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Thermal depoling and relaxation property of (Na,K)NbO_3 system

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Abstract

(Na,K)NbO_3 ceramics was synthesized by an ordinal solid state reaction method. Thermally stimulated depolarization current (TSDC) pattern of the poled ceramics was measured. Electrically poled $Na_{0.5}K_{0.5}NbO_3$ ceramics generated anomalous large discharge current at around 370 °C during the heating step due to the thermal relaxation of oxygen vacancy. The oxygen vacancy piled up around electrodes and formed the electrically inhomogeneous structure in the ceramics. In addition, the anomalous current of K-riched ceramics was larger than that of Na-riched one. This result suggested that the equilibrium composition of $NaNbO_3$–$KNbO_3$ system was near to Na-riched composition against $Na_{0.5}K_{0.5}NbO_3$.

Keywords: B. Defects; C. Thermal properties; C. Piezoelectric properties; D. Niobates

1. Introduction

(Na,K)NbO_3 is an attractive material as lead-free piezoelectrics. The hot-pressed $Na_{0.5}K_{0.5}NbO_3$ ceramics shows dense and good piezoelectric properties (d_{33} ~160 pC/N) with a high Curie temperature (T_C ~420 °C) [1–4]. However, the piezoelectric property of the poled specimens is affected significantly by their synthesis condition [5], and the property also tends to decrease with long service by depoling. The depoling process includes the deformation of its ferroelectric domain structure and the other discharge process originated from the migration of ion defects. Therefore, the study of poling and depoling property is of importance to understand the piezoelectric property of (Na,K)NbO_3 ceramics.

In our preceding study, the conductivity of $KNbO_3$ ceramics was closely related to the motion of oxygen vacancy by analyzing a.c. impedance spectrum [6], and $Na_{0.5}K_{0.5}NbO_3$ (NKN) ceramics shows the large discharge phenomenon at the heating process, which was caused by the motion of oxygen vacancy in the poled ceramics [7]. Therefore, it was considered that the large leakage current of alkali niobate ceramics was closely related to the defect structure. However, the relation between the existence of oxygen vacancy and piezoelectric and ferroelectric property of alkali niobate was not clarified. Especially, the ferroelectric and its depolarization property have not been investigated in alkali niobate system.

In this study, the variation of the oxygen vacancy-related discharge was measured by thermally stimulated depolarization current measurement with different molar ratio of Na/K samples to investigate the individual attribution of alkali metal, Na and K, and the co-generated oxygen vacancy. In addition, the effect of the existence of oxygen vacancy on the piezoelectric and ferroelectric property of sodium potassium niobate was investigated by reducing the raw materials of alkali content from the composition of $Na_{0.5}K_{0.5}NbO_3$.

2. Experimental procedures

$Na_{0.5}K_{0.5}NbO_3$ (N5K5) ceramics was synthesized by an ordinal solid state reaction method. Na_2CO_3, K_2CO_3 and Nb_2O_5 of high purity (99.99%) raw powders were weighed and mixed with zirconia ball in acetone medium for 24 h. The dried mixture was calcined at 950 °C for 10 h and ball-milled again. The calcined powder was uniaxially pressed into a disk shape under 100 MPa and additionally cold isostatic pressed under 200 MPa. The disks were sintered at 1095 °C for 2 h. In addition, $K_{0.4}Na_{0.6}NbO_3$ (K4N6) and $K_{0.6}Na_{0.4}NbO_3$ (K6N4) ceramics were also synthesized as comparatives with different molar ratio of Na/K.

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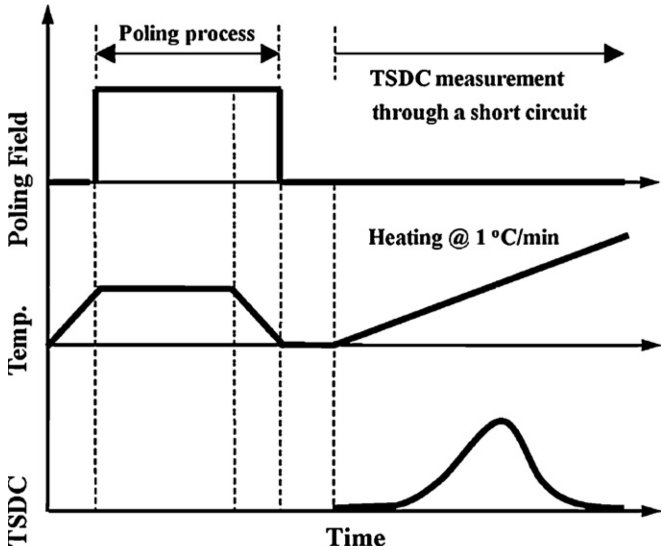

Fig. 1. Thermally stimulated current measurement program of the poled alkali niobate ceramics.

