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*Article*

# Tetragonal-to-Tetragonal Phase Transition in Lead-Free $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) Crystals

**Dabin Lin [1], Zhenrong Li [2,*], Fei Li [2], Changlong Cai [1], Weiguo Liu [1] and Shujun Zhang [3,*]**

[1] Laboratory of Thin Film Techniques and Optical Test, Xi'an Technological University, Xi'an 710032, Shaanxi, China; E-Mails: ldbin2007@live.cn (D.L.); changlongcai@126.com (C.C.); wgliu@163.com (W.L.)

[2] Electronic Materials Research Laboratory, Key Laboratory of Education Ministry/International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China; E-Mail: lifei1216@gmail.com

[3] Materials Research Institute, the Pennsylvania State University, University Park, PA 16802, USA

* Authors to whom correspondence should be addressed; E-Mails: zhrli@mail.xjtu.edu.cn (Z.L.); soz1@psu.edu (S.Z.); Tel.: +86-29-8266-8679 (Z.L.); Fax: +86-29-8266-8794 (Z.L.).

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**Abstract:** Lead free piezoelectric crystals of $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) have been grown by the modified Bridgman method. The structure and chemical composition of the obtained crystals were determined by X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The domain structure evolution with increasing temperature for $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) crystals was observed using polarized light microscopy (PLM), where distinguished changes of the domain structures were found to occur at 400 °C and 412 °C respectively, corresponding to the tetragonal to tetragonal phase transition temperatures. Dielectric measurements performed on $(K_{0.11}Na_{0.89})NbO_3$ crystals exhibited tetragonal to tetragonal and tetragonal to cubic phase transitions temperatures at 405 °C and 496 °C, respectively.

**Keywords:** lead free piezoelectric crystal; phase transitions; domain structure

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## 1. Introduction

The $(K_xNa_{1-x})NbO_3$ (KNN)-based solid solutions have been extensively studied in view of their potential to replace the lead-based piezoceramics from the viewpoint of environmental impact [1–6]. Over the past few years, significant improvements on the piezoelectric properties in KNN-based lead free ceramics have been achieved, with piezoelectric coefficient ($d_{33}$) values being in the order of 200~300 pC/N. Shifting the orthorhombic to tetragonal phase transition temperature downward to room temperature limited their temperature usage range greatly [7–10]. KNN-based single crystals have been grown by various crystal growth methods such as solid state growth, Bridgman, flux, and top-seeded solution growth methods [11–15]. $(K_{0.5}Na_{0.5})NbO_3$ crystals with the thickness of 160 μm were grown by the solid state reaction method using $KTaO_3$ seed crystal [11], while $0.95(K_{0.5}Na_{0.5})NbO_3$-$0.05LiNbO_3$ crystals was grown by the Bridgman method and $d_{33}$ was found to be in the order of 200~400 pC/N [12]. Mn doped $(K_{0.5}Na_{0.5})NbO_3$ crystals with electromechanical coupling factors ($k_{33}$) of 64% and $d_{33}$ of 160 pC/N have been fabricated by the flux method using KF-NaF eutectic composition [13]. The domain structure observation indicated that the enhanced piezoelectric property of KNN crystals by Mn doping was due to the smaller domain size [14]. Recently, Li, Ta modified (K, Na)$NbO_3$ crystals with size of 18 × 18 × 18 $mm^3$ have been grown using the top-seeded solution growth method, possessing high $k_{33}$ of 88% and $d_{33}$ of 255 pC/N, with orthorhombic to tetragonal and tetragonal to cubic phase transitions being at 79 °C and 276 °C, respectively [15].

