were also discussed.

Key words: Electrical properties, Structural characteristics, Lead-free ceramics.

Introduction

Lead-free piezoelectric ceramics have been widely investigated to search the environment-friendly replacement for $(\text{Pb,Zr})\text{O}_3$ (PZT) ceramics. $(\text{K,Na})\text{NbO}_3$ -based ceramics of alternative materials of PZT were considered the most promising candidate due to the high piezoelectric properties and Curie temperature (T_C), compared to other candidates such as bismuth and barium based ceramics [1-7].

The piezoelectric constant (d_{33}), electromechanical coupling coefficient (k_p) and dielectric constant (ϵ_r) of the PZT ceramics were enhanced due to the close to the morphotropic phase boundary (MPB). Similarly to PZT ceramics, many studies reported that the electrical properties of $(\text{K,Na})\text{NbO}_3$ -based ceramics were improved due to the high alignment of ferroelectric dipoles by orthorhombic to the tetragonal phase transition temperature (T_{o-t}) at near room temperature [8-14].

With substitutions of Li^+ and/or Ta^{5+} to $(\text{K}_{0.5}\text{Na}_{0.5})^+$ and/or Nb^{5+} respectively, the electrical properties and strain characteristics are enhanced because the sinterability of KNN is increased and the orthorhombic to tetragonal phase transition temperature (T_{o-t}) is decreased around room temperature. In general, the electrical properties

of materials were strongly affected by the structural characteristics as well as T_{o-t} [15]. Therefore, the dependence of phase transition temperature such as T_{o-t} on the structural characteristics of KNN-based ceramics should be investigated to control and predict the electrical properties and strain characteristics of materials. Additionally, the microstructural homogeneity of Ta^{5+} ion should influence the electrical properties and strain characteristics of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ceramics.

Therefore, the dependence of electrical properties and strain characteristics on the structural characteristics of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ceramics prepared by partial the sol-gel (PSG) method and conventional mixed oxide (CMO) method were investigated in this study.

Experimental

High-purity oxide powders of K_2CO_3 (99%, High Purity Chemicals, Japan), Na_2CO_3 (99%, High Purity Chemicals, Japan), Li_2CO_3 (99%, High Purity Chemicals, Japan), Nb_2O_5 (99.9%, Sigma-Aldrich, USA), Ta_2O_5 (99.9%, High Purity Chemicals, Japan) and $\text{Ta}(\text{OC}_2\text{H}_5)_5$ (99.99%, Sigma-Aldrich, USA) were used as the starting powders. For the CMO method, powders were prepared according to the desired composition of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) and ground with ZrO_2 balls for 24 hrs in ethanol. These powders were calcined at 850°C for 5 hrs to obtain a single

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phase. For the PSG method, $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}]\text{NbO}_3$ powder and $\text{Ta}(\text{OC}_2\text{H}_5)_5$ were dispersed in 2-methoxyethanol and then stirred in a three-neck flask for 24 hrs. The resulting mixture was refluxed at 130 °C for 24 hrs and then hydrolyzed by adding 1 : 4 ration of water and 2-methoxyethanol. The gel was dried and then calcined at 850 °C for 3 hrs. The calcined powders were milled again with ZrO_2 balls for 24 hrs in ethanol and then dried. Dried powders were pressed isostatically to a 15 mm-diameter at 1500 kgf/cm². These pellets were sintered from 1100 °C for 5 hrs in air.

Powder X-ray diffraction (XRD, D/Max-3C, Rigaku, Japan) analysis was used to determine the phase identification. The x-ray diffraction data for a Rietveld analysis was collected over a range of 2θ from 20 ° to 80 ° with a step size of 0.02 ° and a count time of 2 s. The lattice parameters, unit-cell volumes and atomic positions were obtained from Rietveld refinements of XRD patterns using the Fullprof program [16]. The initial structure model for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ compounds was sourced from the previous reports [17, 18]. The parameters such as zero shift, individual scale factor, unit-cell parameters and phase profile parameters (U , V and W) and two asymmetry (orthorhombic and tetragonal) parameters were refined until the apparent convergence of XRD patterns was reached. The vibration of NbO_6 octahedron was confirmed by a Raman spectra meter (T 64000, Horiba, Jobin Yvon, France) with an Ar^+ ion laser operating at 514 nm for excitation.

