

# Effect of Mn doping on the leakage current and polarization properties in $K_{0.14}Na_{0.86}NbO_3$ ferroelectric single crystals

Yuji NOGUCHI<sup>†</sup> and Masaru MIYAYAMA

Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904

Single crystals of  $K_{0.14}Na_{0.86}NbO_3$  (KNN) and Mn-substituted KNN (Mn-KNN,  $K_{0.14}Na_{0.86}Mn_{0.005}Nb_{0.995}O_3$ ) were grown by a flux method, and the effects of Mn substitution on the leakage current, polarization and dielectric properties were investigated along [100]<sub>cubic</sub>. As-grown and annealed (850°C in air) crystals did not show an apparent polarization hysteresis loop due to its large leakage current density ( $\sim 10^{-3}$  A/cm<sup>2</sup>). The annealing at 1100°C in air led to a marked decrease in leakage current density of the order of  $\sim 10^{-6}$  A/cm<sup>2</sup> for KNN crystals. Mn-KNN crystals annealed at 1100°C in air exhibited a low leakage current density of  $\sim 10^{-8}$  A/cm<sup>2</sup>. Electron spin resonance measurements and defect chemistry analysis show that the average valence increase of Mn by oxidation treatment (the annealing in air) absorbs electron hole, the carrier of the leakage current, which is suggested to be the origin of the low leakage current observed for Mn-KNN crystals.

©2010 The Ceramic Society of Japan. All rights reserved.

Key-words : Ferroelectric, Defect, KNN, Piezoelectric, Single crystal

[Received April 27, 2010; Accepted July 15, 2010]

## 1. Introduction

Lead zirconium titanate (PZT) and related materials<sup>(1),2)</sup> have been widely used for ferroelectric and piezoelectric applications such as nonvolatile memories, sensors, actuators and transducers.<sup>(3)–23)</sup> 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 in electronic devices. Thus, the development of lead-free materials with sufficient ferroelectric and piezoelectric properties has been strongly demanded from the environmental and economical points of view. In recent days, lead-free perovskite ferroelectrics of  $BaTiO_3$  (BT),<sup>(24)–40)</sup>  $(Bi,K,Na)TiO_3$ ,<sup>(41)–52)</sup>  $(K,Na)NbO_3$  (KNN)<sup>(53)–70)</sup> and Bi-layered ferroelectrics<sup>(71)–80)</sup> such as  $SrBi_2Ta_2O_9$  and  $Bi_4Ti_3O_{12}$  (BiT) and so on have attracted much attention as alternative materials of  $Pb(Zr,Ti)O_3$ .

Ti-based perovskite ferroelectrics such as  $BT$ <sup>(24)–26)</sup> and  $(Bi,Na,K)TiO_3$ <sup>(41)–43)</sup> have recognized as cost-effective lead-free piezoelectric materials. Recent investigations<sup>(24),25)</sup> have demonstrated that fine-grained BT ceramics with a grain size of  $\sim 100$  nm show a large piezoelectric strain constant  $d_{33}$ , in which engineered domain configurations<sup>(26),81)</sup> probably enhance the piezoelectric properties. However, Curie temperature ( $T_C$ ) of BT is as low as 135°C, and furthermore fine-grained BT ceramics exhibit a tetragonal-orthorhombic transition temperature at around room temperature. This phase transition constitutes an obstacle to the practical applications of BT.

Takenaka et al.<sup>(41),42)</sup> have shown that  $(Bi,Na)TiO_3$  (BNT) is an attractive piezoelectric material because of a high  $T_C$  of 320°C and a large spontaneous polarization. One of the problems to be overcome is that depolarization temperature ( $T_d$ ), i.e., piezoelectric activities disappear or are markedly reduced at  $T_d$ , lies around 200°C for BNT<sup>(44),47),51)</sup> due to structural phase transition from rhombohedral ( $R3c$  symmetry) to tetragonal ( $P4bm$  symmetry).<sup>(82),83)</sup>

It is well known that rhombohedral BNT constitutes a morphotropic phase boundary (MPB) with tetragonal BT. The piezoelectric properties have been enhanced for the ceramics of BNT-BT solid solutions near the MPB composition.<sup>(84)</sup> Although BNT-BT ceramics near the MPB composition have been intensively studied, marked enhancement in piezoelectric properties has not been achieved to date as well as the reported values of the piezoelectric constants etc. are scattered,<sup>(41)–48),51),52)</sup> which seems to be ascribed to the multiple influences of microstructure, grain size and orientation, nonstoichiometry and defects.

Potassium sodium niobate (KNN)<sup>(53),54)</sup> has been regarded as a promising lead-free piezoelectric material, because of its high  $T_C$  of 420°C and superior piezoelectric properties. KNN shows a consecutive structural phase transition from cubic to tetragonal around 420°C and tetragonal to orthorhombic around 200°C. Since Saito et al. have demonstrated that KNN-based ceramics show sufficient piezoelectric properties comparable to commercially-available PZT-based ceramics,<sup>(54)</sup> considerable interest has been devoted to improve the piezoelectric properties of KNN ceramics.

One of the problems in the KNN system, however, is a relatively high leakage current due to lattice defects.<sup>(55),85)</sup> Ceramics and films of KNN often suffer from a high leakage current due to lattice defects, probably originating from the evaporation of K with high volatility.<sup>(55)</sup> Leakage current properties of ceramics are closely related not only to defect structure in grains but also to microstructure. Leakage current interferes with polarization switching and poling process, and a poor insulating property makes piezoelectric material unsuitable for practical applications. To establish the guiding principle of defect control for suppressing leakage current of ferroelectric materials, investigations on single crystals are advantageous to know the influence of defects in ferroelectric lattice on properties.

