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Electric properties of alkali metal doped potassium niobate crystals

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Abstract

Alkali metal (Na, Rb or Cs) doped $KNbO_3$ single crystals are grown using an original pulling down method by means of co-doping with Na (small ionic size), Rb (large ionic sizes) or Cs (large ionic sizes) into $KNbO_3$. Single-phase crystals are successfully grown with orthorhombic system at room temperature, for all the pure and doped $KNbO_3$. Their electric properties, such as the dielectric constant and the impedance, are found to be changed according to the co-doping elements.

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1. Introduction

Potassium niobate crystals $KNbO_3$ (KN) have been interest materials in the ferroelectric and piezoelectric crystals research fields [1,2]. Bulk single crystals of KN were difficult to grow from melts because of the incongruent melting and the twice solid-state phase transformations phenomena (cubic/435 °C/tetragonal/225 °C/orthorhombic) [1]. Recently the KN crystals are of interest again in piezoelectric applications because of their large electric-mechanical coupling factors of more than 50% and the zero temperature coefficients [2].

On the other hand, $NaNbO_3$ (NN) thin films as an anti-ferroelectric material are also of interest because of their high Curie temperature of 365 °C [3–5]. However, it is difficult to fabricate the NN thin films due to the fact that the Na element is easy to evaporate during the fabrication process. Consequently, low-temperature process for NN, such as a sol–gel method, has been adapted [6]. Recently a solid solution of KN and NN, such as $(KNa)NbO_3$ (KNN), is of interest [7–10]. For the KNN, the properties were changed depending on the K/Na ratio [11]. Up to now, the KNN can be fabricated as bulk ceramics and thin films. But the KNN single crystals have rarely been reported. Judging from the phase diagrams as complete solid solution on KN–NN ($KNbO_3$–$NaNbO_3$) [12,13], the composition of grown single crystals is changed during the growth, as the Na ion is quite small compared to the K ion [14]. We have discovered that it would be easier to grow the crystals by doping a large ion, for example, Rb or Cs as a co-dopant of Na, such as $(KNaRb)NbO_3$ (KNRN) or $(KNaCs)NbO_3$ (KNCN) [15,16].

High quality KN single crystals have been grown with low lattice defects in fiber shape. We have developed a new growth method using the pulling down method in the fiber shape KN, KNRN and KNCN crystals [16,17]. This method can even be applied to grow single crystals of solid solutions.

In the present work, we have grown the $KNbO_3$ single crystals co-doped with several alkali metal elements in the fiber shapes. The crystal and electric properties were investigated.

2. Experimental

Crystal growth method is called Floating Zone Pulling Down (Fz-PD) method using Pt tube as a melt feeder of starting material and a keen Pt wire for a seed crystal [18]. The diameter of Pt tube was 3 mm. The ratio of alkali ions and Nb ion was not 50:50 but 54:46 referring to the previous studies on KN [16]. The ratio is determined only for our methods. Different ratio was reported by other groups [16]. Crystals were grown in Ar gas flow condition. The pulling-down rate of 10 mm/h was used and no crystal rotation was employed. The percentages of Na, Rb or Cs in the KNRN or KNCN were up to 10–20 mol%.

Since the starting materials of Rb and Cs carbonates can absorb moisture easily, the starting pellets by the solid-state

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reaction method were decomposed soon even under a dry atmosphere. Therefore we used lower-purity carbonate for the starting materials such as 97% (Rb) and 95% (Cs) [19]. Moisture absorption of lower-purity carbonates is smaller than that of high-purity carbonates (99%). The impurities of lower-purity carbonates are mainly of K and Na, so it is not an issue in using these lower-purity carbonates.

The detailed crystal growth method can be found in one of our previous paper [19]. So far, the double ring Fz heater furnace was used in our experiments [18]. However even a conventional double ellipsoidal mirror furnace was employed, the sizes of crystals would be big enough for characterization.

For the characterization of samples, the grown crystals were cut perpendicularly to the growth direction about 1 mm in diameter and 2 mm in length. The powder X-ray diffraction characterization was carried out, and then the dielectric constant and impedance were analyzed. Ag paste and Ag wire were used for the electrode and lead wire respectively. Dielectric constants were measured at low and high temperature conditions in 10–100 kHz using a LCR meter (Agilent 4984A) and an electric furnace. At low temperature conditions, liquid nitrogen was used as a coolant. Measurement was carried out at heating process from 77 to 273 K. No automatic temperature control was available hence the data between 77 and 100 K was difficult to obtain. On the other hand, at high temperature conditions, the measurements were carried out for heating processes up to 500 °C with 100 K/h, and then cooling with the same rate. Impedance and phase angle were measured at room temperature from 500 kHz to 2 MHz using an impedance analyzer (Agilent 4294A) with a test fixture (Agilent 16034E).

