



Ferroelectric Property and Crystal Structure of KNbO₃ Based Ceramics

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Abstract. Rietveld refinement analysis was carried out to obtain the knowledge on the solid solution structure of the La and Fe co-doped KNbO₃ ceramics. The diffraction data was well fitted with tetragonal space group *P4mm*, and showed that La and Fe located at K and Nb sites in KNbO₃ perovskite, respectively. The sum of both occupancy ratios agreed almost well with the doping content. Furthermore, the effects of MnO₂ addition on the ferroelectric properties and crystal structure of the La and Fe co-doped KNbO₃ ceramics were investigated. MnO₂ addition strongly affected the ferroelectric and piezoelectric properties, because the valence of Mn ions changed from Mn⁴⁺ to some extents of Mn³⁺ and Mn²⁺, which were suggested by XAFS analysis.

Keywords: KNbO₃, LaFeO₃, piezoelectrics, Rietveld analysis, XANES analysis

1. Introduction

Potassium niobate, KNbO₃ is an important candidate of lead-free piezoelectric materials, since the single crystal shows a large electromechanical coupling factor [1]. Compared with KNbO₃ single crystals, preparation of sintered ceramics has a commercial merit from the viewpoints of productivity and shape flexibility. However, the synthesis of highly dense KNbO₃ ceramic body has been considered to be difficult by ordinary pressure sintering [2, 3]. One of the main reasons is that potassium oxide, K₂O, easily volatilizes with increasing temperature during sintering process. As a result, some of unstable secondary phases form in the final product and show deliquesce when exposed to humidity [4]. This is a severe problem for controlling stoichiometry and phase stability of KNbO₃ ceramics.

In the preceding paper, we reported the ferroelectric property of La and Fe co-doped KNbO₃ ceramics for the first time [5]. This new class of KNbO₃ ceramics demonstrated a good sintering behavior and showed 98% of theoretical density even under pressure-less sintering. When the doping amount of La and Fe

equals to 0.002 mol only, KNbO₃ ceramics showed an excellent ferroelectric hysteresis loop with remanent polarization (P_r) of 18 $\mu\text{C}/\text{cm}^2$ and coercive field (E_c) of 9 kV/cm. Moreover, the electrically poled ceramics demonstrated an electromechanical coupling factor (k_p) of 0.17 and piezoelectric constant (d_{33}) of 98 pC/N. However, the origin of enhancement in the sintering behavior of KNbO₃ ceramics by addition of La and Fe has never been clear.

On the other hand, there are many reports that the dielectric properties are controllable by adding MnO₂ into ferroelectrics. Yokosuka et al. reported that substitution for Ca by Mn in Bi₄Sr_xCa_{1-x}Ti₄O₁₅ ceramics played an important role in enhancing the piezoelectricity [6]. Park et al. also reported that mechanical quality factor (Q_m) increased with an addition of MnO₂ in Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ relaxor ferroelectrics, because Mn behaved as an acceptor which worked as a domain-pinning constituent [7]. Therefore, it is also interesting to study the effect of MnO₂ addition on the ferroelectric properties of La and Fe co-doped KNbO₃ ceramics, since Mn as well as Fe is known to be multivalent cations.

In this study, crystallographic evaluation of La and Fe co-doped KNbO₃ ceramics was performed for better understanding of the solid solution structure. Furthermore, the effect of MnO₂ addition on the ferroelectric

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property of the KNbO_3 ceramics was investigated in terms of the valence status of Mn ion.

2. Experimental Procedure

High purity ($\geq 99.9\%$) powders of K_2CO_3 , Nb_2O_5 , La_2O_3 , Fe_2O_3 and MnO_2 were used as the raw materials. These powders were weighed according to the compositional formula of $(\text{K}_{0.998}\text{La}_{0.002})(\text{Nb}_{0.998}\text{Fe}_{0.002})\text{O}_3 + y \text{ wt}\% \text{MnO}_2$, where y varied from 0 to 1.0. The weighed powders were mixed for 24 h in acetone with zirconia balls (5 mm ϕ) using wet ball-milling technique. The dried mixed powders were calcined at 820°C for 4 h, then a pelletized disc was calcined at 850°C for 4 h. The calcined disc was pulverized, sieved through a 300-mesh screen, and pressed under a pressure of 98 MPa into a disc with 12 mm in diameter. The disc was further cold-isostatic-pressed under 200 MPa, then placed on a powder-bed made of the same composition powders, and sintered at 1060°C for 4 h.

The crystal structure of sintered specimens was investigated by the Rietveld refinement analysis of powder X-ray diffraction data. The X-ray absorption fine structure (XAFS) analysis was also carried out using synchrotron X-ray data to evaluate the multi-valence status of Fe and Mn.

