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# Crystal growth and ferroelectric property of $Na_{0.5}K_{0.5}NbO_3$ and Mn-doped $Na_{0.5}K_{0.5}NbO_3$ crystals grown by floating zone method

Yumi Inagaki *, Ken-ichi Kakimoto, Isao Kagomiya

*Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

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**Abstract**

$Na_{0.5}K_{0.5}NbO_3$ (NKN) and Mn-doped NKN crystals, which are one of the promising candidates of lead-free piezoelectric materials, were grown by using a floating zone (FZ) method. The resulting crystal growth was compared with crystal growth that resulted from using a flux method in a previous study. In the crystal grown by FZ method under where the growth rate was controlled to 3 mm/h, thin layers formed parallel and perpendicular directions to the growth direction. In the crystal grown by FZ method, the crystal structure could not be classified as having the orthorhombic lattice of *Amm*2, which was observed in the crystal grown using a flux method. It was found that doped Mn was substituted in the perovskite-type lattice of NKN. Pure NKN crystals showed 90° domains that had a zig-zag shape, whereas Mn-doped NKN crystals were aligned to the domain layers in straight lines. It was confirmed that Mn-doped NKN crystal showed a square *P–E* hysteresis loop.
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*Keywords:* Dielectric properties; Ferroelectric properties; Grain growth; Piezoelectric properties; Single crystal

## 1. Introduction

$Na_{0.5}K_{0.5}NbO_3$ (NKN), which is a solid solution of $KNbO_3$ and $NaNbO_3$, is one of the most promising candidates of lead-free piezoelectric materials because previous research has indicated that NKN has not only an excellent piezoelectric property but also a high Curie temperature ($T_c > 400\,°C$).[1,2] However, only a few reports about NKN system single crystals have been published.[3–6] In the previous study, Mn-doped NKN crystals were successfully grown under a slow cooling treatment by a self-flux method using KF–NaF eutectic composition where the temperature was first held at 1050 °C for 5 h and then 950 °C for an additional 5 h, and a cooling rate of 0.25 °C/min was maintained (Fig. 1(a) and (b)). However, as-grown crystals revealed a relatively high leakage current density of $10^{-3}$ A/cm$^2$. According to Kizaki et al.,[4] Mn-doping and subsequent oxygen annealing is quite effective to improve the leakage current density of NKN crystals. In a crystal growth of the NKN system, oxygen vacancies are generated by the evaporation of alkali oxides which occur during the processing. When the NKN crystals oxidized, the oxygen occupied oxygen vacancies, followed by the formation of electron holes. In the case of Mn substitution for NKN, Mn acts as electron hole absorbant with the increase of Mn valence during oxidation because Mn can exhibit three valences of 2+, 3+ and 4+. Our experimental results also revealed that the leakage current density of annealed Mn-doped NKN crystals were three orders of magnitude lower than that of NKN crystal, however, the function of Mn-doping to NKN crystal is not known yet. The resultant Mn-doped NKN single crystal showed a statured ferroelectric *P–E* hysteresis loop and piezoelectric properties of the piezoelectric strain constant ($d_{33}$) = 161 pC/N, and the longitudinal electro-mechanical coupling factor ($k_{33}$) = 0.64.[5] However, there are some problems with using a flux method for crystal growth such as the contamination of flux in the resultant crystals and the difficulty in producing growth of the large-sized single crystals.

In order to solve these problems, floating zone (FZ) method was employed to synthesize Mn-doped NKN crystals in this study. Also, the crystal growth and the effects of Mn-doping on NKN crystals were investigated. In this method it is not necessary to use a crucible, therefore, FZ methods are able to synthesize crystals and avoid impurities. Another important feature of FZ methods is the ease of growing of large-sized crystals with a longitudinal shape because ceramics rods with longitudinal shapes are used as feed rods. Thus, a lot of piezoelectric single crystals such as $KNbO_3$,[7,8] $LiTaO_3$,[9] and

* Corresponding author. Tel.: +81 52 735 7734; fax: +81 52 735 7734.
*E-mail address:* kakimoto.kenichi@nitech.ac.jp (K.-i. Kakimoto).

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$Na_{1/2}Bi_{1/2}TiO–BaTiO_3$[10] were prepared by a FZ method. However, the growth of NKN system crystals using a FZ method has not been reported. The researches of this study indicated for the first time, that the synthesis of large-sized NKN and Mn-doped NKN crystals can be grown using a FZ method. In this paper, crystal growth resulting from using a FZ method and the effects of Mn-doping on NKN crystal were discussed.