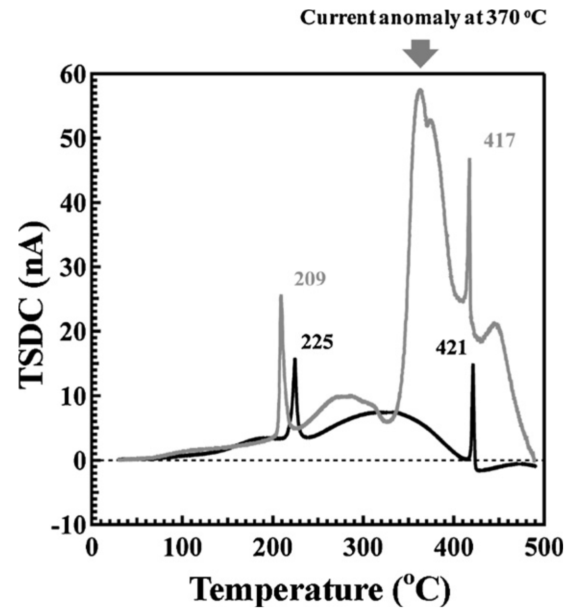

Fig. 3. Thermally stimulated depolarization current patterns of the poled N5K5 ceramics with d_{33} value of 116 pC/N ($N5K5_H$) and 97 pC/N ($N5K5_L$).

The sintered disk ceramics were ground on the top and bottom surfaces. The surfaces were polished by diamond abrasives to obtain the fine surfaces. The dimension of the disk ceramics was approximately 10 mm in diameter and 0.8 mm in thickness. Ag paste was painted on the surfaces and fired to form the electrode. The ceramics was heated up to 150 °C in a silicone oil bath and electrically poled under a field of 3 kV/mm for 0.5 h. After cooling to room temperature, the poling field was turned off and the ceramics was attached to a short circuit via an electrometer. The poled ceramics was heated from room temperature to 500 °C at the rate of 1 °C/min. Then, the thermally stimulated depolarization current was measured by the electrometer at the heating process. The poling and thermal program is shown in Fig. 1. On the other hand, the poled N5K5 ceramics was cut parallel to the electrodes into two parts as shown in Fig. 2. One part was contacted with the negative electrode at the poling treatment and another part was contacted with a ground electrode. These are named as N5K5(−) and N5K5(+), respectively. The *P*–*E* hysteresis loops of the two samples were observed.

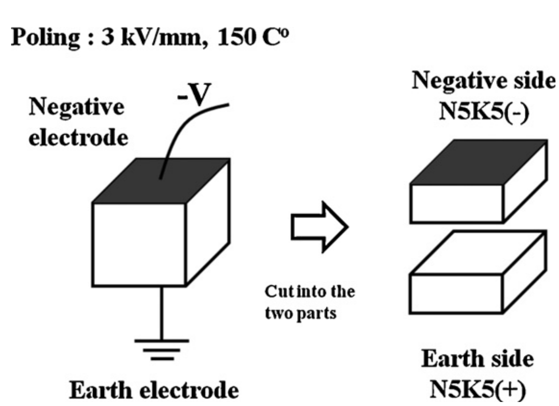

Fig. 2. Schematic illustration for the *P*–*E* hysteresis measurement of the poled N5K5 ceramics.

3. Results and discussion

Fig. 3 shows the TSDC patterns of the poled N5K5 ceramics with 97 pC/N and 116 pC/N of d_{33} values. These ceramics were named as $N5K5_L$ and $N5K5_H$, respectively. The large anomalous current pattern was observed around at 370 °C of $N5K5_L$ with the sharp pyrocurrent patterns around at 209 and 417 °C. The anomalous current generation was contributed of the motion of oxygen vacancy from the poling state to the equilibrium state at the heating measurement. The oxygen vacancy was induced by the sintering process at high temperature, which described as the following equation;

$$2M_M^x + \frac{1}{2}O_O^x \rightarrow M_2O + 2V_M' + V_O^{\bullet\bullet} \quad (1)$$

where M is alkali metal. Therefore, the large TSDC of $N5K5_L$ indicated that the amount of oxygen vacancy was larger in $K5K5_L$ ceramics than that in $K5N5_H$, and the concentrated oxygen vacancy caused the large TSDC current in the thermal relaxation process at the heating process.