In the preceding study,<sup>(55)</sup> the effects of Mn substitution on the leakage current properties for  $K_{0.47}Na_{0.53}NbO_3$  crystals were investigated. Although the defect structure and the relation with the Mn substitution were clarified,  $K_{0.47}Na_{0.53}NbO_3$  crystals did not exhibited an apparent polarization hysteresis due to a large

<sup>†</sup> Corresponding author: Y. Noguchi; E-mail: ynoguchi@crm.rcast.u-tokyo.ac.jp

leakage current. In this study, to reduce leakage current and to examine the effects of Mn substitution on the polarization properties, crystals with a low K content,  $K_{0.14}Na_{0.86}NbO_3$ , were grown by a flux method and the effects of the Mn substitution were investigated in detail.

## 2. Experimental procedure

Crystals of KNN and Mn-KNN with a low K content were grown by a self-flux method in air. For the crystal growth,  $NaNbO_3$  (NN) powder was used as the starting material. NN and Mn-doped NN powder ( $NaMn_yNb_{1-y}O_3$ ;  $y = 0.005$ ) were prepared by a conventional solid-state reaction. Raw materials of  $Na_2CO_3$  (99.95%),  $Nb_2O_5$  (99.99%) and  $Mn_2O_3$  (99.9%) were mixed in stoichiometric composition by a ball milling for 1 h. The mixture was calcined at 800°C for 5 h in air. Powder X-ray diffraction (XRD) data were collected and analyzed by the Rietveld method using the program RIETAN-2000<sup>86)</sup>. Although the space group of NN has been reported to be orthorhombic  $Pbma$ ,<sup>85)</sup> the Rietveld analysis was conducted based on  $Amm2$  orthorhombic symmetry<sup>53)</sup> because of the following reason: the precise refinement of lattice parameters and the comparison with  $K_{0.5}Na_{0.5}NbO_3$  that has  $Amm2$  symmetry.

Calcined powders of NN or Mn-NN ( $y = 0.005$ ) were mixed with KF-NaF eutectic flux, and the mixture was put in a Pt crucible. The weight ratio of NN or Mn-NN ( $x = 0.005$ ) powders, KF, and NaF was 5:2:1. The materials were melted at 1050–1150°C for 5 h and then slowly cooled down to 950–1050°C in air. The crystal was dark blue in color with the size of  $2 \times 2 \times 2$  mm<sup>3</sup>. The annealing at 1100°C for 5 h in air changed colors of the crystals from dark blue to white for KNN and to brown for Mn-KNN. It is suggested that the blue color originates from the presence of  $Nb^{4+}$  in the crystals because of the defect state of  $Nb^{4+}$  inside their band gap. The annealing at 1100°C for 5 h in air resulted in a complete oxidation of  $Nb^{4+}$  to  $Nb^{5+}$ , leading to a color change from blue to white.<sup>87,88)</sup>

The composition of KNN and Mn-KNN crystals determined by inductively coupled plasma atomic emission spectroscopy were  $K_{0.14}Na_{0.86}NbO_3$  and  $K_{0.14}Na_{0.86}Mn_{0.005}Nb_{0.995}O_3$ , respectively. Hereafter, these are denoted as KNN and Mn-KNN crystals. Electron spin resonance (ESR) spectroscopy was employed to study the valence state of Mn in the crystals. Leakage current and polarization were measured at 25°C for the crystals annealed under various oxidation conditions. In these measurements, electric field was applied along the pseudocubic (100)<sub>cubic</sub> direction of the crystals.

## 3. Results and discussion

**Figure 1** shows the XRD patterns of NN and Mn-NN powder obtained by a solid-state reaction and the powders obtained by crushing the crystals of KNN and Mn-KNN. These results indicate that all of the samples were of single phase with perovskite structure. The results of the Rietveld analysis of NN and Mn-NN powders are listed in **Table 1**. The resultant  $R$ -weighted pattern ( $R_{wp}$ ) of 9–11% and the goodness of fit ( $S$ ) of 1.6–1.8 were obtained. Since the distribution of crystalline size for the crushed powders of KNN and Mn-KNN crystals were much difference from the prediction by the simulation, a satisfactory fitting by the Rietveld analysis was not obtained for the crystals.

A marked change in lattice parameters by Mn substitution into NN was not detected in this study. While ionic radius of  $Mn^{3+}$  (coordination number of VI, high spin: 0.0645 nm, low spin: 0.058 nm) is equal to or smaller than those of  $Nb^{5+}$  (VI,

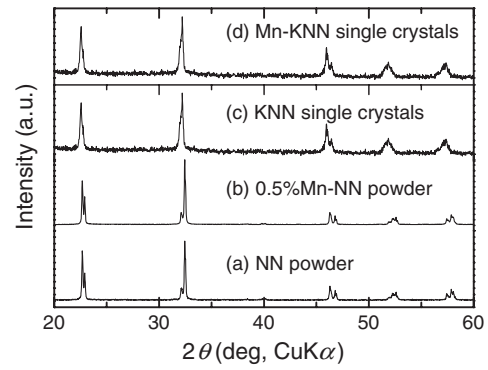


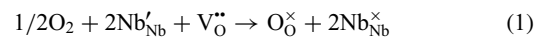
Fig. 1. The XRD patterns of NN and Mn-NN powder obtained by a solid-state reaction and the powders obtained by crushing the crystals of KNN and Mn-KNN.