## 2. Experimental procedure

NKN and Mn-doped NKN ceramics were prepared by a conventional mixed oxide method. The raw materials were high-purity (99.99%) powders of $Na_2CO_3$, $K_2CO_3$, $Nb_2O_5$ and $Mn_2O_3$. These powders were weighed to obtain the compositions according to the formula of $(Na_{0.5}K_{0.5})(Nb_{1-x}Mn_x)O_3$, where $x$ is 0 and 0.005. The weighed powder was mixed with ball-milling media for 1 h in ethanol. The dried mixture was then calcined at 800 °C for 20 h. The calcined powder was granulated using polyvinyl alcohol as a binder and then passed through a sieve with openings of 100 μm. The powder was put into rubber tubes with a columnar with a 6 mm diameter. The packed powders were sealed by using a vacuum pump, followed by cold-isostatic-pressing under 200 MPa. Then, the molded rods were sintered at 1100 °C for 2 h.

The growth apparatus was an infrared convergence-type FZ furnace with two ellipsoidal mirrors (Canon Machinery Inc. FZD0167). Two halogen lamps were set at the focal point of ellipsoid as infrared source. The sintered rods were fixed to the upper and lower shafts. The growth rate was fixed at 3 mm/h and the rotation rate of the upper and lower shafts were fixed at 25 rpm. The crystal growth was carried out under air atmosphere.

The as-grown crystals were annealed at 1100 °C for 6 h in air. The crystal phase of obtained NKN and Mn-doped NKN crystals cut parallel and perpendicular to the growth direction was identified by a X-ray diffraction (XRD) using Cu Kα radiation (Phillips X'pert MPD). The microstructure was observed by scanning electron microscopy (SEM). The phase-transition-temperature of the samples was measured by a differential scanning calorimetry (Shimadzu DSC-60). The measurements were carried out at an elevated temperature. The domain structure of the crystals was observed by polarizing microscopy. For electric measurement, Au electrode was sputtered on both surfaces of the samples. Ferroelectric *P–E* hysteresis loop at 1 Hz and leakage current density were measured using a ferroelectric test system (aixACT TF2000FE-HV).

## 3. Results and discussion

### *3.1. Crystal growth using FZ method*

Fig. 1(c) and (d) shows the appearances of as-grown NKN and Mn-doped NKN crystals grown under the growth rate of 3 mm/h and the rotation rate of the shafts of 25 rpm by using the FZ method, respectively. NKN and Mn-doped NKN crystals grown by a flux method using slow cooling treatment[5] are also shown in Fig. 1(a) and (b). The color of the crystals grown by both a flux method and the FZ method were similar. The as-grown Mn-doped NKN crystals were brownish white in color. On the