The variation of the oxygen vacancy was also observed as the asymmetric *P*–*E* hysteresis loop of the poled ceramics as shown in Fig. 4. The *P*–*E* hysteresis of N5K5(+) shows the asymmetric loop around at the original point of $E = 0$ kV/mm. The value of current peak for the inversion of ferroelectric domain structure, which is circled by broken line in Fig. 4, was different between the positive field and negative field. However, the *P*–*E* hysteresis of N5K5(−) shows the symmetric loop. The difference between N5K5(+) and N5K5(−) is contributed from the concentrated oxygen vacancy. The d_{33} value of each samples were different although the samples were same sintered body at the poling treatment; the d_{33} of N5K5(+) and N5K5(−) were 136 and 111 pC/N, respectively. The oxygen

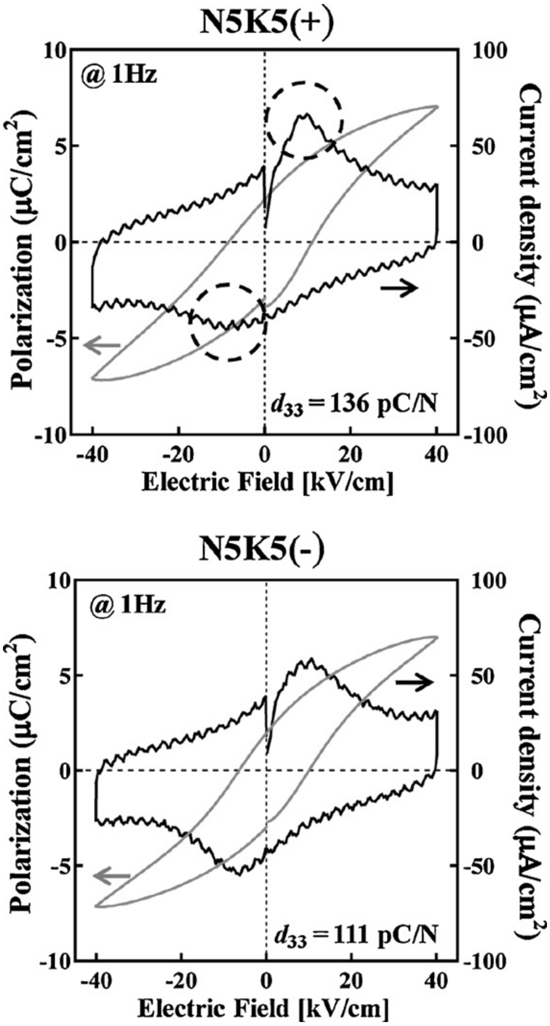

Fig. 4. *P–E* hysteresis loops and the current density patterns of the poled N5K5 ceramics of the part around earth electrode (N5K5(+)) and negative electrode (N5K5(−)).

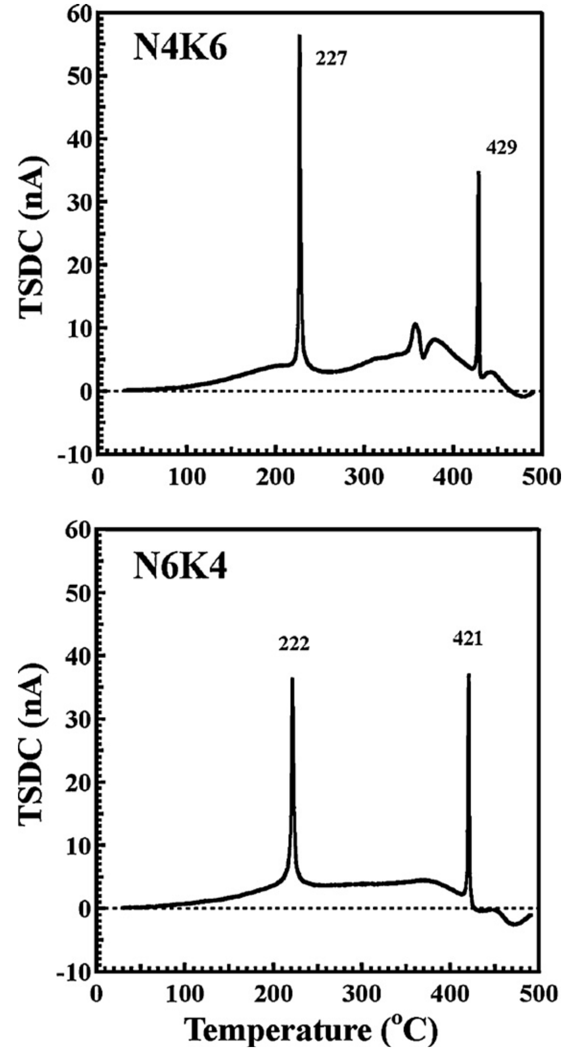

Fig. 5. Thermally stimulated depolarization current patterns of the poled N4K6 and N6K4 ceramics.

vacancy behaved as the space charge and resulted in the asymmetric *P–E* hysteresis and the difference of d_{33} value.