The optical method is one of the most effective ways to observe domain structure and phase transitions. There are many studies on domain structures and phase transitions in lead-free single crystal systems using polarizing light microscopy (PLM) [16–18]. Wada *et al.* [16–19] reported that the piezoelectric properties were associated with the domain size in $KNbO_3$ and $BaTiO_3$ single crystals, while Lin *et al.* [18,19] studied the domain structure evolution of poled and unpoled [001]-oriented KNN crystals in a temperature range of −195 to 405 °C using PLM. It was reported that two tetragonal phases existed in pure $NaNbO_3$ and $(K_xNa_{1-x})NbO_3$ ($x < 0.1$) crystals, confirmed by optical observations [20]. However, the phase transition is yet unclear in the $(K_xNa_{1-x})NbO_3$ ($0.1 < x < 0.2$) system, as shown in Figure 1. In this paper, KNN crystals were grown by the modified Bridgman method. The evolution of tetragonal domain structures was studied by the observation of domain configurations using PLM based on the principles of optical crystallography and symmetry. Finally, the tetragonal to tetragonal phase transition that is determined by the changes of tetragonal domain structure was discussed.

## 2. Results and Discussion

Figure 2 shows the Bridgman-grown KNN crystals. It is difficult to obtain large size $(K_xNa_{1-x})NbO_3$ (KNN) crystals due to the spontaneous nucleation and the composition segregation during crystal growth. The composition of the as-grown KNN crystals was found to significantly deviate from the starting composition [21], because of the high volatility of potassium and sodium oxides during the crystal growth.

**Figure 1.** Phase diagram of $NaNbO_3$-$KNbO_3$ solid solution. Reprinted with permission from [22], Copyright 1976 ICUr.

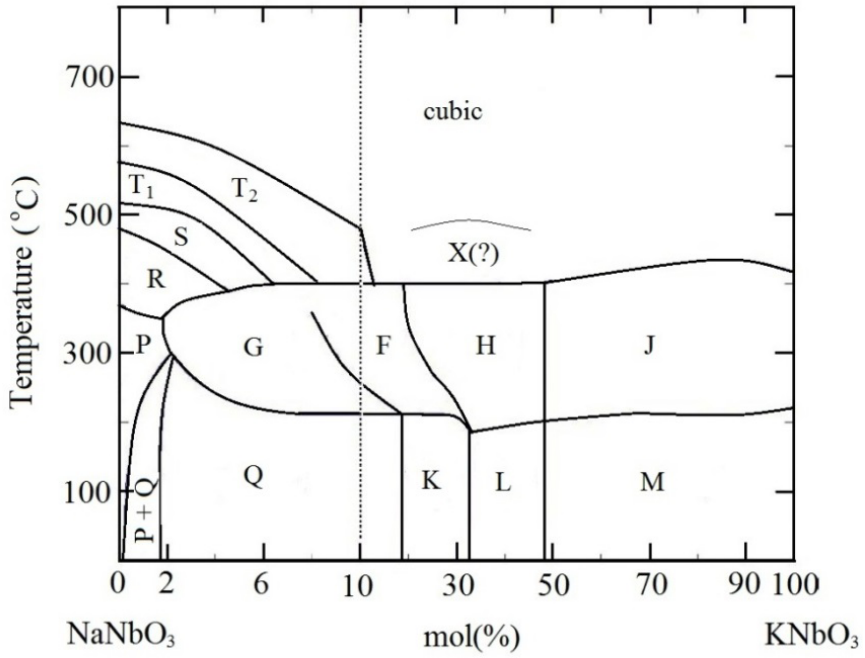
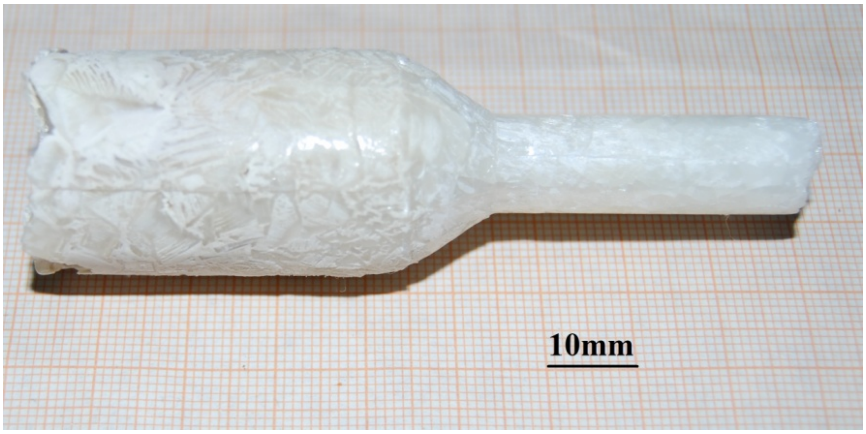