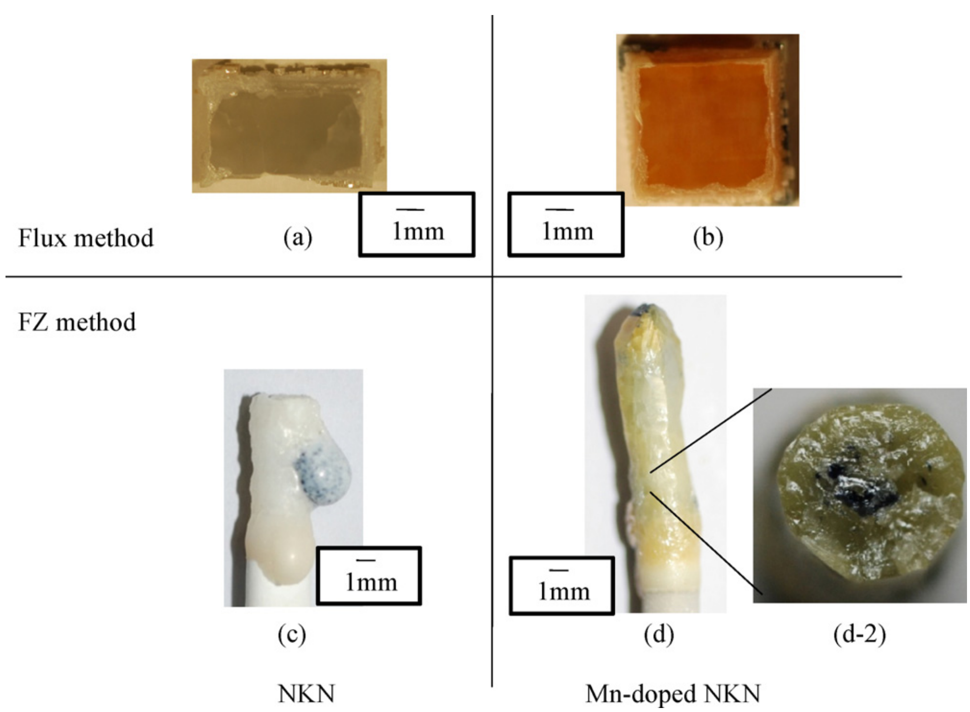


Fig. 1. NKN and Mn-doped NKN crystals: (a) NKN crystal grown by FZ method, (b) Mn-doped NKN crystal grown by FZ method, (c) NKN crystal grown by flux method, and (d) Mn-doped NKN crystal grown by flux method, (d-2) Mn-doped NKN crystal grown by FZ method cut out along to perpendicular to the growth direction.

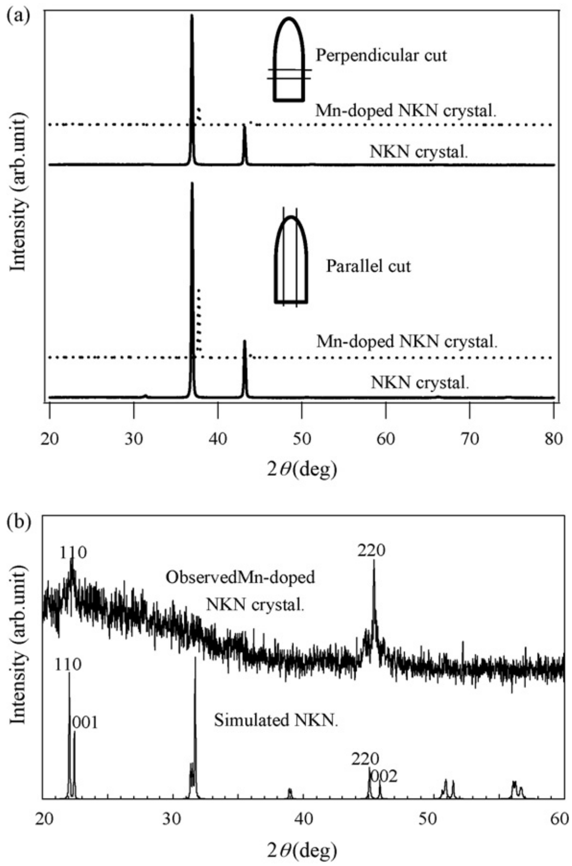


Fig. 2. XRD patterns of NKN and Mn-doped NKN crystals grown by (a) FZ method and (b) flux method.

other hand, NKN crystals were white in color. There was no significant change in color after the crystals were annealed in NKN and Mn-doped NKN crystals grown by the FZ method. A lot of grains were observed in the surface of NKN crystals, whereas a number of grains decreased along the growth direction in the surface of Mn-doped NKN crystals. The lengths of the NKN and

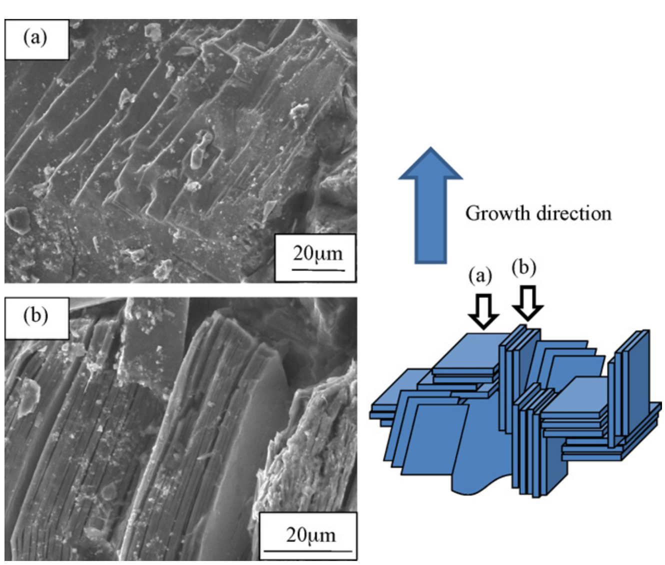


Fig. 3. Microstructure of NKN crystal grown by FZ method.