Table 1. The results of the Rietveld analysis of NN( $NaNbO_3$ ) and Mn-NN( $NaMn_{0.005}Nb_{0.995}O_3$ )

Samples	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	Volume (nm <sup>3</sup> )	<i>R</i> <sub>wp</sub> (%)	<i>S</i> (—)
NN	0.38819(3)	0.55162(4)	0.55731(4)	0.11934(1)	10.53	1.78
Mn-NN	0.38817(2)	0.55165(4)	0.55728(4)	0.11933(1)	9.79	1.64

0.064 nm), the radius of  $Mn^{2+}$  (VI, high spin: 0.083 nm, low spin: 0.067 nm) is larger than that of  $Nb^{5+}$ .<sup>89)</sup> The unchanged lattice parameters and volume by the Mn substitution and ionic-size consideration suggest that the majority of Mn ions for the powder calcined at 800°C in air are substituted at the  $Nb^{5+}$  site as  $Mn^{3+}$  with the high-spin configuration, which is different from the substitution of  $Mn^{2+}$  with the low-spin configuration for  $K_{0.5}Na_{0.5}NbO_3$  powders.<sup>55)</sup>

**Figure 2** shows the leakage current density ( $J$ ) measured at 25°C along [100]<sub>cubic</sub> of KNN and Mn-doped crystals. Both as-grown crystals exhibited a high  $J$  over  $10^{-3}$  A/cm<sup>2</sup> due to electrical conduction through 4d electron of  $Nb^{4+}$ .<sup>90)</sup> For KNN crystals, the annealing at 850°C in air changed color of the crystals from dark blue to light blue and led to a decrease in  $J$  to  $\sim 10^{-4}$  A/cm<sup>2</sup>. This annealing was not, however, sufficient for decreasing leakage current due to the remanence of  $Nb^{4+}$ . The annealing at 1100°C for 5 h in air yielded a white crystal with a low  $J$  of the order of  $10^{-7}$  A/cm<sup>2</sup>, which shows that the valence increase of  $Nb^{4+}$  ( $Nb_{Nb}^{4+}$ ) to  $Nb^{5+}$  ( $Nb_{Nb}^{5+}$ ) are almost accomplished by the oxidation treatment at 1100°C in air. This oxidation reaction (first stage) is expressed by



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

The first stage oxidation by air annealing yields a marked decrease of  $Nb^{4+}$  responsible for high  $J$ , while a large amount of  $V_O^{\bullet\bullet}$  is still present in these KNN crystals, probably originating from K vacancies formed during high-temperature crystal growth.<sup>55,68)</sup> It has been reported that the annealing under high-pressure oxygen ( $P_{O_2} = 35$  MPa) atmosphere at 750°C for 10 h (the second stage oxidation) leads to a significant increase in  $J$  to  $\sim 10^{-5}$  A/cm<sup>2</sup>  $K_{0.5}Na_{0.5}NbO_3$  crystals.<sup>55)</sup> It is reasonable to consider that the oxidation by the high- $P_{O_2}$  annealing indeed decreases  $V_O^{\bullet\bullet}$ . The higher  $J$  induced by the second stage oxidation leads to a conclusion that the leakage current properties at room temperature of oxidized KNN crystals is governed by electron-hole ( $h^+$ ) conduction ( $p$  type) as expressed by

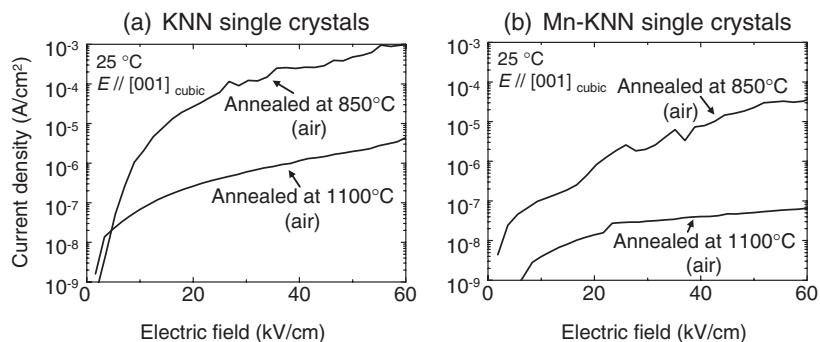


Fig. 2. The leakage current density ( $J$ ) measured at 25°C along  $[100]_{\text{cubic}}$  of KNN and Mn-doped crystals.

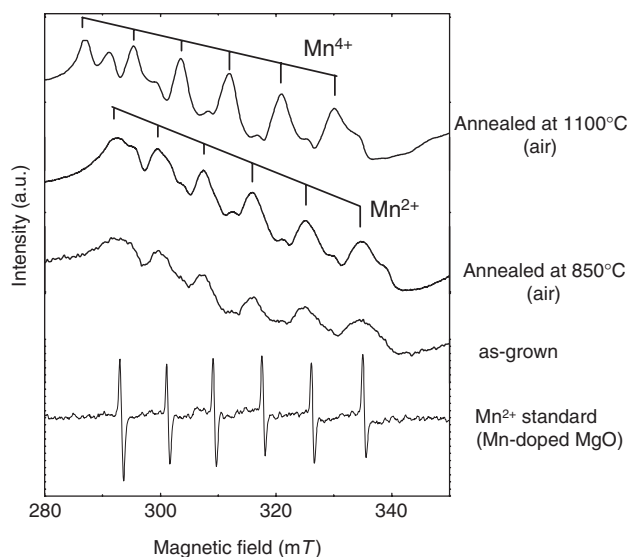
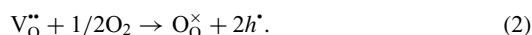


Fig. 3. Relation between leakage current density ( $J$ ) and oxidation degree.



