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Growth and Characterization of $K_3LiNb_6O_{17}$ Single Crystals

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Starting from the stoichiometric composition of $K_2CO_3 : Li_2CO_3 : Nb_2O_5$=3 : 2 : 5 with the mole ratio, $K_3LiNb_6O_{17}$ single crystals were grown using the Czochralski method. Although the starting melt composition corresponds to the $K_3Li_2Nb_5O_{15}$ crystals, the chemical composition of the as grown crystals appears to be $K_{2.95}Li_{1.33}Nb_{6.17}O_{17}$ or $K_{2.60}Li_{1.17}Nb_{5.44}O_{15}$ which relatively contain fewer Li ions than $K_3Li_2Nb_5O_{15}$ crystals. We investigated the influence of the deficiency of the Li ions in the tetragonal tungsten bronze structure through the measurements of D-E loop, temperature dependent dielectric constant, differential thermal analysis and temperature dependent X-ray diffraction pattern.

Key words: Czochralski method, Potassium lithium niobate, Tungsten bronze structure

I. Introduction

Tungsten bronze (TB) type ferroelectric crystals such as $Sr_{1-x}BaxNb_2O_6$, $KBa_2Nb_5O_{15}$, $KSr_2Nb_5O_{15}$ and $K_3Li_2Nb_5O_{15}$ have attracted attention for electro-optic, photorefractive and surface acoustic wave (SAW) applications.[1-3] Among those crystals, $K_3Li_2Nb_5O_{15}$ (KLN-1) crystals are known as a potentially useful material for linear and nonlinear optical application comparing to $LiNbO_3$ and $KNbO_3$ crystals. Furthermore, the KLN-1 crystals are a good candidate for blue light emitting material through second harmonic generation which takes place at room temperature and enables non-critical phase matching.[4]

However, application of the KLN-1 crystals is limited because many difficulties are encountered during crystal growth. KLN-1 is easy to crack near phase transition temperature when it is cooled down to room temperature after growth. Also, a change of composition, which is related to the crystal growth condition, strongly affects to the Curie temperature and the optical properties because of high volatilization in growth temperature. Furthermore, the possibility of the growth of $K_3LiNb_6O_{17}$ (KLN-2) crystals which is caused by the high volatilization of the Li and K ions has been reported by Tanaka *et al.*[5] for the KLN-2 polycrystalline sample (ceramic). The structure of the KLN-2 is considered to be the same as that of the KLN-1 crystals and belongs to the TB type phase. However, the physical properties of the KLN-2 crystals still remain uncovered.

In this study, we report the crystal growth of KLN-2 and the influence of the deficiency of the Li ions on structural and ferroelectric properties, and phase transition behaviors in the KLN-2 crystals with the tetragonal TB type structure.

II. Experimental Procedure

The KLN-2 crystals were grown using the Czochralski method from a stoichiometric melt composition of $K_2CO_3 : Li_2CO_3 : Nb_2O_5$=3 : 2 : 5 with the mole ratio. The oxide powders were mixed by ball milling and the mixed powder heated at 400, 600°C for 12 hours in air. After this pretreatment, the mixture was sintered at 900°C, put into a platinum crucible and melted at about 1,100°C by induction heating in air for 24 hours. The melt was cooled down to about 1,075°C, and the crystal was pulled from the melt using a seed crystal with [001] orientation. The pulling rate was about 1 mm/hour, and the rotating rate was 10 rpm. The as-grown crystals show pale yellow and the typical morphology of the TB type under the above growth conditions with dimension of 6×6×100 mm^3, as shown in Fig. 1(a).

The crystal composition determined by using a inductively coupled plasma emission spectrophotometer (ICP, Shimadzu ICP-1000 III, Japan). The structure of the as-grown crystals were determined by a X-ray diffraction (XRD, Rigaku RAD III, Japan). In order to measure the temperature dependent XRD pattern, the temperature control system was attached to the XRD equipment and was controlled within the accuracy of ±2°C.

The samples were cut along a and c axis and polished with 0.3 μm alumina powder. For electric measurement, gold electrode was evaporated on the two main surfaces. The D-E loop was observed using a ferroelectric test system (RT66A, USA) at room temperature. The temperature dependence of the dielectric constant was measured by an impedance analyzer (Hewlett-Packard 4194A, USA) for several frequency over the temperature range from room temperature to 500°C. The differential thermal analysis (DTA, Seiko SSC/5200, Japan) were studied with cooling and heating rate of 10°C/min.