**Figure 2.** The $(K_xNa_{1-x})NbO_3$ (KNN) crystals grown by the modified Bridgman method.

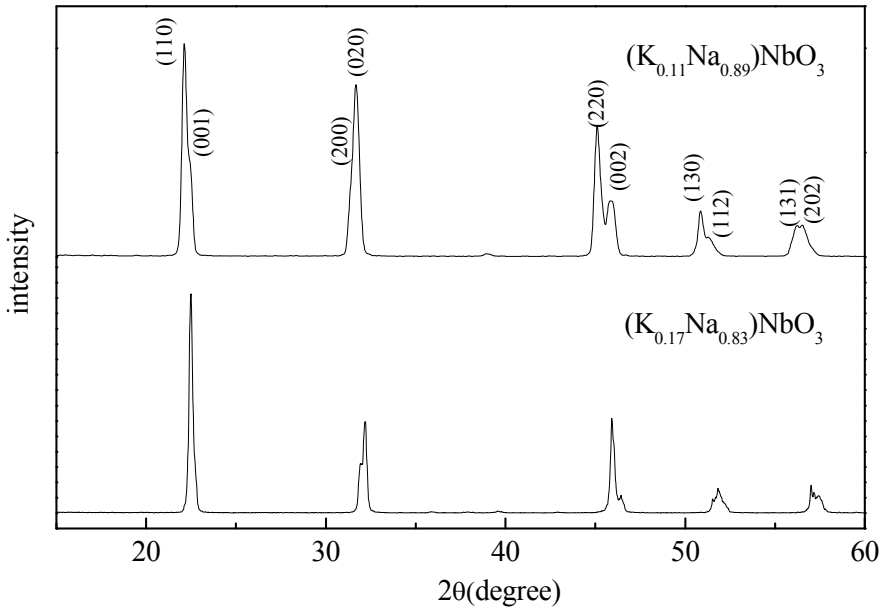



In order to determine the composition homogeneity of the KNN crystals, three different locations on crystal plates with size of 3 × 3 × 0.4 $mm^3$ were analyzed by electron probe microanalysis (EPMA), as listed in Table 1. The crystal samples were found to possess homogeneous compositions, but with potassium content far below their nominal composition. Figure 3 gives the room temperature X-ray diffraction pattern of the ground $(K_{0.17}Na_{0.83})NbO_3$(KNN) crystals powder, showing the pure perovskite phase. Miller indices of KNN ground powder as shown in Figure 3 are determined according to the $KNbO_3$ XRD pattern (PDF #32-0822).

**Table 1.** Composition calculated the electron probe microanalysis (EPMA) results of the obtained KNN crystals.

| Sample | Na | K | Nb | Formula |
|---|---|---|---|---|
| Raw material | 50 | 50 | 100 | $(K_{0.5}Na_{0.5})NbO_3$ |
| Sample 1 | 90.62 | 10.88 | 100 | $(K_{0.11}Na_{0.89})NbO_3$ |
| | 89.65 | 11.44 | 100 | $(K_{0.11}Na_{0.89})NbO_3$ |
| | 88.76 | 12.04 | 100 | $(K_{0.12}Na_{0.88})NbO_3$ |
| Sample 2 | 83.71 | 18.50 | 100 | $(K_{0.18}Na_{0.82})NbO_3$ |
| | 83.54 | 16.76 | 100 | $(K_{0.17}Na_{0.83})NbO_3$ |
| | 82.99 | 15.77 | 100 | $(K_{0.16}Na_{0.84})NbO_3$ |