Silver electrodes were formed on both surfaces of each sintered disk by firing at 700 °C for 10 min. The samples were polarized in a silicon oil bath at 100 °C by applying a DC electric field (4 kVmm⁻¹ for 20 min). The piezoelectric coefficient (d_{33}) was measured using a piezo- d_{33} meter (ZJ-3BN, Institute of Acoustics, Chinese Academy of Sciences, China). The electro-mechanical coupling coefficient (k_p) was determined by the resonance and anti-resonance method on the basis of IEEE standards using an impedance analyzer (HP 4192A, Palo Alto, CA, USA). The dielectric constant was measured as a function of temperature by an LCR meter (HP 4284A, Agilent, USA).

Results and discussion

Crystal structural characteristics

Fig. 1 shows the XRD patterns of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ (LKNNT) ($0.05 \leq x \leq 0.25$) specimens sintered at 1100 °C for 5 hrs with Ta^{5+} content. A single phase with a perovskite structure was detected through the entire range of compositions. The volume fraction (V.F.) of orthorhombic and V.F. of the tetragonal were calculated from Rietveld refinement. The V.F. of the orthorhombic phase ($Amm2$) of the LKNNT prepared conventional mixed oxide (CMO) method was decreased with Ta^{5+} content, while the V.F. of tetragonal phase ($P4mm$) was increased, which was confirmed at 2θ

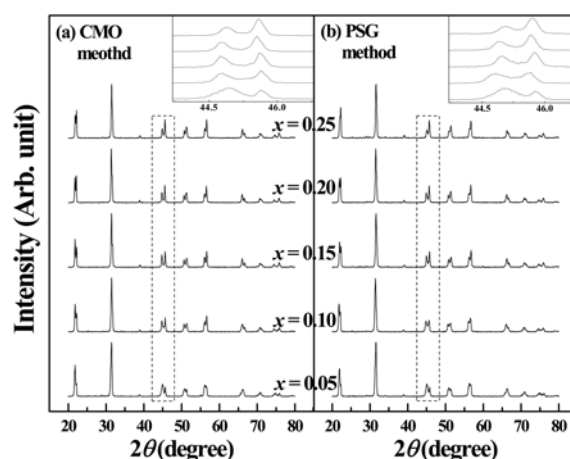


Fig. 1. X-ray diffraction patterns of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100 °C for 5 hrs prepared by (a) conventional mixed oxide (CMO) method and (b) partial sol-gel (PSG) method.

from 43 ° to 47 ° for all specimens. The XRD patterns of specimens prepared by the partial sol-gel (PSG) method showed a similar tendency to the behaviour of the XRD patterns of the LKNNT specimens prepared by the CMO method. For the analysis of structural characteristics, the Rietveld refinement procedures were performed to evaluate the structural characteristics. Using the two types of the initial structure mode of the orthorhombic (ICSD # 18502) and tetragonal (ICSD # 2852), the lattice parameters and atomic positions for each space group were obtained from the Rietveld refinement. From these results, the four types of bond lengths ($2 \times d_1$, $2 \times d_2$, d_3 , d_4) for the orthorhombic phase ($Amm2$) and the three types of bond lengths (d_1 , d_2 , $4 \times d_3$) for the tetragonal phase ($P4mm$) were obtained in an NbO_6 octahedra, respectively.

These changes of bond lengths affect the distortion of NbO_6 octahedra which was calculated in Eq. (1) [19];

$$\Delta = \frac{1}{6} \sum \left\{ \frac{(R_i - \bar{R})}{\bar{R}} \right\}^2 \quad (1)$$

where R_i is the individual bond length, and $\bar{R}$ is the average bond length of the oxygen octahedral. With increasing of Ta^{5+} content, the average octahedral distortion (Δ) between the orthorhombic and tetragonal phase of the LKNNT specimens prepared by the CMO method and PSG method was decreased due to the increase of the volume fraction of the tetragonal phase.