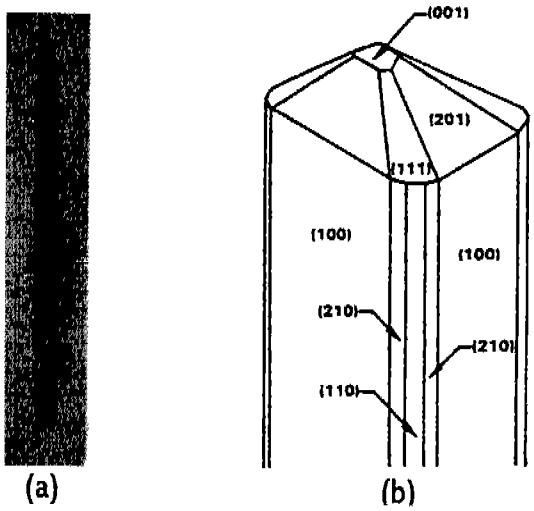

Fig. 1. The photography of as-grown and detailed morphology of the KLN-2 crystals. The as-grown crystals show transpa-rent with yellowish color.

II. Results and Discussion

TB type crystals have two different types, unfilled and filled TB type structure. The general site occupancy formula can be written as $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. The site A_1, A_2, C, B_1 and B_2 can be either partially or fully occupied by different cations. In the case of the KLN-1 crystals, the B_1 and B_2 sites are occupied by Nb, while A_1 and A_2 sites are occupied by K and C sites are occupied by Li. Namely, the KLN-1 crystals are known as completely filled TB type ones.[6]

However, we have found that the deficiency of Li ions in the C sites is dominant in the as-grown crystals by means of ICP composition analysis. The results are 11.9±0.8 wt% for K, 0.95±0.16 wt% for Li, and 59.1±1.8 wt% for Nb, and the molecular formula can be written in the form $K_{2.95}Li_{1.33}Nb_{6.17}O_{17}$ (=$K_{2.60}Li_{1.17}Nb_{5.44}O_{15}$, KLN-2), although the starting melt composition corresponds to the stoichiometry of the

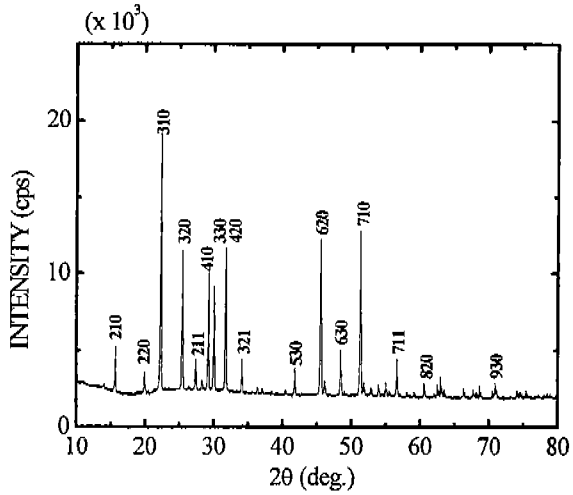

Fig. 2. The powdered XRD pattern of the as-grown crystals at room temperature.

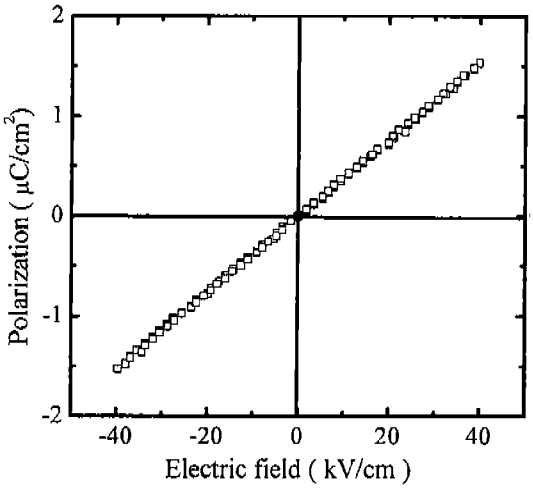

Fig. 3. D-E loop of the KLN-2 crystal at room temperature.