Mn-doped NKN crystals were 9.3 and 12.5 mm, respectively. As for crystal structure, although the crystals grown by a flux method were orthorhombic NKN (*Amm*2)[11] and the orthorhombic (1 1 0) face was obtained[5] (Fig. 2(b)), the reflections of NKN and Mn-doped NKN crystals grown by the FZ method could not be assigned by the Miller indices to the orthorhombic NKN as shown in Fig. 2. In addition, NKN and Mn-doped NKN crystals seem to have crystallographic anisotropy. Therefore, it is expected that one of the lattice parameters of the NKN crystals grown by the FZ method was longer than the other lattice parameters. The lattice parameters of NKN ceramics and single crystals grown by a flux method are the orthorhombic and exhibit lattice constants of $a = 4.0$ Å, $b = 5.6$ Å, $c = 5.7$ Å,[11] which are similar to each other. Additionally, the structures of the NKN and Mn-doped NKN crystals cut in parallel and perpendicular directions were quite similar. This is due to thin-layered grain growth as shown in Fig. 3. Tabular layers 50–200 μm in width and approximately 2 μm in thickness were grown parallel and perpendicular to the growth direction. Fig. 2 showed that the structure of crystal growth when the crystal was cut parallel or perpendicular to the growth direction is the same. These similarities in the crystal structure can be attributed to the arrangement of tabular, which can be seen in Fig. 3. Generally, the configuration of crystals depends on the level of the driving force for

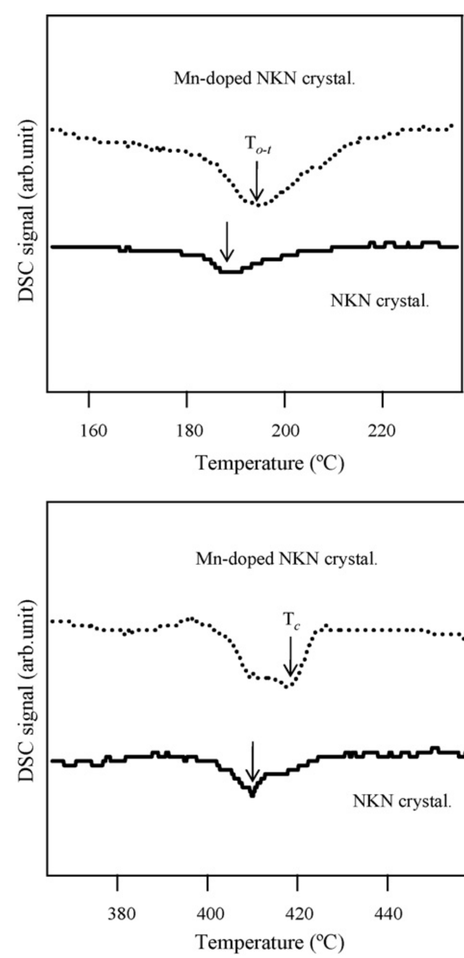


Fig. 4. DSC signals of NKN and Mn-doped NKN crystals grown by FZ method.

crystal growth. The driving force for crystal growth using a solvent such as in the flux method is the degree of supersaturation, but in the case of FZ method, the driving force is the temperature gradient because a solvent is not used to grow the crystals. Also, the shape of the crystal tends to be polyhedron when the driving force for crystal growth is high. On the other hand, when the driving force for crystal growth is low, the grown particles tend to have large crystallographic anisotropy. Thus, it is considered that the driving force for crystal growth, which is temperature gradient of the growth rate of 3 mm/h was high because the particles grown in both NKN and Mn-doped NKN crystals were polyhedron shaped, e.g., tabular layers, as shown in Fig. 3.

### 3.2. *Effect of Mn-doping on NKN crystals*

Mn-doped NKN crystals were brownish white in color, but a part of doped Mn was concentrated at the center of the crystal (Fig. 1(d-2)). In general, a FZ method is used for purifying single crystals because impurity tends to segregate out from the crystal during crystal growth. At the beginning of crystal growth, impurity is not contained in the solidified part; subsequently, impurity is segregated out in the crystal. For this reason, a part of Mn seems to have been separated out from the crystal in this experiment. However, a DSC measurement confirmed that Mn was substituted in the perovskite-type structure of NKN because the orthorhombic–tetragonal phase-transition-temperature ($T_{o\text{–}t}$) and $T_c$ shifted to a higher temperature by Mn-doping as shown in Fig. 4. $T_{o\text{–}t}$ and $T_c$ of Mn-doped NKN crystals were 194.1 and 417.9 °C, respectively. On the other hand, $T_{o\text{–}t}$ and $T_c$ of NKN crystal were 189.7 and 410.1 °C, respectively. From these results, it was found that Mn was substituted in the structure of NKN, but a part of doped Mn was segregated out due to the function of purification.