When KNN crystals absorb oxygen into the lattice, the oxygen occupies  $V_{\text{O}}^{\bullet\bullet}$  as  $\text{O}_{\text{O}}^{\times}$  accompanied by the formation of  $2h^{\bullet}$ . The higher  $J$  induced by oxidation treatment provides direct evidence that  $h^{\bullet}$  conduction plays a detrimental role in the leakage current properties of KNN crystals. The  $p$ -type conduction at room temperature has been observed for oxide ferroelectrics such as  $\text{PbTiO}_3$ ,<sup>91)</sup>  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT),<sup>92,93)</sup> and La-substituted BiT.<sup>94)</sup>

The same tendency of  $J$  was observed for Mn-doped crystals. Mn-KNN crystals annealed at 850°C in air (with bluish brown) showed a relatively high  $J$  of  $\sim 10^{-5}$  A/cm<sup>2</sup>, which was by about one order of magnitude lower than those of KNN crystals with the same annealing treatment. Mn-KNN crystals annealed at 1100°C in air showed a low  $J$  of  $\sim 10^{-8}$  A/cm<sup>2</sup>, indicating that the Mn substitution and subsequent oxygen annealing are effective for suppressing leakage current of KNN crystals. It has been reported that high- $P_{\text{O}_2}$  annealing led to an increase in  $J$  also for Mn-doped  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  crystals.<sup>55)</sup> The increase in  $J$  by the oxidation treatment clearly demonstrates that, in an oxidized state,  $h^{\bullet}$  act as detrimental carrier for the leakage current of Mn-KNN crystals as well as KNN ones.

In order to clarify the valence state of Mn, ESR investigations were performed for the crushed powders of Mn-KNN crystals. **Figure 3** shows the X-band ESR spectra of the crystals observed at  $-160^\circ\text{C}$ . As-grown crystals exhibited the hyperfine structure

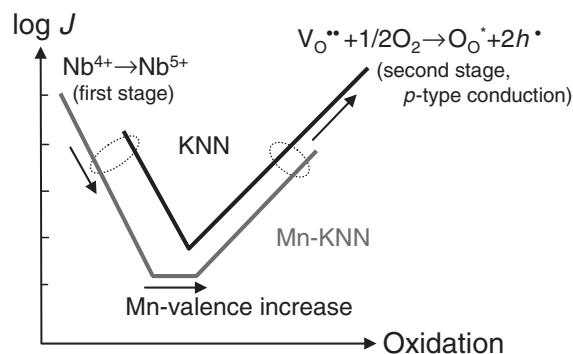
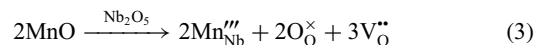


Fig. 4. X-band ESR spectra of the crushed powder of Mn-KNN crystals observed at  $-160^\circ\text{C}$ .

with six prominent lines of typical isolated  $\text{Mn}^{2+}$ ,<sup>95)</sup> which is almost the same as the spectrum observed for  $\text{Mn}^{2+}$  standard samples (Mn-doped MgO). In these crystals, Mn is substituted at the  $\text{Nb}^{5+}$  site as  $\text{Mn}^{2+}$  ( $\text{Mn}_{\text{Nb}}^{\prime\prime}$ ) accompanied by the formation of  $V_{\text{O}}^{\bullet\bullet}$  as expressed by



The crystals annealed at 850°C and 1150°C in air indicate a superimposed signal originating from  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$ .<sup>96)</sup> These results clearly show that  $\text{Mn}^{2+}$  is partially oxidized to higher valent cations and that  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$  occupy the  $\text{Nb}^{5+}$  site with a mixed valent state ( $\text{Mn}^{3+}$  is silent in X-band ESR measurements). The intensity of  $\text{Mn}^{4+}$  signal increased with increasing annealing temperature in air. These ESR investigations provide definite evidence that the oxidation treatment by the annealing in air increases average Mn valence in Mn-KNN crystals.

Here, the effects of the Mn substitution in KNN crystals are discussed. The structural analysis and ESR investigations have demonstrated that Mn in the crystals with a relatively reduced state is present at the  $\text{Nb}^{5+}$  site as  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ .  $\text{Mn}^{2+}$  at the perovskite  $B$  site has been observed also for  $\text{PbTiO}_3$ ,<sup>96)</sup>  $\text{KNbO}_3$ ,<sup>97)</sup> and  $\text{NaNbO}_3$ .<sup>98)</sup> ESR analysis has revealed that the annealing in air increases average Mn valence.

The relation between  $J$  and oxidation degree is schematically depicted in **Fig. 4**. When as-grown crystals of KNN and Mn-KNN are oxidized gradually (first-stage oxidation),  $J$  drops rapidly due to the valence increase of niobium from  $\text{Nb}^{4+}$  to  $\text{Nb}^{5+}$ . For the crystals annealed at 850°C in air, KNN ( $\text{K}_{0.14}\text{Na}_{0.86}\text{NbO}_3$ ) crystals exhibited a low  $J$  compared with  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  crystals. KNN crystals with a low K content seem to have a low vacancy concentration of K, which results in a high

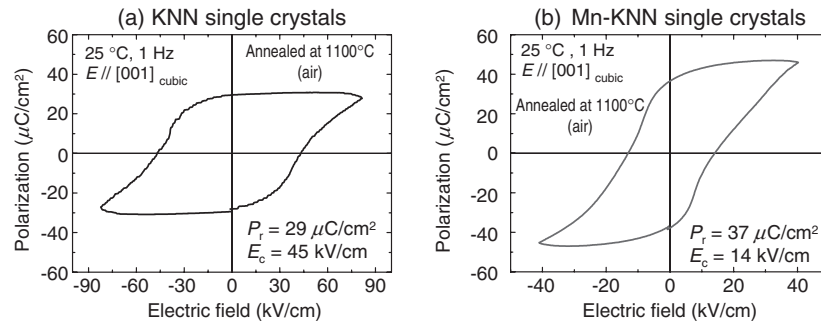
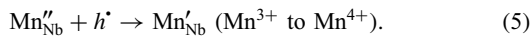
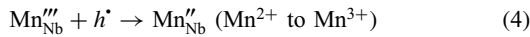


Fig. 5. Polarization hysteresis loops of KNN Mn-KNN crystals annealed at 1100°C in air ( $E \parallel [100]_{\text{cubic}}$ ).

concentration of  $Nb^{4+}$  due to charge neutrality restriction and thereby leads to a high  $J$ . In addition, the value of  $J$  of Mn-KNN crystals was lower than that of KNN even in the first-stage oxidation. This result suggest that Mn ions at the  $Nb^{5+}$  site acts as acceptors to decrease  $Nb^{4+}$ , and then gives a lower  $J$  observed for Mn-KNN crystals.