KLN-1 crystals. Compared with KLN-1 crystals, 42% of Li and 13% of K are expected to be vacant in the as-grown KLN-2 crystals. Therefore, the KLN-2 crystals are the unfilled TB type structure. However, it still remains as tetragonal structure. Because the morphology of the KLN-2 crystals is same with the KLN-1 and other tetragonal TB type crystals, they are square in shape and exhibit four well defined facets as shown in Fig. 1. Also the powdered XRD pattern of the as-grown crystals at room temperature is similar to that of Tanaka *et al.*[5] as shown in Fig. 2. The estimated lattice constant are a=b=12.593 Å, c=3.988 Å which is slightly different to the previously reported value.[5-6] The difference is due to the difference in composition.

We have found that the deficiency of the Li ions in C-sites strongly affects to the ferroelectric and thermal properties of the KLN-2 crystals. The results of the D-E loop measurement of the KLN-2 crystals are shown in Fig. 3. As increasing bias field up to 40 kV/cm, the sample does not show a hysteresis both along a and c-axis at room temperature.

Fig. 4 and 5 show the temperature dependence of DTA signal and XRD pattern in the temperature range from room temperature to 500°C. In this measuring temperature range, the temperature dependent DTA signal and XRD pattern do not indicate any signature for a phase transition on cooling and heating process. As consistent with the literature,[7-9] it has been reported that K_2O-Li_2O-Nb_2O_5 ternary system can be divided into three regions by Nb_2O_5 concentration. The region, belonging to the as-grown KLN-2 crystals, where the Nb_2O_5 concentration ranges from 0.55 to 0.68 does not show ferroelectric property. Recently, from the Raman and Infrared spectroscopy, Xia et al.[10] reported that comparing lattice vibration spectra of the KLN-1 with those of other TB type crystals, the influence of the Li ions in the C-sites on the internal vibration of $[NbO_6]^{7-}$ is dominating. Moreover, they found the broadening of the anti-symmetric vibration modes which may be the origin of the ferroelectricity in the KLN-1 crystals strongly depends on the Li ions in

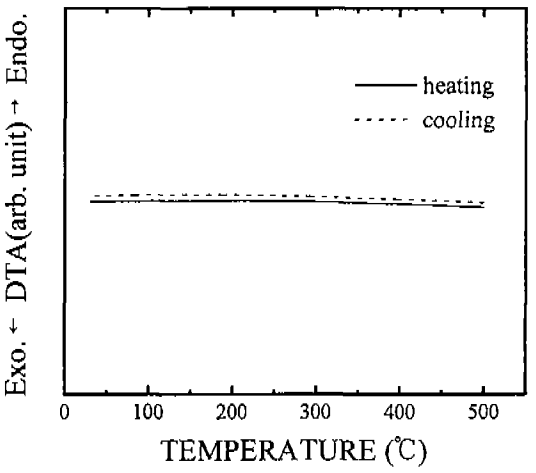

Fig. 4. The temperature dependence of the DTA signal of the KLN-2 crystals.

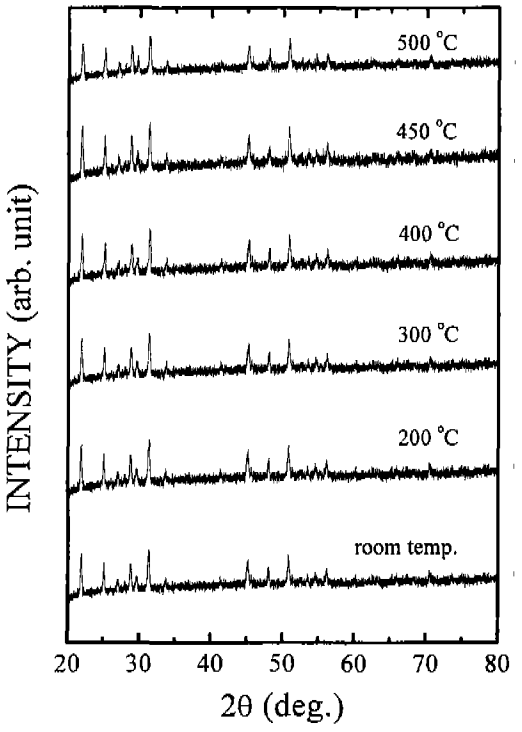

Fig. 5. The temperature dependence of the XRD patterns of the KLN-2 crystals.

the C-sites. Consequently, summarizing our experimental results and previous works[4,7-10], although it is rather difficult to exactly explain the influence of the deficiency of the Li ions on the anti-symmetric vibration in the KLN-2 crystals, the ferroelectric phase transition is not observed in the KLN-2 crystals owing to the effect of the deficiency of the Li ions in the C-sites.