Silver electrodes were formed on both sides of specimens for dielectric measurement. The temperature dependence of the dielectric properties was measured using a LCR meter at 1 kHz in the temperature range from 500°C to room temperature. P - E hysteresis loops and electric-field-induced strain loops were measured by an aixACT TF2000FE-HV ferroelectric test unit. Specimens for the piezoelectric measurements were poled at 100°C in a silicon oil bath with field strength of 1 kV/mm for 60 min. The planar electromechanical coupling factors k_p were determined from the resonant and antiresonant frequencies measured by an impedance analyzer (Agilent 4294A). Piezoelectric d_{33} constants were directly measured at room temperature using the quasi-static method by a d_{33} meter (Academia Sinica ZJ-4B).

3. Results and Discussion

Figure 1 shows the measured powder X-ray diffraction pattern and its fitting result by the Rietveld analysis using RIETAN-2000 program [8]. The powder specimen was prepared from La and Fe co-doped (0.1 mol) KNbO_3 ceramics to check the occupation sites of La and Fe. The diffraction data was well fitted with tetragonal space group $P4mm$. Our previous study found that the crystal system of KNbO_3 changed from

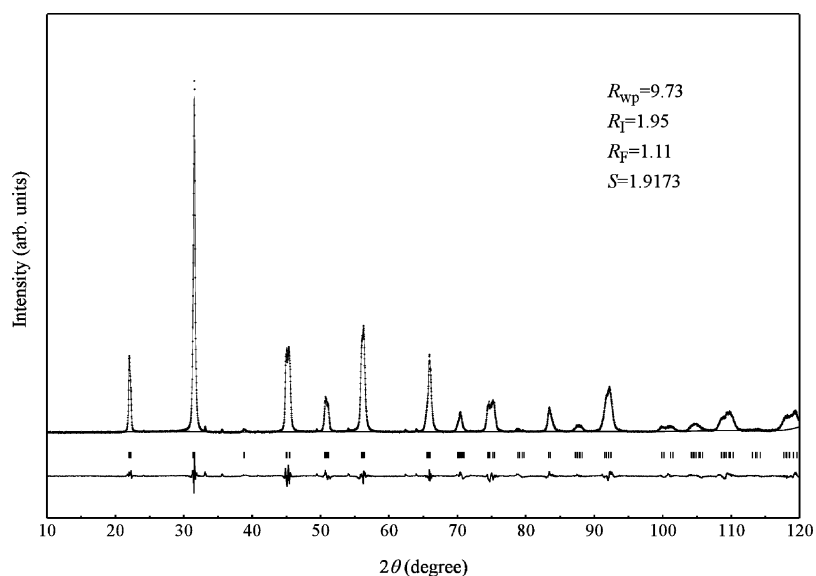


Fig. 1. Observed (symbols) and calculated (solid line) X-ray diffraction patterns by the Rietveld analysis for the La and Fe co-doped (0.1 mol) KNbO_3 ceramics.

orthorhombic space group *Amm*2 to tetragonal symmetry with increasing doping content of La and Fe. The Rietveld analysis showed that La and Fe located at K and Nb sites in KNbO₃ perovskite, respectively. Calculated site occupancy of La ions was 0.098 at K site and that of Fe ions was 0.101 at Nb site. Each occupancy ratio agreed almost well with their doping contents. Therefore, KNbO₃ formed a solid solution represented as a formula of (K_{1-x}La_x)(Nb_{1-x}Fe_x)O₃ which

matched with the initially assumed formula in the starting mixture composition. However, the occupancy of K ions was calculated to be 0.825, which indicates that massive loss of K₂O occurred in the sintering process.

Figure 2 shows the X-ray absorption near edge structure (XANES) data obtained from La and Fe co-doped (0.002 mol) KNbO₃ ceramics with addition of MnO₂ (0.5 wt%). The absolute excitation energy (E_0) in Fe *K*-edge spectra, which was defined as inflection points