The vibration of the NbO_6 octahedra on the $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)-based ceramics was determined by the Raman spectrum mode [20]. The Raman spectrum of the LKNNT specimens prepared by the CMO method and PSG method with Ta^{5+} content is shown in Fig. 2. The A_{1g} and F_{2g} modes indicate the double-degenerate symmetric O-Nb-O stretching vibration and triply-degenerate symmetric O-Nb-O bending vibration, respectively [20]. The peaks of the F_{2g} mode shift to a

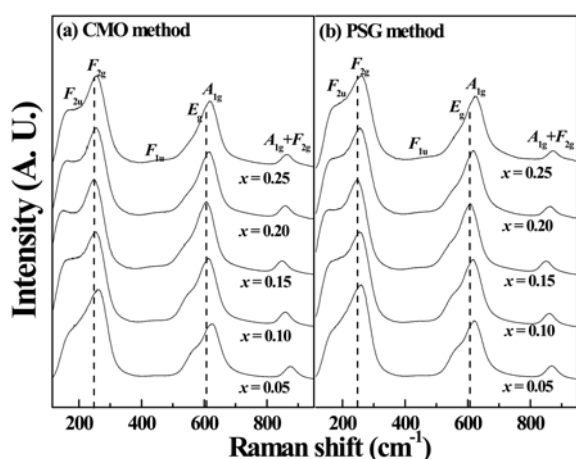


Fig. 2. Raman spectrum of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100°C for 5 hrs prepared by (a) conventional mixed oxide (CMO) method and (b) partial sol-gel (PSG) method.

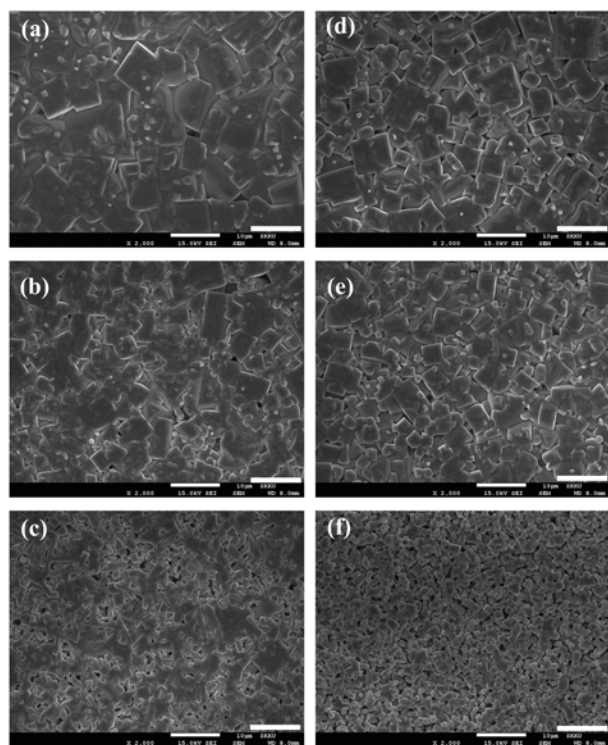


Fig. 3. SEM micrographs of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100°C for 5 hrs prepared by conventional mixed oxide (CMO) method ((a) $x = 0.05$, (b) $x = 0.15$, (c) $x = 0.25$) and partial sol-gel (PSG) method ((d) $x = 0.05$, (e) $x = 0.15$, (f) $x = 0.25$) (Bar = $10\mu\text{m}$).

lower wave number up to $x = 0.15$, and then increased with further addition of Ta^{5+} content. These results could be explained by the fact that the orthorhombic-tetragonal phase boundary of the LKNNT specimens was observed around $x = 0.15$.