Even though the configuration of both NKN and Mn-doped NKN crystals were the same as shown in Fig. 2, the domain structures which were included in one tabular particle were different from each other. Fig. 5 shows domain patterns of NKN and Mn-doped NKN crystals grown by the FZ method. In NKN crystals, zig-zag shaped 90° domain structures were observed, and the domain width was about 0.7 μm and the length was 10 μm. When the NKN system crystals were grown by a flux method, the domain structure was similar to the NKN crystals grown by the FZ method having zig-zag shaped 90° domain structures[6] (Fig. 5). On the other hand, the domain structure of Mn-doped NKN crystals grown by the FZ method was aligned to the thin layers as indicated in possible schematics in Fig. 5. The domain-wall width of Mn-doped NKN crystals was the same as NKN crystals of 0.7 μm, but the length was longer than NKN

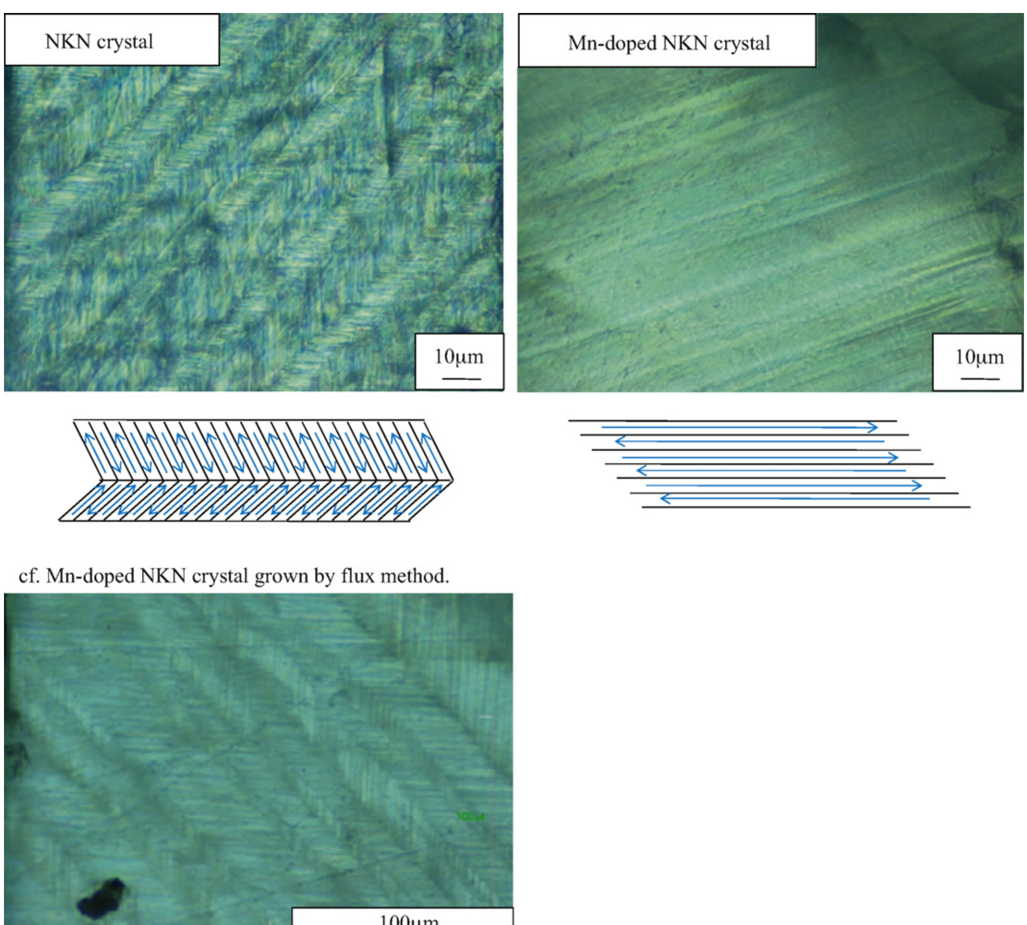


Fig. 5. Domain structure of NKN and Mn-doped NKN crystals grown by FZ method.