Fig. 5 shows the TSDC patterns of the poled N4K6 and N6K4 ceramics at the heating process. The small current anomaly was observed on the TSDC pattern of N4K6 at 357 °C. The peak temperature of N4K6 was close to the temperature of the large anomaly observed for TSDC pattern of $N5K5_L$. Therefore, the current was also contributed of the motion of oxygen vacancy. On the other hand, the TSDC pattern of N6K4 ceramics was flat around the temperature. This means that the relatively large amount of oxygen vacancy was existed in N4K6 and N5K5 ceramics, i.e. the oxygen vacancy existed in the ceramics which was synthesized from the raw materials of the equivalent molar amount of Na and K, against the ceramics which was synthesized from the Na-riched raw material. Dai et al. showed that the piezoelectric property of $KNbO_3$–$NaNbO_3$ solid solution showed the maximum value at the Na-riched composition of $K_{0.48}Na_{0.52}NbO_3$ [8]. Therefore, the K-riched sample of N4K6 and the N5K5 must be relatively large amount of oxygen vacancy as well as Na ion vacancy to approach the equilibrium composition near around

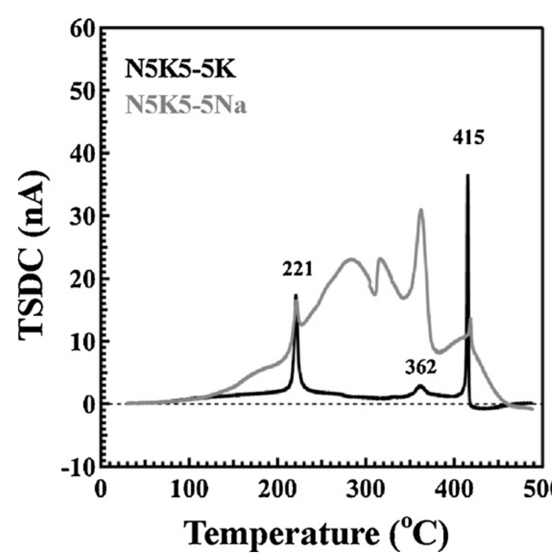

Fig. 6. Thermally stimulated depolarization current patterns of the poled K-lacked N5K5 (N5K5-5K) and Na-lacked N5K5 (N5K5-5Na) ceramics.

$K_{0.48}Na_{0.52}NbO_3$ at the sintering process. When the defects of alkali metals and oxygen were introduced by reducing the amount of raw materials of K_2CO_3 and Na_2CO_3 at the synthesis, the TSDC was quite varied. Fig. 6 shows the TSDC patterns of the poled N5K5-5K and N5K5-5Na ceramics at the heating process. The TSDC of $Na_{0.45}K_{0.50}NbO_3$ (N5K5-5Na) ceramics shows the large broad pattern was observed. On the other hand, the TSDC of $Na_{0.50}K_{0.45}NbO_3$ (NKN-5K) ceramics shows relatively flat current pattern although the small anomaly was detected around at 362 °C. This result suggests that the equilibrium composition of the $NaNbO_3$–$KNbO_3$ system was near to Na-riched composition against N5K5. In addition, the difference of the molar ratio of Na/K in alkali niobate ceramics was closely correlated to the generation of oxygen vacancy.

4. Conclusion

TSDC pattern of the poled sodium potassium niobate ceramics includes the large anomaly, which was caused by the relaxation of oxygen vacancy. The current anomaly of the poled ceramics with low d_{33} value showed the large TSDC of the relaxation of oxygen vacancy at around 370 °C. The oxygen vacancy was piled up around the electrodes in the poling treatment, and the ferroelectric properties of each the electrode sides were quite different by the concentration of the oxygen vacancy. The oxygen vacancy lead to the low piezoelectric property. The relaxation current of oxygen vacancy was larger of the K-riched ceramics than that of Na-riched ceramics. This result suggests that the equilibrium composition of the $NaNbO_3$–$KNbO_3$ system was near to Na-riched composition against $Na_{0.5}K_{0.5}NbO_3$.

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