Defect control for polarization properties in $K_{0.5}Na_{0.5}NbO_3$ single crystals

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ABSTRACT

Single crystals of $K_{0.47}Na_{0.53}NbO_3$ (KNN) and Mn-substituted KNN (Mn-KNN, $K_{0.53}Na_{0.47}Mn_{0.004}Nb_{0.996}O_y$) were grown by a flux method, and the influence of lattice defects on the polarization and leakage current properties was investigated. As-grown KNN did not show an apparent polarization hysteresis loop due to its large leakage current ($\sim10^{-3}$ A/cm^2). 0.4 at.%-Mn-KNN annealed at 1100°C in air exhibited a low leakage current ($\sim10^{-8}$ A/cm^2), a relatively large remanent polarization of 40 μC/cm^2 and a coercive field of 12 kV/cm at 25°C. The oxidation of Mn and Nb ions during annealing in air was found to play an essential role in the low leakage current in Mn-KNN. Mn substitution followed by annealing under moderate oxidation condition was effective for reducing leakage current in addition to enhancing polarization property.

Keywords: ferroelectric, piezoelectric, potassium sodium niobate, KNN, defect, single crystal

1. INTRODUCTION

Lead zirconium titanate (PZT) ceramics have been widely used for piezoelectric applications such as sensors, actuators and transducers etc.. PZT based ceramics, however, contain a large amount of toxic lead, and the use of lead elements in electronic materials would be restricted in the near future. Thus, the development of lead-free piezoelectric materials with sufficient ferroelectric and piezoelectric properties has been strongly demanded from the environmental and economical points of view.

Potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$: KNN) has been regarded as a promising lead-free piezoelectric material, because of its high Curie temperature and superior piezoelectric properties.[1-5] However, ceramics and films of KNN suffer from a high leakage current due to lattice defects, probably originating from the evaporation of K with high volatility. [6-8] Leakage current properties are closely related not only to defect structure in grains but also to microstructure of samples. To know the effects of lattice defects on the leakage current, investigations on single crystals are expected to be advantageous. In this study, KNN single crystals were grown by a flux method, and the effects of Mn substitution on the leakage current, polarization and piezoelectric properties were investigated.

2. EXPERIMENTAL

KNN and Mn-doped KNN ceramics were prepared by a conventional mixed oxide method. Raw materials of K_2CO_3, Na_2CO_3, Nb_2O_5 and Mn_2O_3 were mixed by a ball milling for 1 h. The mixture was calcined at 800°C for 5 h in air.

Crystals of KNN and Mn-KNN were grown by a flux method in air. The calcined powders of KNN and Mn-KNN were mixed with KF-NaF eutectic flux, and the mixture was put in a Pt crucible. The materials were melted at 1050°C for 5 h and then slowly cooled down to 950°C. The crystal was dark blue in color with the size of 2×2×2 mm^3. The annealing at 1100°C in air changed colors of the crystals from dark blue to white for KNN and to brown for Mn-KNN. The compositions of KNN and Mn-KNN crystals determined by inductively coupled plasma emission spectroscopy were $K_{0.47}Na_{0.53}NbO_3$ and $K_{0.53}Na_{0.47}Mn_{0.004}Nb_{0.996}O_y$, respectively.