crystals. Note with interest that only the domain structures of Mn-doped NKN crystals grown by the FZ method had a different kind of pattern from the other samples. The difference in domain structures between NKN and Mn-doped NKN crystals are considered to have arisen from due to the intra-granular stress. Generally, Mn is known to be substituted in the *B*-site of the perovskite-type structure,[4] therefore the substitution of Mn changes the shape of the $BO_6$ unit in perovskite-type structure and the internal stress in the crystal. Raman spectroscopy measurement confirmed that the internal stress of NKN crystal was higher than that of Mn-doped NKN crystal in the case using flux method.[12] Thus, it is expected that when FZ method is used for the crystal growth of Mn-doped NKN crystals, Mn substitution significantly releases the internal stress compared to NKN crystal. As a result, the Mn-doped NKN crystals grown by the FZ method with small internal stress had a straight domain pattern in spite of the zig-zag shaped domain patterns of the other samples.

### 3.3. Ferroelectric property of NKN and Mn-doped NKN crystals grown by FZ method

Fig. 6 shows ferroelectric *P–E* hysteresis loops and leakage current densities of NKN and Mn-doped NKN crystals grown by the FZ method. The leakage current densities of both NKN and Mn-doped NKN crystals were the same degree of $10^{-5}$ A/cm$^2$. However, the ferroelectric properties of both samples were different. NKN crystals showed a ferroelectric *P–E* hysteresis loop with the remanent polarization ($P_r$) of 27 μC/cm$^2$ and the coercive field ($E_c$) of 22.2 kV/cm, and Mn-doped NKN crystals showed the square *P–E* hysteresis loop with $P_r$ of 106 μC/cm$^2$ and $E_c$ of 14.8 kV/cm. The $P_r$ of Mn-doped NKN crystals grown by a flux method was 52 μC/cm$^2$ when the applied electric field was 55 kV/cm and that of Mn-doped NKN ceramics showed 30 μC/cm$^2$ when the applied electric field was 25 kV/cm.[5] Compared to the crystals grown by a flux method, the $P_r$ of the crystals grown by the FZ method was large. It is considered that large $P_r$ of Mn-doped NKN crystals grown by FZ method is attributed to the domain structure which was changed by doped Mn which was substituted in the *B*-site of perovskite-type structure of the NKN crystals. The shape and internal stress of the $NbO_6$ unit in the perovskite-type structure was controlled by Mn substitution, which may result in the large $P_r$.

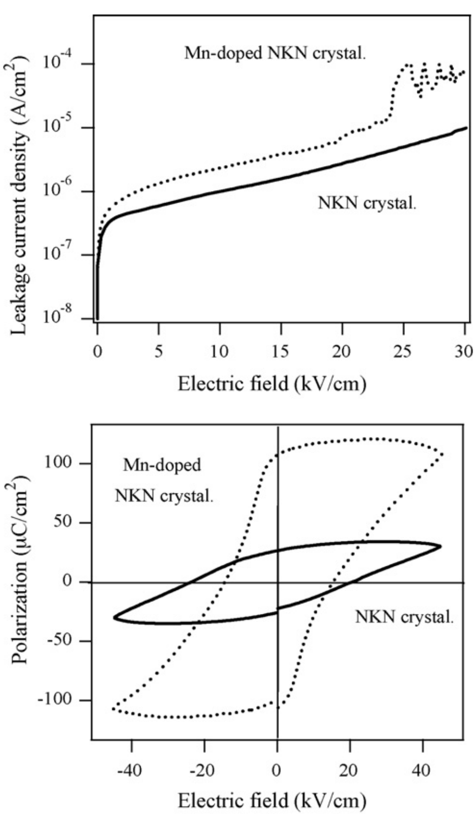


Fig. 6. Ferroelectric *P–E* hysteresis loop and leakage current density of NKN and Mn-doped NKN crystals grown by FZ method.

## 4. Conclusion

NKN and Mn-doped NKN crystals were grown by the FZ method under the growth rate of 3 mm/h and the rotation rate of 25 rpm in air. The crystal structure of the crystals grown by the FZ method indicated crystallographic anisotropy and was not assigned by the orthorhombic *Amm*2, which is adopted by NKN crystals grown by a flux method. Tabular layers arranged in particular directions were caused by the driving force for crystal growth depended on the growth rate of 3 mm/h. In addition, it was found that the doped Mn was substituted in the perovskite-type structure. As a result, the domain structures and ferroelectric properties were affected by Mn substitution.

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