**Figure 3.** The XRD pattern of $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) crystals.




In ferroelectric material, the domain structure changes are related to the polarization vector and crystallography symmetry. Figure 4a–f summarized the eight compatible domain patterns in tetragonal phase state, including two kinds of 180° domain patterns, two kinds of 90° and 180° mixed domain patterns, and four kinds of 90° domain structures. Any change of crystallography symmetry will allow the polarization vector to move the domain structure from one state to another, leading to the phase transition. The domain patterns of [001]-oriented $(K_{0.11}Na_{0.89})NbO_3$ crystals from 310 °C to 510 °C during heating are given in Figure 5a–d, where only 90° domain walls were observed. At 310 °C, the tetragonal domain structures with similar pattern shown in Figure 4b were observed, with domain boundary parallel to [110] direction, as shown in Figure 5a. Upon further heating, tetragonal to tetragonal phase transitions occurred at 400 °C, where new tetragonal domain structures with similar pattern, shown in Figure 4d, were observed, with domain boundary parallel to the [110] direction, as shown in Figure 5b. The tetragonal-cubic phase transition was observed, as shown in Figure 5d. Until 530 °C, the $(K_{0.11}Na_{0.89})NbO_3$ crystals were in total extinction.

**Figure 4.** The compatible domain patterns in tetragonal phase state: (**a**) parallel and antiparallel 180° domain patterns; (**b**) two kinds of 90° and 180° mixed domain patterns; (**c**)–(**f**) four kinds of 90° domain patterns.

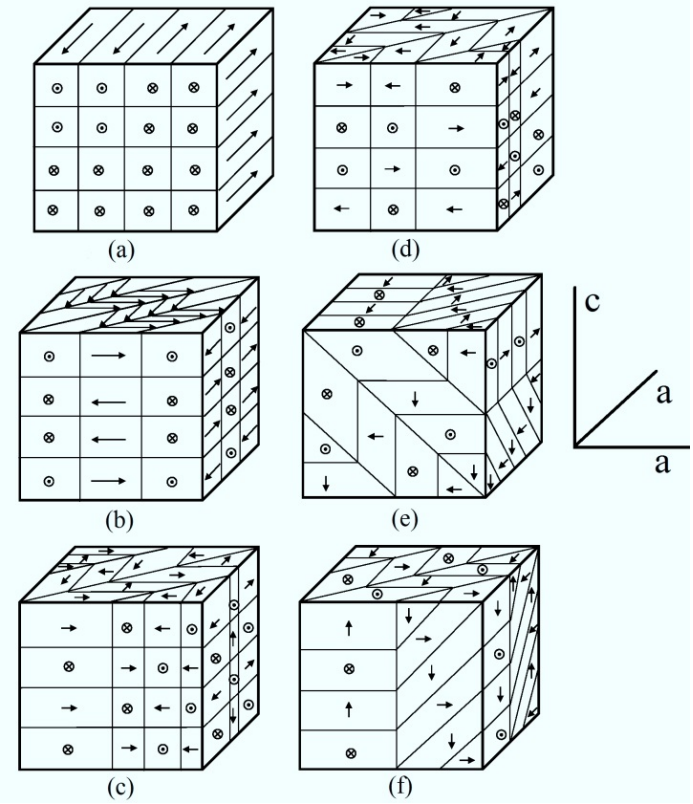



**Figure 5.** Temperature dependent domain structures in $(K_{0.11}Na_{0.89})NbO_3$ crystal: (**a**) 310 °C; (**b**) 400 °C; (**c**) 450 °C; (**d**) 510 °C.