Gold electrodes were sputtered onto the surfaces of the crystals. The leakage current and polarization hysteresis properties were measured at 25°C using an FCE-2STD (TOYO Corporation, Japan). The dielectric properties were measured using an impedance analyzer HP4194A (Agilent Technologies, USA) in the temperature range from 30°C to 500°C. Electric-field-induced strain was measured using a contact-type displacement sensor at 1 Hz. In these measurements, electric field was applied along the pseudocubic $[100]_C$ direction of the orthorhombic crystals. [9,10] Electron spin resonance (ESR) investigation were performed for crushed powers of Mn-KNN crystals at -160°C.
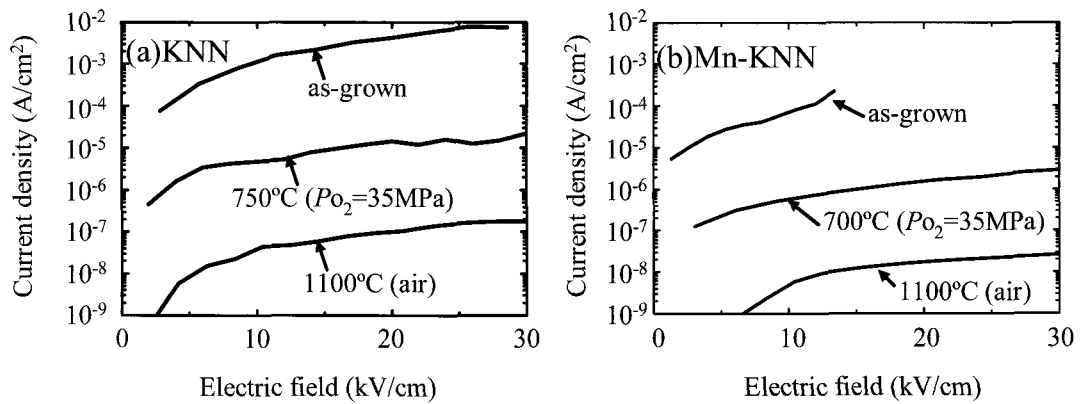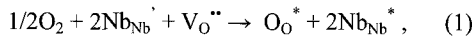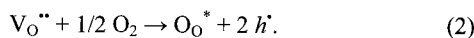
3. RESULT AND DISCUSSION

Fig.1 Leakage current properties of
(a) KNN and (b) Mn-KNN crystals annealed under various oxidation conditions.
Electric field was applied along the $[100]_C$ direction.

Figure 1(a) shows the leakage current density (J) of KNN crystals measured at 25°C. As-grown crystals exhibited a high J over 10^{-3} A/cm^2 due to electrical conduction through the conduction band (d band) attributed to Nb^{4+}, as suggested by the blue color of the crystals. [6,11-13] The annealing at 1100°C in air yielded a white crystal with a low J of the order of 10^{-7} A/cm^2, which implies that the valence increase from Nb^{4+} (Nb$_{Nb}$') to Nb^{5+} (Nb$_{Nb}$$^\times$) is accomplished by the oxidation treatment. This oxidation reaction is expressed by

$$1/2O_2 + 2Nb_{Nb}' + V_O^{\cdot\cdot} \rightarrow O_O^\times + 2Nb_{Nb}^\times, \quad (1)$$

where $V_O^{\cdot\cdot}$ indicates the vacancy at the oxide-ion site and $O_O^\times$ is O^{2-} at the oxide-ion site.

Further oxidation by annealing under a high-pressure oxygen (P_{O2} = 35 MPa) atmosphere at 750°C for 10 h gave rise to a significant increase in J to ~10^{-5} A/cm^2. The air annealing yielded a marked decrease of Nb^{4+} responsible for high J, while a large amount of $V_O^{\cdot\cdot}$ is likely to exist, probably originating from K vacancies formed during high-temperature crystal growth. It is reasonable to consider that further oxidation by the high-P_{O2} (35 MPa) annealing indeed decreased $V_O^{\cdot\cdot}$, as expressed by
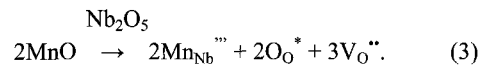
$$V_O^{\cdot\cdot} + 1/2 O_2 \rightarrow O_O^\times + 2 h^\cdot. \quad (2)$$

When KNN absorbs oxygen into the lattice, the oxygen occupies $V_O^{\cdot\cdot}$ as $O_O^\times$ accompanied by the formation of $h^\cdot$. A significant increase in J by the high-P_{O2} annealing demonstrates that the hole ($h^\cdot$) arising from oxygen absorption into the lattice is the dominant carrier for the leakage current of oxidized KNN crystals.

The same tendency of J was observed for Mn-KNN crystals. Figure 1(b) shows the J of Mn-KNN crystals measured at 25°C. As-grown crystals of Mn-KNN showed a high J over 10^{-4} A/cm^2. The annealing at 1100°C in air led to a decrease in J to ~10^{-8} A/cm^2. The

high-P_{O2} annealing increased J, as can be observed also for KNN crystals.