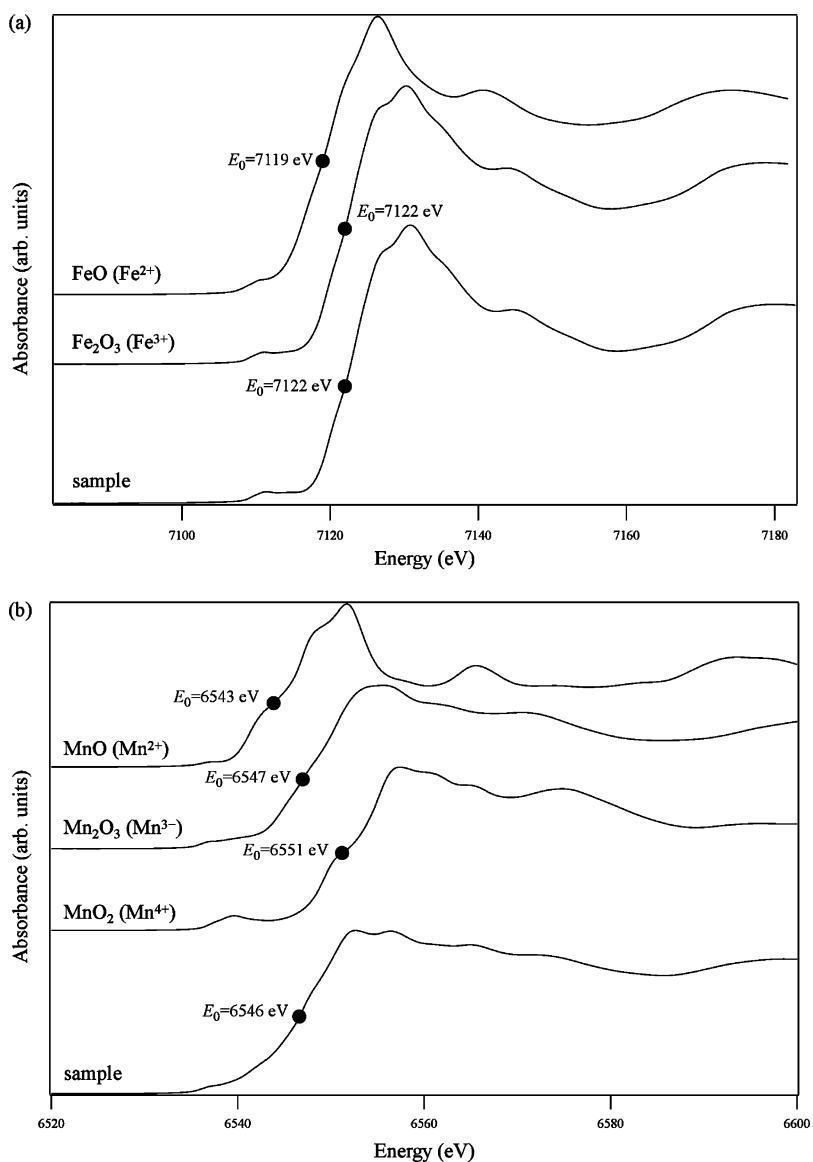


Fig. 2. XANES spectra of the (a) Fe *K*-edge and (b) Mn *K*-edge of the La and Fe co-doped (0.002 mol) KNbO₃ ceramics with addition of MnO₂ (0.5 wt%).

indicated by solid circles, was measured to be 7119 and 7122 eV for standard samples of FeO (Fe^{2+}) and Fe_2O_3 (Fe^{3+}), respectively. The KNbO_3 solid solution showed E_0 of 7122 eV, and well agreed with the value of standard Fe_2O_3 (Fe^{3+}). This informs that the valence of Fe at Nb site was unchanged from its doping status and equaled to +3. On the other hand, the E_0 values obtained from Mn *K*-edges for three kinds of standards MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}) and MnO_2 (Mn^{4+}) were 6543, 6547 and 6551 eV, respectively. The KNbO_3 solid solution demonstrated a mixture edge shape, indicating the change from initial doping status of MnO_2 (Mn^{4+}). A fitting calculation determined that the mixture ratio of $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$ equaled to be 37.1/50.3/12.6 %. This result suggests that a part of Mn ions changed from Mn^{4+} to Mn^{3+} and Mn^{2+} . Especially, Mn^{3+} has an ionic radius of 0.645 Å, which is almost identical to 0.64 Å of Nb^{5+} , indicating a possibility that Mn^{3+} as well as Fe has dissolved into Nb site.

As shown in Fig. 3, the addition of MnO_2 altered the temperature dependence of dielectric constant (ϵ_r) of La and Fe co-doped KNbO_3 ceramics. Two peaks observed at 395 and 200°C corresponded to phase transitions from cubic to tetragonal (Curie temperature, T_c) and tetragonal to orthorhombic symmetry, respectively. These transition temperatures were independent on Mn content. On the other hand, ϵ_r increased significantly by addition of MnO_2 . At $y = 0.50$, ϵ_r showed the highest value of 3581 at T_c . However, a steep increase of ϵ_r above 500°C is observed at the same time. This may

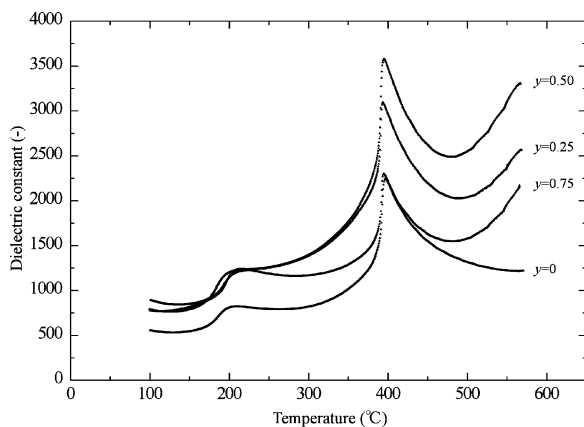


Fig. 3. Temperature dependence of dielectric constants of the La and Fe co-doped (0.002 mol) KNbO_3 ceramics with various MnO_2 contents of y from 0 to 0.75 wt%.