Immediately after completing Nb oxidation (all  $Nb^{4+}$  ions become  $Nb^{5+}$ ), further oxidation (second-stage oxidation) increases  $J$  due to the formation of  $h^*$  according to Eq. (2). In contrast, for Mn-doped crystals, Mn acts as a buffering species for suppressing an increase of  $h^*$  by oxidation. After  $Nb^{4+}$  is completely oxidized to  $Nb^{5+}$ ,  $Mn^{2+}$  absorbs  $h^*$  generated in further oxidation process by the valence increase of Mn as expressed by



Thus a low  $J$  is maintained for Mn-KNN in a wide oxidation range as a result of the increase in average Mn valence, while oxidation forces KNN to accommodate  $h^*$ , resulting in a higher  $J$ . The  $h^*$ -absorbing function originating from the Mn-valence increase is a possible origin of the lower  $J$  observed for Mn-KNN crystals.

**Figure 5** shows the polarization hysteresis loops measured at 25°C along  $[100]_{\text{cubic}}$  of KNN and Mn-KNN crystals annealed at 1100°C in air. KNN crystals exhibited a remanent polarization ( $P_r$ ) of 29  $\mu\text{C}/\text{cm}^2$  and a coercive field ( $E_c$ ) of 45 kV/cm. A well-developed polarization hysteresis was observed for Mn-KNN crystals, and a relatively larger  $P_r$  of 37  $\mu\text{C}/\text{cm}^2$  and a small  $E_c$  of 14 kV/cm were obtained. This  $P_r$  value was larger than those of reported KNN-based ceramics.<sup>(88),(99)</sup> The crystals annealed at 850°C did not show an apparent hysteresis loop due to their high  $J$ .

**Figure 6** shows the temperature dependence of dielectric permittivity ( $\epsilon_r$ ) and loss ( $\tan \delta$ ) measured along  $[100]_{\text{cubic}}$  at 1 MHz of KNN and Mn-KNN annealed at 1100°C in air. The  $\epsilon_r$  as a function of temperature exhibited two anomalies corresponding to the successive phase transitions: orthorhombic to tetragonal ( $T_{O-T}$ ) and tetragonal to cubic (Curie temperature,  $T_C$ ). The  $T_{O-T}$  and the  $T_C$  of KNN were 173°C and 365°C, respectively. These  $T_{O-T}$  and  $T_C$  were lower than those of  $K_{0.5}Na_{0.5}NbO_3$  ( $T_{O-T} = 190^\circ\text{C}$ ,  $T_C = 390^\circ\text{C}$ ),<sup>(53)</sup> which is probably due to a smaller K content for KNN crystals ( $K_{0.14}Na_{0.86}NbO_3$ ). The substitution of Mn led to a slight increase in both  $T_{O-T}$  and  $T_C$ , and Mn-KNN crystals exhibited a  $T_{O-T}$  of 177°C and a  $T_C$  of 376°C. The Mn substitution did not change the absolute values of  $\epsilon_r$  in the orthorhombic and tetragonal states markedly, while the Mn substitution decreased  $\tan \delta$  in the tetragonal state. For practical case,  $T_{O-T}$  is decreased to around room temperature by the doping of Li and/or Ta etc.,<sup>(53),(54)</sup> and the dielectric and

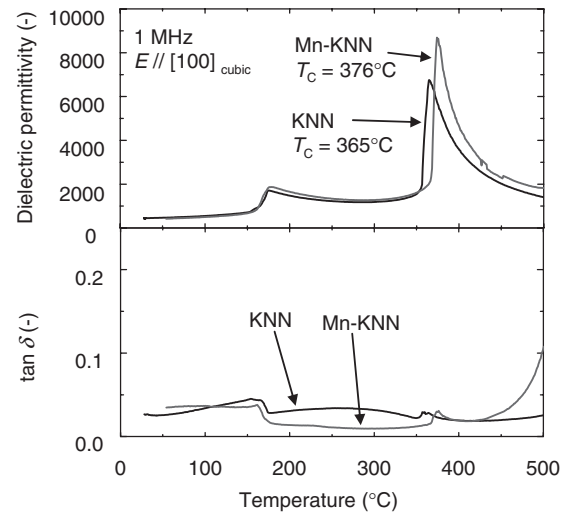


Fig. 6. The temperature dependence of dielectric permittivity ( $\epsilon_r$ ) and loss ( $\tan \delta$ ) measured along  $[100]_{\text{cubic}}$  at 1 MHz of KNN and Mn-KNN annealed at 1100°C in air.

piezoelectric properties in the tetragonal state plays an important role. Our investigations show that the Mn substitution is effective for decreasing  $\tan \delta$  in the tetragonal state in addition to for suppressing leakage current at room temperature.