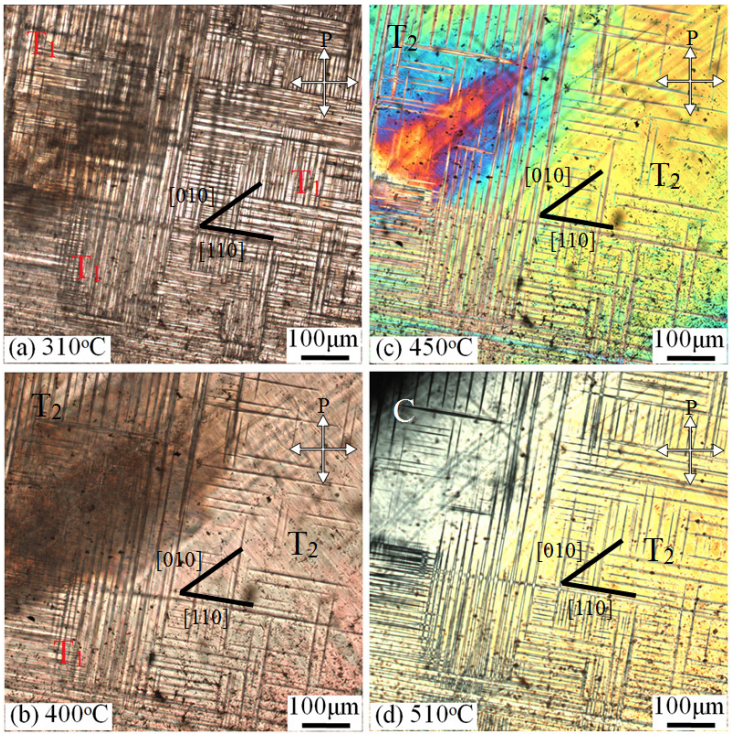


Figure 6a–d show the domain pattern of [001]-oriented $(K_{0.17}Na_{0.83})NbO_3$ crystals from 400 °C to 472 °C during heating. At 400 °C, the tetragonal domain structures, similar to the domain pattern shown in Figure 4d, were observed with domain boundary parallel to the [110] direction. At 412 °C, a new tetragonal phase with similar patterns shown in Figure 4e appeared with domain boundary parallel to the [100] direction and extinctions along the [110] directions, as shown in Figure 6b. The new tetragonal domain structure occupies the whole sample at 450 °C, as observed in Figure 6c. At 472 °C, the tetragonal-cubic phase transition was observed, as shown in Figure 6d. This tetragonal to tetragonal phase transition was also observed optically in pure $NaNbO_3$ crystal and $(K_xNa_{1-x})NbO_3$ ($x < 0.1$) crystal [20], revealing that two tetragonal phases co-exist in $(K_xNa_{1-x})NbO_3$ ($0.1 < x < 0.2$).

**Figure 6.** Temperature dependent domain structures in $(K_{0.17}Na_{0.83})NbO_3$ crystal: (**a**) 400 °C; (**b**) 412 °C; (**c**) 450 °C; (**d**) 472 °C.

