Effect of Nb$_2$O$_5$ content on dielectric characteristics of tungsten–bronze-structured KLN ceramics

Shu-Lun Xu$^a$, Joon-Hyung Lee$^a$, Jeong-Joo Kim$^a$,*, Hee Young Lee$^b$, Sang-Hee Cho$^a$

$^a$ Department of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, South Korea
$^b$ Department of Materials Science and Engineering, Yeungnam University, Gyungsan, Kyungpook 712-749, South Korea

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Abstract

The effect of excess Nb$_2$O$_5$ on the dielectric characteristics of tungsten–bronze-structured polycrystalline K$_3$Li$_2$Nb$_5$O$_{15}$ (KLN) ceramics was studied. During sintering, the evaporation of K and Li was inevitable, which caused an effective increase of Nb content in the crystal. Even though the initial composition was below the boundary, where the crystal structure of KLN changed from tetragonal to orthorhombic, the composition passed over the boundary due to evaporation. The composition shift took away the dielectric relaxation near the phase transformation temperature. Ti addition was effective in suppressing the evaporation of K and Li and revived the phase transformation. The evaporation of cations was explained from the viewpoint of lattice stability.

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1. Introduction

Among various tungsten–bronze-structured materials, potassium lithium niobate K$_3$Li$_2$Nb$_5$O$_{15}$ (KLN) is well known to have excellent ferroelectric, piezoelectric, and optical properties [1,2]. The tungsten–bronze-structure consists of a skeleton framework of MO$_6$ octahedra, which share corners to form three different types of tunnels parallel to the c-axis in the unit cell formula of [(A1)$_2$(A2)$_4$C$_4$][(B1)$_2$(B2)$_8$]O$_{30}$ [3]. Various tungsten–bronze families exist. One of the basic differences between tungsten bronzes can be attributed to A and/or C-site cation occupancy, which is determined by ionic valence, coordination number, and radius. KLN is completely filled, where K$^+$ occupies both A1 and A2 sites, Li$^+$ occupies C-site, and Nb occupies both B1 and B2 sites [4]. When all of the cation sites are completely filled, forming stoichiometric KLN, it is found that the lattice is electrostatically unstable [5] and expels K and Li ions leaving behind vacancies in the lattice in order to reduce the lattice energy, which finally produces the second phases of KNbO$_3$ and Li$_3$NbO$_4$ [12]. Nb-rich compositions form a single phase indicating that the ions are stabilized electrostatically due to the formation of vacancies. This is the reason why solid solutions exist only in the Nb-rich region of the ternary [6].

It is difficult to grow high quality KLN crystals of suitable size from the melt because of the high volatility of K and Li in the melt. Additionally cracks are easily generated during the cooling process of the crystals [7]. In spite of these shortcomings, studies have focused on crystal growing and its properties, and research on polycrystalline KLN has not been conducted so far. In this study, polycrystalline KLN ceramics were fabricated. Various compositions with different Nb$_2$O$_5$ content along the 30 mol% K$_2$O isopleth were synthesized, and their dielectric characteristics were examined. The effect of Ti substitution on dielectric characteristics was also examined.

2. Experiment

High purity chemicals of K$_2$CO$_3$ (99.99%), Li$_2$CO$_3$ (99.99%), Nb$_2$O$_5$ (99.9%) and TiO$_2$ (99.9%) were used
for starting raw materials. The compounds with a basic formula of $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$, where $x = 0, 0.2, 0.4, 0.6$, were synthesized by the conventional solid-state reaction method. Compositions with $x = 0, 0.2, 0.4, 0.6$ will be marked KLN50, KLN52, KLN54, and KLN56, respectively, when the numbers represent the mol% of Nb. The required amounts of raw materials were weighed and wet mixed with ZrO$_2$ balls in ethyl alcohol for 24 h. After drying, the mixtures were calcined at 1000 °C for 0 h in air and crushed by ball milling under the same conditions conducted for mixing. The powders were isostatically pressed into pellets under a pressure of 200 MPa for 3 min. Sintering was carried out in the temperature range 960–1080 °C for 4 h in air. In order to examine the effect of TiO$_2$ substitution on dielectric characteristics, TiO$_2$ added powder was also prepared by the solid-state reaction method.

Powder X-ray diffraction with nickel-filtered Cu-Ka radiation (MAC Science Co., M03XHF) was performed for phase identification. An Ag electrode was screen-printed on both surfaces of the sintered samples, and dielectric properties were analyzed by an Impedance Gain Phase Analyzer (HP4194) as a function of temperature.