#### 4. Summary

$K_{0.14}Na_{0.86}NbO_3$  crystals were grown by a flux method and the effects of Mn substitution on leakage current, polarization and dielectric properties were investigated along the  $[100]_{\text{cubic}}$  direction. The leakage current of  $K_{0.14}Na_{0.86}NbO_3$  crystals depended strongly on oxidation degree. A high leakage current of the crystals in a reduced state is suggested to originate from  $d$ -electron conduction through  $Nb^{4+}$ , while electron hole generated by oxidation is shown to be a detrimental carrier of leakage current of  $K_{0.14}Na_{0.86}NbO_3$  crystals in an oxidation state. The substitution of Mn is demonstrated to be effective for suppressing leakage current, and the increase in averaged Mn valence is indicated to play an important role in electron-hole absorption during oxidation for reducing leakage current. Mn-substituted crystals exhibited a superior polarization hysteresis with a  $P_r$  of 37  $\mu\text{C}/\text{cm}^2$  and a small  $E_c$  of 14 kV/cm.

**Acknowledgments** This study was partly supported by Grant-in-Aid for Scientific Research on Priority Areas “Novel States of Matter Induced by Frustration” (19052002), the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

## References

- 1) K. Uchino and S. Nomura, *Ferroelectrics*, **50**, 517–522 (1983).
- 2) L. Bellaiche and D. Vanderbilt, *Phys. Rev. Lett.*, **83**, 1347–1350 (1999).
- 3) C. H. Lee, S. I. Lee and S. J. Kim, *J. Ceram. Soc. Japan*, **116**, 158–162 (2008).
- 4) K. Ishii and S. Tashiro, *J. Ceram. Soc. Japan*, **116**, 1214–1221 (2008).
- 5) D. Byrne, A. Schilling, J. F. Scott and J. M. Gregg, *Nanotechnology*, **19**, 165608 (2008).
- 6) Z. H. Yao, H. X. Liu, Y. Liu, Z. Li, X. B. Cheng, M. H. Cao and H. Hao, *J. Ceram. Soc. Japan*, **116**, 1150–1153 (2008).
- 7) Y. J. Wang, K. F. Cheung, S. W. Or, H. L. W. Chan and H. S. Luo, *J. Ceram. Soc. Japan*, **116**, 540–544 (2008).
- 8) M. Miyake, J. F. Scott, X. J. Lou, F. D. Morrison, T. Nonaka, S. Motoyama, T. Tatsuta and O. Tsuji, *J. Appl. Phys.*, **104**, 064112 (2008).
- 9) N. Yasuda, K. Ozawa, M. M. Rahaman, H. Ohwa, Y. Yamashita, M. Iwata and Y. Ishibashi, *Jpn. J. Appl. Phys.*, **47**, 7650–7654 (2008).
- 10) T. Ogawa, *Jpn. J. Appl. Phys.*, **47**, 7655–7658 (2008).
- 11) J. Takarada, K. Imoto, K. Yamamoto, M. Date, E. Fukada and Y. Tajitsu, *Jpn. J. Appl. Phys.*, **47**, 7698–7701 (2008).
- 12) M. Kobune, W. Adachi, K. Kitada, A. Mineshige, T. Yazawa, H. Yamaguchi and K. Honda, *Jpn. J. Appl. Phys.*, **47**, 7664–7668 (2008).
- 13) V. Sivasubramanian, S. Tsukada and S. Kojima, *Jpn. J. Appl. Phys.*, **47**, 7740–7744 (2008).
- 14) W. F. Guo, A. L. Ding and H. F. Wang, *J. Ceram. Soc. Japan*, **117**, 891–894 (2009).
- 15) A. Kumar, G. L. Sharma, R. S. Katiyar, R. Pirc, R. Blinc and J. F. Scott, *J. Phys.: Condens. Matter*, **21**, 382204 (2009).
- 16) G. He, T. Iijima and H. Funakubo, *J. Ceram. Soc. Japan*, **117**, 698–702 (2009).
- 17) M. Iwata, K. Kuroda, Y. Hasegawa, R. Aoyagi, M. Maeda and Y. Ishibashi, *Jpn. J. Appl. Phys.*, **48**, 09KF07 (2009).
- 18) M. Iwata, K. Sakakibara, R. Aoyagi, M. Maeda and Y. Ishibashi, *J. Ceram. Soc. Japan*, **117**, 954–957 (2009).
- 19) T. Miyazaki, S. Sou, N. Sakamoto, N. Wakiya and H. Suzuki, *J. Ceram. Soc. Japan*, **117**, 950–953 (2009).
- 20) T. Miyoshi, *J. Ceram. Soc. Japan*, **117**, 899–903 (2009).
- 21) J. F. Scott, H. J. Fan, S. Kawasaki, J. Banys, M. Ivanov, A. Krotkus, J. Macutkevicius, R. Blinc, V. V. Laguta, P. Cevc, J. S. Liu and A. L. Khokin, *Nano Lett.*, **8**, 4404–4409 (2008).
- 22) T. Ohno, B. Malic, H. Fukazawa, N. Wakiya, H. Suzuki, T. Matsuda and M. Kosec, *J. Ceram. Soc. Japan*, **117**, 1089–1094 (2009).
- 23) X. L. Xie and Z. H. Yao, *J. Ceram. Soc. Japan*, **117**, 208–210 (2009).
- 24) H. Takahashi, Y. Numamoto, J. Tani and S. Tsurekawa, *Jpn. J. Appl. Phys.*, **45**, 7405–7408 (2006).
- 25) T. Karaki, K. Yan, T. Miyamoto and M. Adachi, *Jpn. J. Appl. Phys.*, **46**, L97–L98 (2007).
- 26) S. Wada, T. Muraishi, K. Yokoh, K. Yako, H. Kamemoto and T. Tsurumi, *Ferroelectrics*, **355**, 37–49 (2007).
- 27) C. H. Wang, *J. Ceram. Soc. Japan*, **116**, 797–802 (2008).