Fig. 6 shows the temperature dependence of the real part (ε') and imaginary part (ε") of dielectric constant in the temperature range from room temperature to 500°C

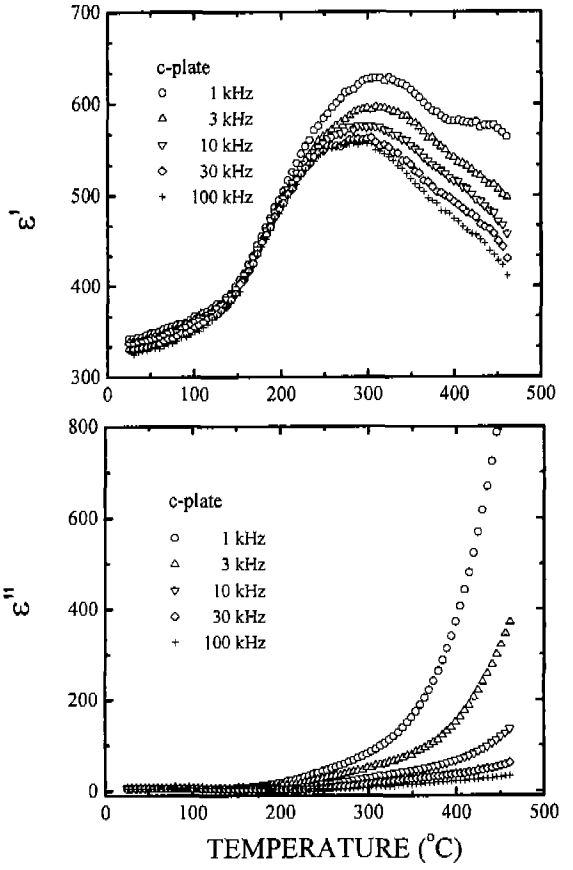

Fig. 6. The temperature dependence of the real and imaginary part of the dielectric constant of the KLN-2 crystals along c-axis for several frequencies.

for several frequencies along c-axis. Contrary to the temperature de-pendent DTA and XRD experimental results, the temperature dependence of ε' shows a broad anomaly near 300°C. However, the temperature dependence of ε" does not show anomaly but rapidly increases in the low frequency regions with increasing temperature. Compared with other ferroelectric crystal,[11] the temperature dependence of ε" show different aspect with a typical ferroelectric phase transition. This aspect is more similar to ionic conduction than ferroelectric phase transition. In addition, it is supported by the D-E loop, temperature dependent DTA and XRD experiments. On the other hands, ionic conduction may be originated from the deficiency of Li ions in the C sites or K ions in the A sites. It has been already reported by Tanaka *et al.*[12] in polycrystalline sample of KLN-2. As mentioned above, the KLN-2 crystals have the unfilled TB structure in which about 42% of the Li-sites and 13% of the K-sites are vacant. Therefore, the Li and K ions in this material are expected to move over the crystals through the Li and K vacant sites. Consequently, we can conclude that the origin of dielectric anomaly near 300°C may be originated from ionic conduction.

IV. Conclusions

Large size and crack free $K_3LiNb_6O_{17}$ single crystals were grown using the Czochralski method. From the chemical composition analysis and XRD experiments, the as-grown crystals appear to be $K_3LiNb_6O_{17}$ which relatively contains fewer Li ions than $K_3Li_2Nb_5O_{15}$ crystals. From experiment results, we concluded that the absence of the ferroelectric phase transition in $K_3LiNb_6O_{17}$ crystals originates from the deficiency of Li ions in the C-sites, thereby resulting in an unfilled tetragonal TB type structure.

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