Fig. 3 shows SEM micrographs of the polished and thermal etched surfaces of LKNNT specimens. For the specimens with the same content of Ta^{5+} , the grain size of the LKNNT specimens prepared by the PSG method

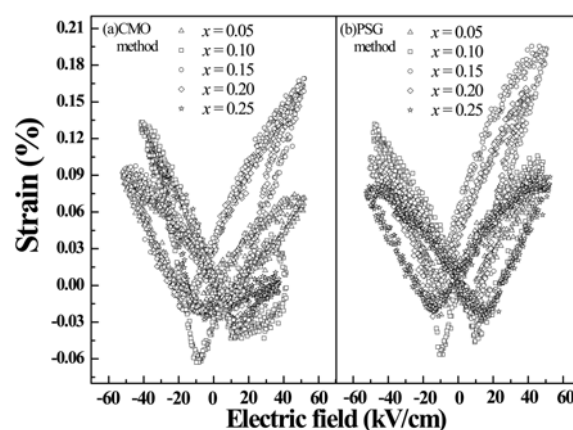


Fig. 4. Typical bipolar S - E curve of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100°C for 5 hrs prepared by (a) conventional mixed oxide (CMO) method and (b) partial sol-gel (PSG) method.

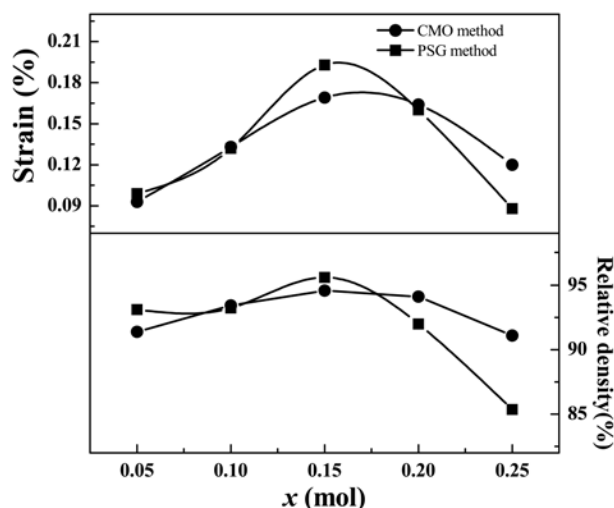


Fig. 5. Dependence of maximum strain on the relative density of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100°C for 5 hrs prepared by (a) conventional mixed oxide (CMO) method and (b) partial sol-gel (PSG) method.

was smaller with a uniform grain than that of the LKNNT specimens prepared by the CMO method. With increasing of Ta^{5+} content, the grain size was decreased due to the inhibition of grain growth. The grain size was remarkably decreased with Ta^{5+} content and pores were observed at the composition of $x = 0.25$, which was in agreement with the relative density of the sintered specimens (Fig. 5).

Strain characteristics and electrical properties

Fig. 4 shows the bipolar field-induced strain (S - E) curves of LKNNT ceramics with Ta^{5+} content. From the measured S - E curves, S_{max} is plotted in Fig. 5. With increasing of Ta^{5+} content, S_{max} was increased up to $x = 0.15$ and then decreased. The S_{max} of the LKNNT specimens prepared by the PSG method was larger than that of the LKNNT specimens prepared by the CMO method, because the relative density and micro-

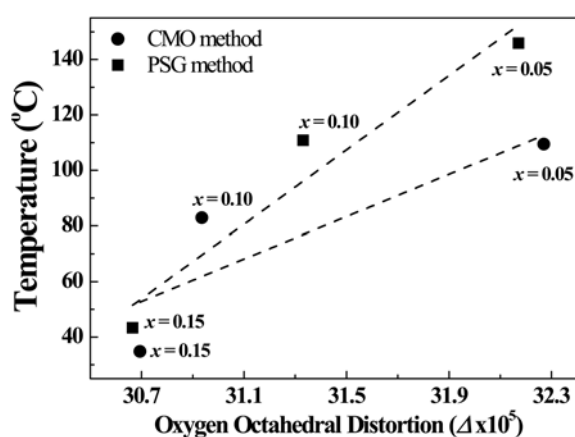


Fig. 6. Dependence of phase transition temperature on the average octahedral distortion of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100 °C for 5 hrs prepared by (a) conventional mixed oxide (CMO) method and (b) partial sol-gel (PSG) method.