- 28) C. H. Wang, *J. Ceram. Soc. Japan*, **116**, 632–636 (2008).
- 29) T. Hoshina, K. Takizawa, J. Y. Li, T. Kasama, H. Kakemoto and T. Tsurumi, *Jpn. J. Appl. Phys.*, **47**, 7607–7611 (2008).
- 30) Y. Sakai, T. Futakuchi and M. Adachi, *Jpn. J. Appl. Phys.*, **47**, 7630–7634 (2008).
- 31) H. Maiwa, *Jpn. J. Appl. Phys.*, **47**, 7646–7649 (2008).
- 32) K. Sugimura and K. Hirao, *J. Ceram. Soc. Japan*, **117**, 1039–1043 (2009).
- 33) S. M. Moon, X. H. Wang and N. H. Cho, *J. Ceram. Soc. Japan*, **117**, 729–731 (2009).
- 34) R. Matoba, Y. Hayashi and H. Takizawa, *J. Ceram. Soc. Japan*, **117**, 388–391 (2009).
- 35) T. Hoshina, Y. Kigoshi, S. Hatta, H. Takeda and T. Tsurumi, *Jpn. J. Appl. Phys.*, **48**, 09KC01 (2009).
- 36) T. Watanabe, H. Saito and K. Takeda, *Jpn. J. Appl. Phys.*, **48**, 09KF02 (2009).
- 37) S. Lee, C. A. Randall and Z. K. Liu, *J. Am. Ceram. Soc.*, **92**, 222–228 (2009).
- 38) R. D. Levi, M. M. Samantary, S. Trolier-McKinstry and C. A. Randall, *J. Appl. Phys.*, **104**, 104117 (2008).
- 39) N. Inoue, T. Okamatsu, A. Ando, H. Takagi, T. Hashimoto, C. Moriyoshi and Y. Kuroiwa, *Jpn. J. Appl. Phys.*, **48**, 09KF03 (2009).
- 40) K. Nishida, H. Kishi, M. Osada, H. Funakubo, M. Nishide, H. Takeuchi, T. Katoda and T. Yamamoto, *Jpn. J. Appl. Phys.*, **48**, 09KF11 (2009).
- 41) T. Takenaka and K. Sakata, *Ferroelectrics*, **95**, 153–156 (1989).
- 42) T. Takenaka, K. Sakata and K. Toda, *Ferroelectrics*, **106**, 375–380 (1990).
- 43) K. Yamamoto, M. Suzuki, Y. Noguchi and M. Miyayama, *Jpn. J. Appl. Phys.*, **47**, 7623–7629 (2008).
- 44) Y. Hiruma, T. Watanabe, H. Nagata and T. Takenaka, *Jpn. J. Appl. Phys.*, **47**, 7659–7663 (2008).
- 45) N. Kumada, Y. Morozumi, Y. Yonesaki, T. Takei, N. Kinomura and T. Hayashi, *J. Ceram. Soc. Japan*, **116**, 1238–1240 (2008).
- 46) Y. Noguchi, I. Tanabe, M. Suzuki and M. Miyayama, *J. Ceram. Soc. Japan*, **116**, 994–1001 (2008).
- 47) H. Nagata, *J. Ceram. Soc. Japan*, **116**, 271–277 (2008).
- 48) D. Rout, K. S. Moon, V. S. Rao and S. J. L. Kang, *J. Ceram. Soc. Japan*, **117**, 797–800 (2009).
- 49) Y. Noguchi, S. Teranishi, M. Suzuki and M. Miyayama, *J. Ceram. Soc. Japan*, **117**, 32–36 (2009).
- 50) N. Yasuda, S. Hashimoto, H. Ohwa, O. Sakurada, K. Fujita, Y. Yamashita, M. Iwata and Y. Ishibashi, *Jpn. J. Appl. Phys.*, **47**, 7650–7654 (2008).
- 51) Y. Hiruma, H. Nagata and T. Takenaka, *Jpn. J. Appl. Phys.*, **47**, 7659–7663 (2008).
- 52) Y. Isikawa, Y. Akiyama and T. Hayashi, *Jpn. J. Appl. Phys.*, **48**, 09KD03 (2009).
- 53) Y. P. Guo, K. Kakimoto and H. Ohsato, *Appl. Phys. Lett.*, **85**, 4121–4123 (2004).
- 54) Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, *Nature*, **432**, 84–87 (2004).
- 55) Y. Kizaki, Y. Noguchi and M. Miyayama, *Appl. Phys. Lett.*, **89**, 142910 (2006).
- 56) R. Sasaki, R. Suzuki, S. Uraki, H. Kakemoto and T. Tsurumi, *J. Ceram. Soc. Japan*, **116**, 1182–1186 (2008).
- 57) R. Suzuki, S. Uraki, E. Li, T. Hoshina and T. Tsurumi, *J. Ceram. Soc. Japan*, **116**, 1199–1203 (2008).
- 58) Z. W. Chen, J. Q. Hu and X. H. He, *J. Ceram. Soc. Japan*, **116**, 661–663 (2008).
- 59) Y. Sun, D. Q. Xiao, L. Wu, D. M. Lin, J. N. Zhu, P. Yu, X. Li, Y. Y. Wang, Y. Li, Y. Z. Lin, Y. Zhuang and Q. Wei, *J. Ceram. Soc. Japan*, **116**, 536–539 (2008).
- 60) K. Kakimoto, T. Ito and H. Ohsato, *Jpn. J. Appl. Phys.*, **47**, 7669–7672 (2008).
- 61) M. Ishikawa, Y. Kadota, N. Takiguchi, H. Hosaka and T. Morita, *Jpn. J. Appl. Phys.*, **47**, 7673–7677 (2008).
- 62) S. Wada, M. Nitta, N. Kumada, D. Tanaka, M. Furukawa, S. Ohno, C. Moriyoshi and Y. Kuroiwa, *Jpn. J. Appl. Phys.*, **47**, 7678–7684 (2008).
- 63) E. Z. Li, H. Kakemoto, T. Hoshina and T. Tsurumi, *Jpn. J. Appl. Phys.*, **47**, 7702–7706 (2008).
- 64) C. Moriyoshi, J. Kato, Y. Terado, S. Wada, M. Takata and Y. Kuroiwa, *Jpn. J. Appl. Phys.*, **47**, 7745–7748 (2008).
- 65) M. S. Kim, S. J. Jeong, I. S. Kim and J. S. Song, *J. Ceram. Soc. Japan*, **117**, 592–595 (2009).
- 66) C. H. Wang, *J. Ceram. Soc. Japan*, **117**, 680–684 (2009).
- 67) M. Abazari and A. Safari, *J. Appl. Phys.*, **105**, 054101 (2009).
- 68) Y. Inagaki, K. Kakimoto and I. Kagomiya, *Jpn. J. Appl. Phys.*, **48**, 09KF02 (2009).