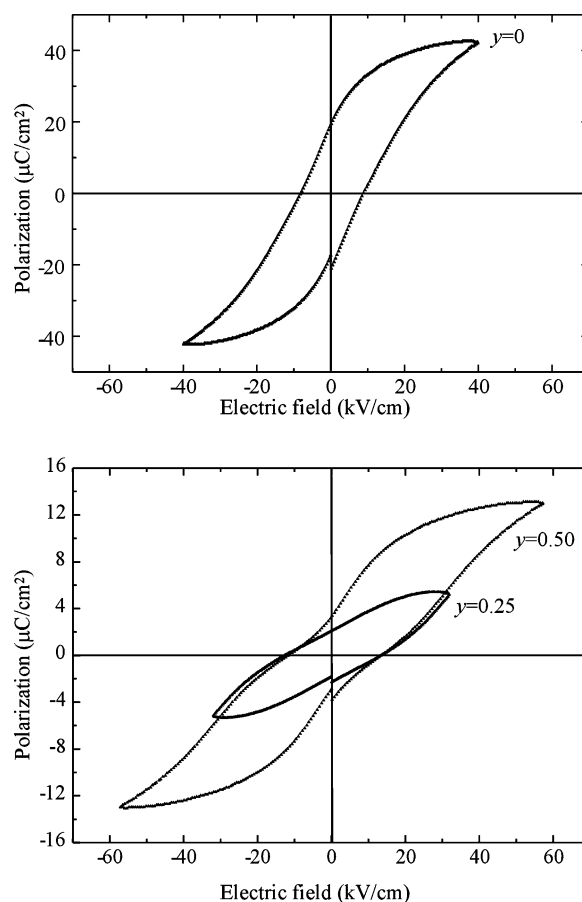


Fig. 4. P - E hysteresis loops of the La and Fe co-doped KNbO_3 ceramics with various MnO_2 contents.

imply that the Mn-containing samples also show high ionic conductivity, indicating that charge imbalance has occurred by partial Mn incorporation into Nb site.

Ferroelectric P - E hysteresis loops of samples with different MnO_2 content are shown in Fig. 4. Noteworthy is that the P - E hysteresis loop is deformed in the Mn-containing samples. By addition of MnO_2 , La and Fe co-doped KNbO_3 ceramics reduced remanent polarization (P_r) significantly. The observed P_r values were 18, 2 and 3 $\mu\text{C}/\text{cm}^2$ for the samples with MnO_2 additive of 0, 0.25 and 0.50 wt%, respectively. This constriction shape seems to be related to space charges formed by the fluctuation of Mn valence. A part of internal electric field must have been formed within the specimens by addition of MnO_2 . However, the ferroelectric property was recovered with increasing Mn content. This indicates that mixture effects worked in the property change. It is considered that one is

Table 1. Piezoelectric property of La and Fe co-doped (0.002 mol) KNbO₃ ceramics.

y	d_{33} (pC/N)
0	98
0.25	67
0.50	90

domain-wall pinning caused by oxygen vacancies to lower the ferroelectric property and the other is the presence of residual Mn-containing phases at grain boundaries to enhance the electric-field resistance. Table 1 compares the piezoelectric properties of the samples with different amounts of MnO₂ addition. The piezoelectric constant d_{33} was varied as similar to the case for the ferroelectric loop, although the planar electromechanical coupling factor (k_p) was not hardly affected by addition of MnO₂.

4. Conclusion

It was found by the Rietveld analysis that La and Fe were soluble at K and Nb sites, respectively in KNbO₃ structure to form (K_{1-x}La_x)(Nb_{1-x}Fe_x)O₃ solid solution. This analysis also indicated that the solid solution was off-stoichiometry in terms of K. MnO₂ addition altered the ferroelectric and piezoelectric properties of KNbO₃ solid solution. XANES analysis clearly showed valence change occurred in Mn ions.

This valence change was considered to have occurred in order to fit better into the Nb site by reducing the ionic size of Mn, which resulted in the formation of partial space charge in the specimens. The selection of soluble cations at K site to compensate for loss of K may be desirable for the property enhancement in La and Fe co-doped KNbO₃ ceramics.

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