Note that the J of Mn-KNN annealed at 1100°C in air was of the order of 10^{-8} A/cm^2, which was lower than that of KNN annealed at 1100°C in air. This result shows that Mn substitution is effective for suppressing leakage current of KNN crystals.

In order to clarify the valence state of Mn, electron spin resonance (ESR) investigations were performed for crushed powders of Mn-KNN crystals. Figure 2 shows the X-band ESR spectra of the crystals observed at -160°C. As-grown crystals exhibited the hyperfine structure with six prominent lines of typical isolated Mn^{2+}. In these crystals, Mn is substituted at the Nb^{5+} site as Mn^{2+} (Mn$_{Nb}$''') accompanied by the formation of $V_O^{\cdot\cdot}$ as expressed by

$$\begin{array}{c} Nb_2O_5 \\ 2MnO \rightarrow 2Mn_{Nb}''' + 2O_O^\times + 3V_O^{\cdot\cdot}. \end{array} \quad (3)$$

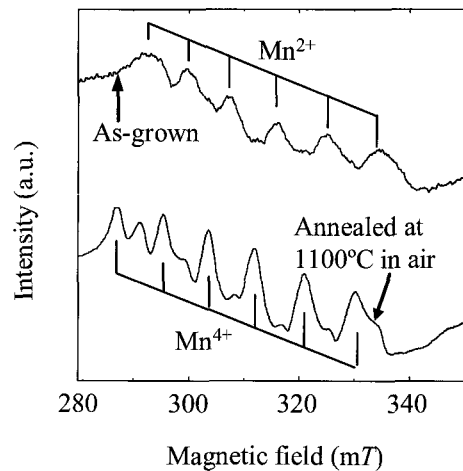Note that the crystals annealed at 1100°C in air
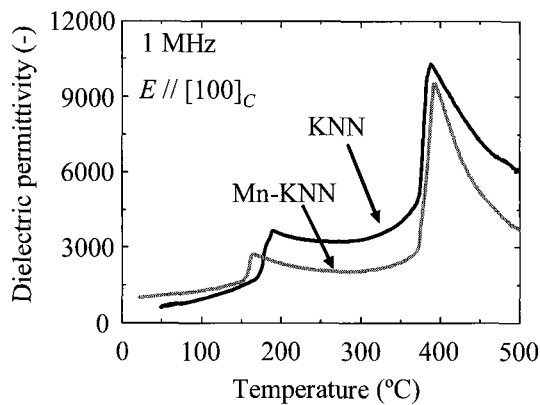

Fig.2 X-band ESR spectra of Mn-KNN crystals observed at -160°C.

Fig.3 Temperature dependence of dielectric Permittivity of KNN and Mn-KNN crystals annealed at 1100°C in air.
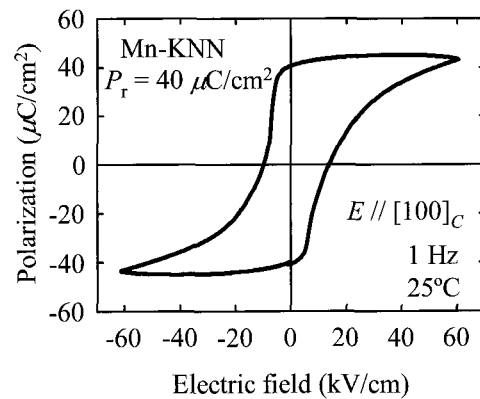

Fig.4 Polarization hysteresis loop of Mn-KNN crystals annealed at 1100°C in air.

Fig.5 Electric-field-induced strain of KNN and Mn-KNN crystals annealed at 1100°C in air.

indicate a superimposed signal originating from Mn^{2+} and Mn^{4+}. This spectrum clearly show that Mn^{2+} is partially oxidized to higher valent cations and that Mn^{2+}, Mn^{3+}, and Mn^{4+} occupy the Nb^{5+} site with mixed valent state (Mn^{3+} is silent in X-band ESR measurements). These ESR investigations provide definite evidence that oxidation by air annealing increases average Mn valence in Mn-doped crystals.