- 48, 09KC09 (2009).
- 69) D. Tanaka, T. Tsukada, M. Furukawa, S. Wada and Y. Kuroiwa, *Jpn. J. Appl. Phys.*, **48**, 09KD08 (2009).
- 70) N. M. Hagh, K. Kerman, B. Jadidian and A. Safari, *J. Eur. Ceram. Soc.*, **29**, 2325–2332 (2009).
- 71) K. Ishii and S. Tashiro, *J. Ceram. Soc. Japan*, **116**, 1304–1308 (2008).
- 72) A. Watanabe, T. Fukui, K. Nogi, Y. Kizaki, Y. Noguchi and M. Miyayama, *J. Ceram. Soc. Japan*, **114**, 97–101 (2006).
- 73) H. Funakubo, *J. Ceram. Soc. Japan*, **116**, 1249–1254 (2008).
- 74) T. Shigyo, H. Kiyono, J. Nakano, H. Itoh and J. Takahashi, *Jpn. J. Appl. Phys.*, **47**, 7617–7622 (2008).
- 75) M. Iwata, A. Toya, R. Aoyagi, M. Maeda and Y. Ishibashi, *Jpn. J. Appl. Phys.*, **47**, 7749–7752 (2008).
- 76) J. N. Kim, Y. S. Choi and B. E. Park, *J. Ceram. Soc. Japan*, **117**, 1032–1034 (2009).
- 77) H. H. Park, H. S. Lee, H. H. Park, R. H. Hill and Y. T. Hwang, *J. Ceram. Soc. Japan*, **117**, 604–607 (2009).
- 78) X. H. He, M. G. Zheng and Z. W. Chen, *J. Ceram. Soc. Japan*, **117**, 217–220 (2009).
- 79) M. S. Islam, J. Kano, S. Tsukada, Q. R. Yin and S. Kojima, *Jpn. J. Appl. Phys.*, **48**, 09KC10 (2009).
- 80) H. Ogawa, S. Kawada, M. Kimura, Y. Higuchi and H. Takagi, *Jpn. J. Appl. Phys.*, **48**, 09KD05 (2009).
- 81) S. E. Park and T. R. Shrout, *J. Appl. Phys.*, **82**, 1804–1811 (1997).
- 82) G. O. Jones and P. A. Thomas, *Acta Crystallogr., Sect. B: Struct. Sci.*, **58**, 168–178 (2002).
- 83) G. O. Jones and P. A. Thomas, *Acta Crystallogr., Sect. B: Struct. Sci.*, **56**, 426–430 (2000).
- 84) T. Takenaka, K. Maruyama and K. Sakata, *Jpn. J. Appl. Phys.*, **30**, 2236–2239 (1991).
- 85) G. Shirane, R. Newnham and R. Pepinsky, *Phys. Rev.*, **96**, 581–588 (1954).
- 86) F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **321–324**, 198–203 (2000).
- 87) B. T. Matthias and J. P. Remeika, *Phys. Rev.*, **82**, 727–729 (1951).
- 88) M. Matsubara, T. Yamaguchi, K. Kikuta and S. Hirano, *Jpn. J. Appl. Phys.*, **44**, 258–263 (2005).
- 89) R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.*, **32**, 751–767 (1976).
- 90) R. Courths, P. Steiner, H. Hochst and S. Hufner, *Appl. Phys. A.*, **21**, 345–352 (1980).
- 91) M. V. Raymond and D. M. Smyth, *J. Phys. Chem. Solids*, **57**, 1507–1511 (1996).
- 92) M. Takahashi, Y. Noguchi and M. Miyayama, *Jpn. J. Appl. Phys.*, **41**, 7053–7056 (2002).
- 93) Y. Noguchi, T. Matsumoto and M. Miyayama, *Jpn. J. Appl. Phys.*, **44**, L570–L572 (2005).
- 94) M. Soga, Y. Noguchi, M. Miyayama, H. Okino and T. Yamamoto, *Appl. Phys. Lett.*, **84**, 100–102 (2004).
- 95) I. I. Yu and M. Senna, *Appl. Phys. Lett.*, **66**, 424–426 (1995).
- 96) K. Hayashi, A. Ando, Y. Hamaji and Y. Sakabe, *Jpn. J. Appl. Phys.*, **37**, 5237–5240 (1998).
- 97) K. Kakimoto, I. Masuda and H. Ohsato, *Jpn. J. Appl. Phys.*, **43**, 6706–6710 (2004).
- 98) J. Kubacki, A. Molak and E. Talik, *J. Alloys Compd.*, **328**, 156–161 (2001).
- 99) J. Tashiro, A. Sasaki, S. Akiba, S. Satoh, T. Watanabe, H. Funakubo and M. Yoshimoto, *Thin Solid Films*, **415**, 272–275 (2002).