3. Results and discussion

Single-phase fiber shape crystals can be grown with 1–2 mm in diameter and 5–10 mm in length. Crystals were grown along the *c*-axis (shortest axis in the orthorhombic system). The *c*-axis can be estimated from a rectangle crystal habit easily. The grown crystals were found to be in good quality by using the cross-nicols observation. In fiber shape crystals, a self-poling effect would be expected as observed in $LiNbO_3$ [20]. Unfortunately the self-poling effect was difficult to observe in the present crystals.

Fig. 1 shows two typical as-grown KNRN and KNCN single crystals. Both crystals show the same brownish and transparent color. The crystal growth conditions in details were reported in our previous paper [19]. While the KN single crystals in long length can be grown, the KNRN and KNCN crystals are difficult to grow to long size by our present system. The revised growth system is reported in another paper [21].

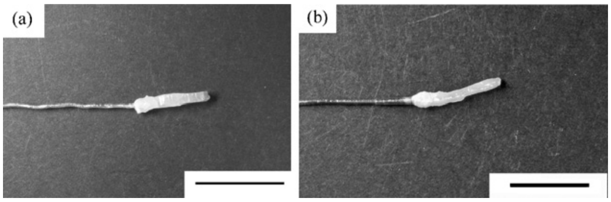

Fig. 1. Typical as-grown single crystals. (a) KNRN: $(KNaRb)NbO_3$ and (b) KNCN: $(KNaCs)NbO_3$. Scale: 10 mm.

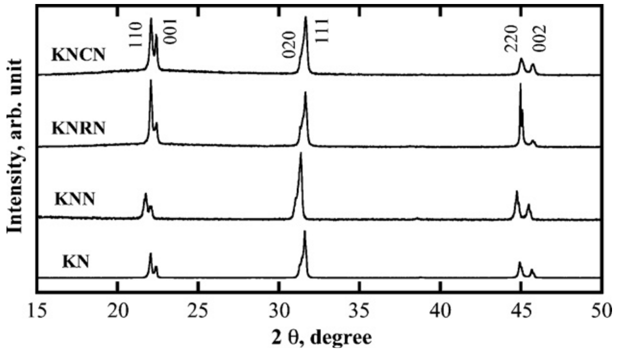

Fig. 2. Powder X-ray diffraction patterns. KN: $KNbO_3$, KNN: $(KNa)NbO_3$, KNRN: $(KNaRb)NbO_3$ and KNCN: $(KNaRb)NbO_3$.

Fig. 2 shows the powder X-ray diffraction patterns of KN, KNN, KNRN and KNCN. The orthorhombic crystal-phase system can be formed at room temperature on the KNRN and KNCN, as well as KN. The peak positions were shifted to lower angles on the KNN. This means that the Na ions can occupy the Nb site and enlarge the crystal lattice. The peak positions of KNRN and KNCN were not changed compared to the KN. While the chemical composition and the lattice volume of alkali metals changed the KNN dramatically [19], little change was observed on the KNRN and KNCN, i.e., the co-doping of Rb or Cs with Na minimizes the change on the chemical composition.

Fig. 3 shows the temperature dependence of dielectric constants in 10–100 kHz on the KN, KNN, KNRN and KNCN along the *c*-axis. On the KN, KNN and KNRN, the high-temperature dielectric constants were also shown in one of our previous paper [15]. Poling was not carried out since the self-poling effect would be expected [20]. At low temperature, the peaks corresponding to the phase transformation from rhombohedral to orthorhombic structures were observed around 240 K. Clear difference among the different co-doping crystals was not observed. At high temperature, the peaks corresponding to the phase transformation (such as among the orthorhombic, tetragonal and cubic structures) can also be

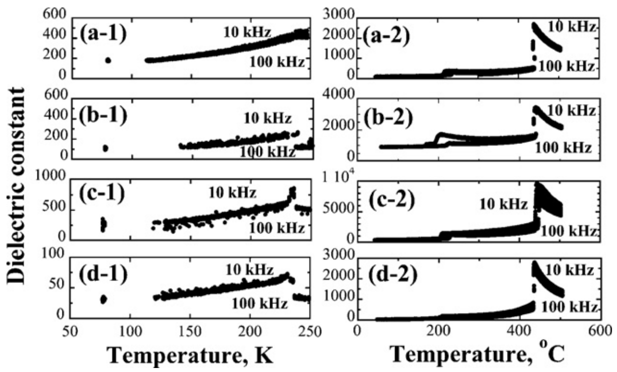

Fig. 3. Temperature dependence of dielectric constants in 10–100 kHz. (a) KN: $KNbO_3$, (b) KNN: $(KNa)NbO_3$, (c) KNRN: $(KNaRb)NbO_3$ and (d) KNCN: $(KNaRb)NbO_3$ (left: low temperature, right: high temperature).

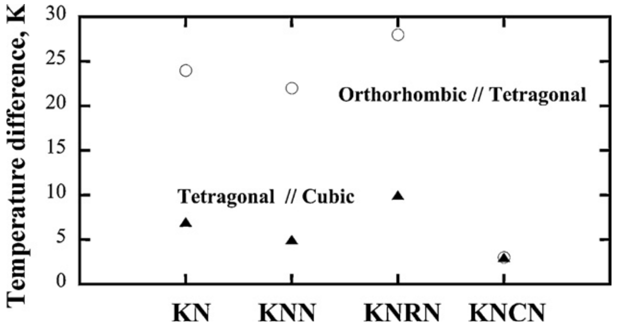

Fig. 4. Difference of phase transformation temperature during the heating and cooling processes on the KN, KNN, KNRN and KNCN.