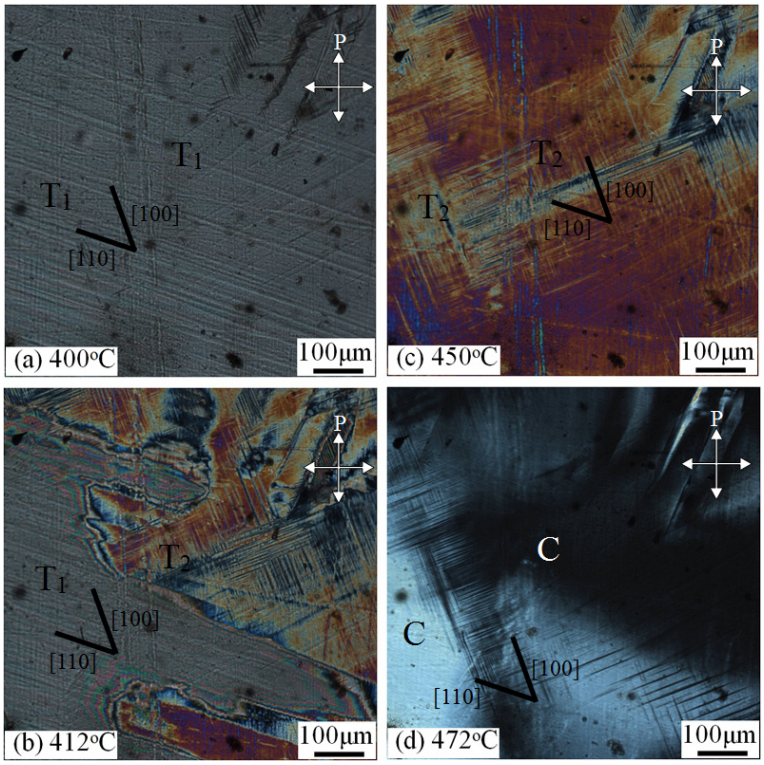



Figure 7 shows the temperature dependence of the dielectric permittivity and dielectric loss for [001]-oriented $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) crystals, measured at 1 kHz frequency. For $(K_{0.11}Na_{0.89})NbO_3$ crystals, three phase transition temperatures, including the orthorhombic to tetragonal, tetragonal to tetragonal, and tetragonal to cubic were found to locate at 206 °C, 405 °C, and 496 °C, respectively. For $(K_{0.17}Na_{0.83})NbO_3$ crystals, the first dielectric peak at 208 °C corresponds to the orthorhombic to tetragonal phase transition, while the second dielectric anomaly at 424 °C indicates the tetragonal to cubic phase transition. The existence of tetragonal to tetragonal phase transitions in $(K_{0.17}Na_{0.83})NbO_3$ crystals observed by PLM, cannot be confirmed by either dielectric or X-ray measurement [20,23] due to the fact that the structural perturbation is very small. The tetragonal to tetragonal ($T_{T1-T2}$) and tetragonal to cubic ($T_C$) phase transition temperatures in $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) observed by domain observation and dielectric permittivity are summarized in

Table 2. As reported in previous work [19,20,22,23], the $T_C$ determined by dielectric measurement, X-ray and optic method are inconsistent.

**Figure 7.** Temperature dependence of dielectric permittivity for $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) single crystal at 1 kHz.