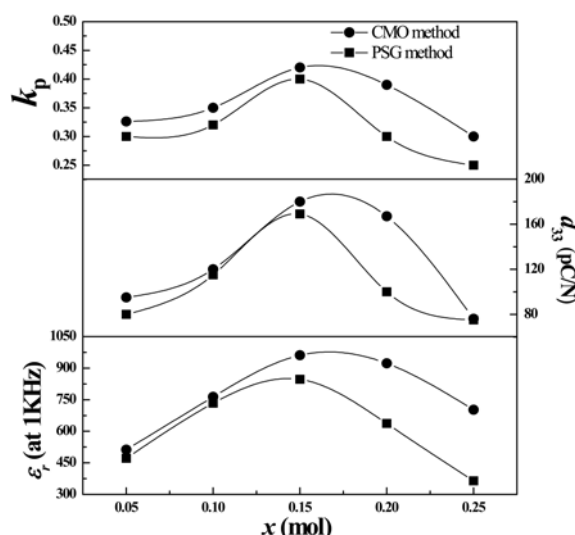


Fig. 7. Electrical properties (k_p , d_{33} and ϵ_r) of $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) sintered at 1100 °C for 5 hrs prepared by conventional mixed oxide (CMO) method and partial sol-gel (PSG) method.

structure of the LKNNT specimens prepared by the PSG method were higher and more homogeneous than those of the LKNNT specimens prepared by the CMO method.

For the specimens prepared by the CMO method and PSG method, with an increase of Ta^{5+} content, the orthorhombic-tetragonal phase transition temperature ($T_{\text{O-T}}$) was shifted to near room temperature up to $x = 0.15$ and then disappeared with the further addition of Ta^{5+} content. These results could be attributed to the average oxygen octahedral distortion, as shown in Fig. 6. With decreasing of average oxygen octahedral distortion, the $T_{\text{O-T}}$ of LKNNT specimens was decreased.

The piezoelectric constant (d_{33}), electromechanical coupling coefficient (k_p) and dielectric constant (ϵ_r) of the specimens are shown in Fig. 7. With increasing of

Ta^{5+} content, the d_{33} , k_p and ϵ_r of the LKNNT specimens prepared by the CMO method increased up to $x = 0.15$ and those of the LKNNT specimens prepared by the PSG method showed a similar tendency due to the $T_{\text{O-T}}$ at near room temperature (Fig. 6) [8, 9]. However, the d_{33} , k_p and ϵ_r of the LKNNT specimens prepared by the CMO method were larger than those of the LKNNT specimens prepared by the PSG method. These results could be explained by the fact that the $T_{\text{O-T}}$ of LKNNT specimens prepared by the CMO method shifted more toward room temperature than the LKNNT specimens prepared by PSG method.

Conclusions

For the $[\text{Li}_{0.055}(\text{K}_{0.5}\text{Na}_{0.5})_{0.945}](\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ($0.05 \leq x \leq 0.25$) specimens sintered at 1100 °C for 5 hrs, the morphotropic phase boundary (MPB) between orthorhombic ($Amm2$) and tetragonal ($P4mm$) phases was detected. With increasing of Ta^{5+} content, the volume fraction of the tetragonal ($P4mm$) phase of the sintered specimens was increased. The S_{max} of LKNNT specimens prepared by the partial sol-gel method was larger than that of the LKNNT specimens prepared by the conventional mixed oxide method. The average oxygen octahedral distortion was decreased with Ta^{5+} content. The phase transition temperature ($T_{\text{O-T}}$) was decreased with decreasing of average oxygen octahedral distortion. The electrical properties (ϵ_r , d_{33} and k_p) strain characteristics of the LKNNT specimens increased with Ta^{5+} content up to $x = 0.15$, and then decreased due to the $T_{\text{O-T}}$ at near room temperature.

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