Here, we discuss the origin of the low leakage current in Mn-KNN crystals. Electron spin resonance (ESR) investigations combined with XRD structural analysis have demonstrated that Mn ions are present as Mn^{2+} at the Nb site in as-grown crystals. [14-16] Air annealing increased a valence state of Mn^{2+} to Mn^{3+} and Mn^{4+}. This reaction is expressed by

$$Mn_{Nb}''' + h^{\bullet} \rightarrow Mn_{Nb}''$$
$$Mn_{Nb}'' + h^{\bullet} \rightarrow Mn_{Nb}'. \qquad (4)$$
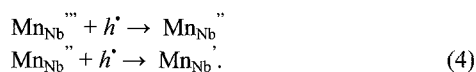
In KNN crystals, $h^{\bullet}$ is indicated to be the dominant carrier for leakage current, as discussed above. For Mn-KNN, the valence increase in Mn can absorb $h^{\bullet}$ generated during air annealing according to the Eq. (4), which leads to a low leakage current for Mn-KNN.

Figure 3 shows the temperature dependence of dielectric permittivity (ε_r) of KNN and Mn-KNN annealed at 1100°C in air. The ε_r as a function of temperature exhibited two sharp peaks corresponding to the two phase transitions: orthorhombic to tetragonal (T_{ot}) and tetragonal to cubic (T_{tc}) during heating. The T_{ot} and T_{tc} of Mn-KNN were 160°C and 390°C, respectively. This T_{tc} was nearly the same as that of KNN crystals, whereas the T_{ot} was lower than that of KNN (190°C). The ε_r at room temperature were about 600 for KNN and 740 for Mn-KNN.

Figure 4 shows the polarization hysteresis loop of Mn-KNN annealed at 1100°C in air. A saturated polarization was observed. A remanent polarization (P_r) of 40 $\mu C/cm^2$ and a coercive field (E_c) of 12 kV/cm
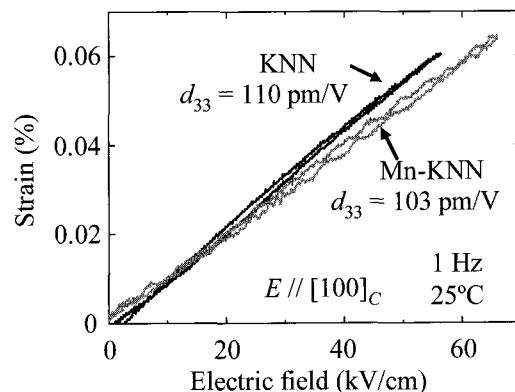
were obtained. This P_r value was larger than those reported for KNN-based ceramics. [7,17-19] Other crystals did not show an apparent hysteresis loop due to their high J.

Figure 5 shows electric-field-induced strain of KNN and Mn-KNN single crystals annealed at 1100°C in air. The strain of these crystals increased linearly with increasing applied electric field and no hysteresis were observed. The piezoelectric d_{33} values calculated from the slope were 110 pm/V for KNN and 103 pm/V for Mn-KNN. KNN-based ceramics have been reported to exhibit a hysteresis behavior of strain curve, leading to a relatively larger strain over 0.08% under an applied electric field of 40-50 kV/cm. [17,20] The polarization rotation of non-180-deg domains seems to be partially responsible for the larger strain observed for KNN-based ceramics. This polarization rotation was not observed for the single crystals, leading to the smaller strain than those of KNN-based ceramics.

4. CONCLUSION

Crystals of KNN and Mn-KNN were grown by a flux method, and the effects of Mn substitution on the leakage

current, polarization and piezoelectric properties were studied. KNN showed a relatively large leakage current, while Mn substitution and following annealing in air were effective for suppressing leakage current. Mn-KNN annealed in air exhibited a large P_r of 40 $\mu C/cm^2$. Piezoelectric strain of KNN and Mn-KNN crystals increased linearly with increasing applied electric field and showed no hysteresis in the strain curve. The piezoelectric d_{33} values calculated from the slope were 110 pm/V for KNN and 103 pm/V for Mn-KNN, respectively.

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