3. Results and discussion

Fig. 1 shows the X-ray diffraction result of the calcined powder. In the stoichiometric KLN50 sample, major peaks of KLN [8] and the second phases of Li$_3$NbO$_4$ [9] and KNbO$_3$ [10] around $2\theta = 15$ and 45° coexisted, and the second phases disappeared in Nb-rich KLN. Peak splitting near $2\theta = 22$ and 32° was observed in KLN50 and KLN52. However, one of the two peaks disappeared and appeared to be one in KLN54 and KLN56. According to the X-ray diffraction data, the peak splitting near $2\theta = 22$ and 32° provides evidence of tetragonal KLN [8] and one peak at the same position corresponds to Nb excess KLN $(K_3LiNb_6O_{17})$ [11] in which excess Nb occupies the C-site which Li has occupied [4]. It has been reported that the crystal structure changes from tetragonal tungsten–bronze to orthorhombic tungsten–bronze near 55 mol% of Nb [12]. However, because the degree of orthorhombic distortion is so small, the X-ray results are indexed on the basis of a fully tetragonal structure [12]. Therefore, the Nb excess KLN of $K_3LiNb_6O_{17}$ can be recognized as orthorhombic KLN. Given the result of peak variation as a function of Nb content, we can conclude that the crystal structure changed from tetragonal to orthorhombic as the content of Nb increased. On the other hand, the X-ray diffraction result of the sintered samples in Fig. 2 showed that the second phases of Li$_3$NbO$_4$ and KNbO$_3$ disappeared in KLN50 and the split peaks near $2\theta = 22$ and 32° observed in KLN50 and KLN52 became one peak. This indicates that the crystal structure has changed during sintering.

Fig. 3 shows the dielectric response of sintered specimens as a function of temperature. Even though the temperature of the phase transformation from tetragonal to orthorhombic is known to be around 400–500 °C depending on the content of Nb, as the content of Nb increases the phase transition temperature decreases and the maximum dielectric constant at the phase transition temperature decreases, no dielectric relaxation was observed in the temperature range measured. Considering the dielectric characteristics of Fig. 3 in conjunction with the X-ray diffraction of Fig. 2, we can imagine that the crystal structure has changed to orthorhombic, since the orthorhombic KLN does not appear to be ferroelectric, which implies that there will be no dielectric relaxation at the phase transformation temperature.

![Fig. 1. X-ray diffraction patterns of KLN calcined at 1000 °C for 0 h as a function of Nb$_2$O$_5$ content.](image1)

![Fig. 2. X-ray diffraction patterns of KLN sintered at (a) 950, (b) 990, (c) 1010, and (d) 1020 °C for 4 h as a function of Nb$_2$O$_5$ content.](image2)
Weight loss of KLN50 during sintering was measured. About $1.0 \pm 0.52\%$ of weight loss was observed. If we assume that a loss of 1% occurred only by Li evaporation, it corresponds to an effective increase of the content of Nb from 50 to 53.38 mol%. If the loss occurred only by K evaporation, it corresponds to 51.02 mol% of Nb. Therefore, we believe that the original composition shifted to an Nb-rich area due to the evaporation of Li and/or K. Accordingly, if the composition has moved to an Nb-excess area over 55 mol% by evaporation, dielectric relaxation will not occur, which can be defined as the disappearance of ferroelectric characteristics. Because the specimen contains the light element of Li, quantitative analysis of the composition shift by the evaporation was not available.

In order to prevent the weight loss, specimens were sintered in an Li and K atmosphere; i.e., the powders with the same composition were surrounded in a covered crucible. However, it was ineffective. The evaporation of K and Li is believed to be closely related to the instability of the lattice. Our study [5] of the stability of a crystal structure based on electrostatic potentials of ions at each site of KLN, which were calculated using a software program [13], showed a tendency that more vacancies in the KLN crystal make the structure stable. As the composition moves to the Nb-rich area, the Madelung energy decreased; i.e., the number of vacancies at A and C sites were inversely proportional to the Madelung energy. When 1 mol% excess Nb$_2$O$_5$ was added, it had an effect of reducing the Madelung energy of 1250 J, which implies that the structure stabilized electrostatically. This in turn suggests that a more completely filled tungsten–bronze structure is less stable electrostatically than a structure with empty sites due to the repulsive forces between cations. According to Pauling’s rule, a crystalline structure will be stabilized when the distance between cations increases. Therefore, it is thought most of the expelled ions of K and Li have evaporated. From this point of view, we can reduce the electrostatic repulsion by substituting ions with a different valence state.

Fig. 4 shows the dielectric characteristics of Ti added KLN52. Different from the Fig. 3, dielectric relaxation was observed, and the phase transformation temperature decreased as the content of Ti increased. Calculated lattice energy for the case of Ti substitution into the C-site similar to the way that the excess Nb occupies C-site [4], addition of 1 mol% TiO$_2$ had an effect of reducing the Madelung energy of 50000 J. This surely contributed to the formation of a stable lattice as well as to reduced activity of the elements in the structure, which played a partial role in suppression of the evaporation rate.

4. Conclusion

In this study, we examined the dielectric characteristics of polycrystalline KLN. This was the first such study ever conducted. The crystal structure of KLN changed from tetragonal to orthorhombic near 55 mol% of Nb. The weight loss by evaporation of K and Li was inevitable. Evaporation made the composition shift to an Nb-rich area that inhibited the phase transformation and dielectric relaxation near the phase transformation temperature. Ti addition was effective in suppressing the evaporation of K and Li and restored the phase transformation. These results suggest a method to hold ions in the structure, which easily evaporate, at high temperatures.
Acknowledgements

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References

[8] JCPDS card #34-0122 for K$_3$Li$_2$Nb$_5$O$_{15}$