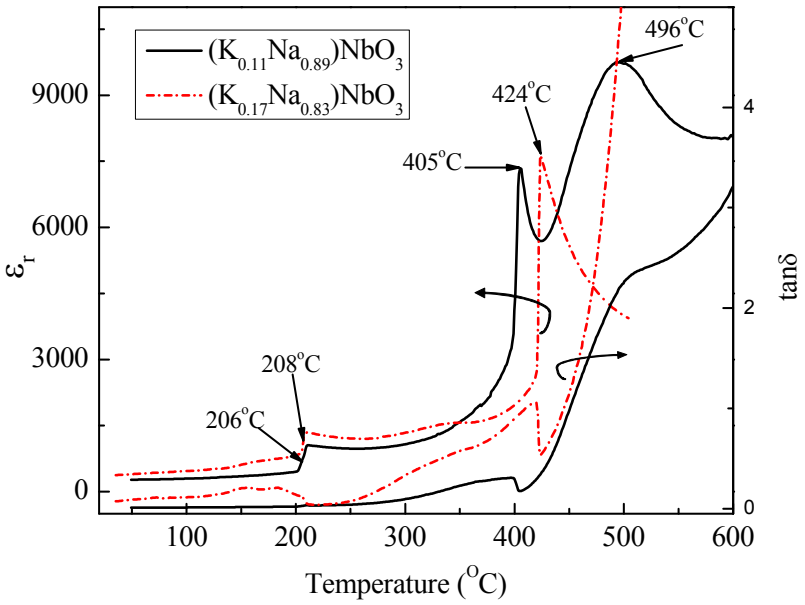



**Table 2.** The phase transition temperatures obtained by domain observation and dielectric permittivity.

| crystals | Domain observation | | Dielectric permittivity | |
|---|---|---|---|---|
| | $T_{T1-T2}$ (°C) | $T_C$ (°C) | $T_{T1-T2}$ (°C) | $T_C$ (°C) |
| $(K_{0.11}Na_{0.89})NbO_3$ | 400 | 510 | 405 | 496 |
| $(K_{0.17}Na_{0.83})NbO_3$ | 412 | 472 | – | 424 |

## 3. Experimental Section

Single crystals of $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) were grown using a modified Bridgman method. The powders of $Na_2CO_3$, $K_2CO_3$ and $Nb_2O_5$ were used as raw materials for crystal growth. Raw materials were mixed by ball milling using $ZrO_2$ media for 5 h and then calcined at 800 °C for 2 h. The synthesized powders with perovskite structure were put into a platinum (Pt) crucible with a lid. The highest temperature during growth was 1380 °C. The temperature gradient was about 50–60 °C/cm in the solid-liquid interface. After soaking for 24 h, the crucible was lowered down at the rate of 0.5 mm/h. The cooling rate was 50 °C/h to room temperature after the growth.

The crystal structure was analyzed by using X-ray diffraction (XRD RIGAKU D/MAX-2400, Rigaku, Tokyo, Japan). The elemental analyses were carried out by electron probe microanalysis (EPMA JEOL JXA-8100, JEOL, Tokyo, Japan). Optical observation of the domain structures was performed by using a polarizing light microscope (Olympus BX51, OLYMPUS, Tokyo, Japan) with an heating-cooling stage (LINKAM THMS600, Linkam, Tadworth, UK). The samples used in this study were unpoled [001]-oriented crystals with 40 μm in thickness and optical surface polish. At each testing temperature, the sample was maintained for 2 min, in order to get stabilized domain structures.

The phase structures were confirmed by the observation of ferroelectric domain configurations under polarization microscopes, based on the principle of optical crystallography and symmetry. After the observation, silver electrodes were painted onto both surfaces of the samples for electrical measurements. The temperature dependence of the dielectric permittivity of KNN single crystal was measured using a multi-frequency LCR meter (HP4284A), which connected to a computer controlled furnace.

## 4. Conclusions

The composition homogeneity of the as-grown $(K_xNa_{1-x})NbO_3$ crystals by the modified Bridgman method was analyzed by electron probe microanalysis (EPMA). The K/Na ratio of $(K_xNa_{1-x})NbO_3$ ($x$ = 0.11 and 0.17) crystals deviated significantly from the nominal composition with K/Na ratio of 1. For $(K_{0.11}Na_{0.89})NbO_3$ crystals, tetragonal to tetragonal and tetragonal to cubic phase transition temperatures were found to locate at 405 °C and 496 °C by dielectric measurement, respectively. Two distinguished changes of the domain structures were found to occur at 400 °C and 510 °C, corresponding to the two phase transition temperatures. For $(K_{0.17}Na_{0.83})NbO_3$ crystals, the optical observation of the domain configurations revealed the occurrence of tetragonal to tetragonal and tetragonal to cubic phase transitions at 412 °C and 472 °C respectively, while only tetragonal to cubic phase transition at 424 °C was obtained from the dielectric temperature behavior. A similar phenomenon was also reported for $(K_xNa_{1-x})NbO_3$ ($x < 0.1$) single crystal by the optical method [20].

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## Author Contributions

Dabin Lin, Zhenrong Li and Shujun Zhang designed the experiments and co-wrote the manuscript. Dabin Lin performed the experiments. All authors analyzed the data and discussed the results.

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