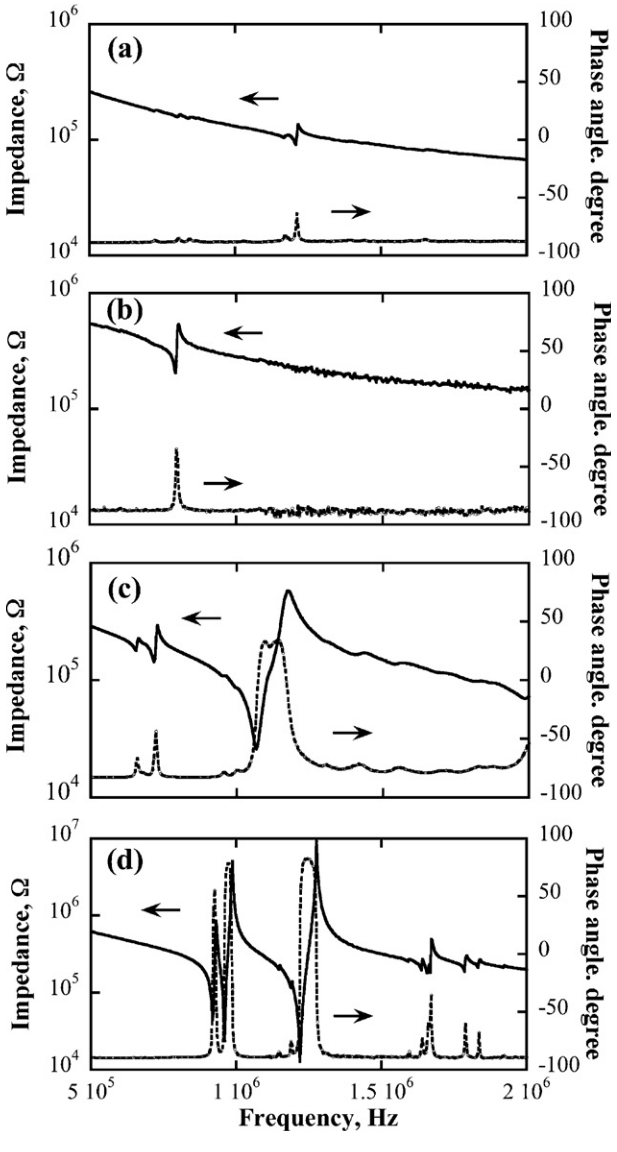

Fig. 5. Frequency dependence of impedance and phase angle. (a) KN: $KNbO_3$, (b) KNN: $(KNa)NbO_3$, (c) KNRN: $(KNaRb)NbO_3$ and (d) KNCN: $(KNaRb)NbO_3$.

observed. The values of high-temperature dielectric constant of KNN is larger compared to the KN, KNRN and KNCN. Since the composition change of KNN crystal is expected to be the largest, we consider these dielectric constant values are almost the same for all co-doping crystals. In all crystals, twice phase transformations were observed clearly around 235 °C and 435 °C, respectively. Hysteresis in temperature was observed during the heating and cooling processes, especially at the low-temperature transformation around 235 °C.

Fig. 4 shows the difference of phase transformation temperature during the heating and cooling processes at high temperature. The absolute temperatures of phase transformations had already been shown in previous paper [19]. The temperature difference between the orthorhombic and tetragonal structures is larger compared to the difference between the tetragonal and cubic structures. The temperature difference was the smallest for the KNCN, but the reason is not clear in this stage.

Fig. 5 shows the frequency dependence of impedance and phase angle on the KN, KNN, KNRN and KNCN. The resonant and anti-resonant peaks, which reflect the piezoelectric properties, can be observed in all samples. The peaks are corresponding to the vibration mode along the longitudinal direction of samples. Since the poling was not carried out for these samples, the resonant and anti-resonant peaks on KN and KNN are not as large as expected. However, the resonant and anti-resonant peaks of the KNRN and KNCN are considerably large. The phase angle also changes from −90° to 50° without poling. Thus the co-doping of Rb or Cs with Na enhances the piezoelectric properties.

4. Summary

Alkali metal (Na, Rb or Cs) doped $KNbO_3$ single crystals were grown using our own developed pulling down method. The co-doping as small ionic size of Na with a large ionic size of Rb or Cs into $KNbO_3$ was employed. The pure and doped $KNbO_3$ crystals with single-phase can be grown in orthorhombic structure at room temperature. Their electric properties, such as the dielectric constant and the impedance, were changed accordingly with the co-doping of Rb or Cs with Na. Large phase-angle change was also observed in the impedance due to the co-doping.

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