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# Microstructure evolution and dielectric properties of $K_3Li_2Nb_5O_{15}$ and $PbTiO_3$ composites

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**Abstract**

Investigations of composite materials with two different crystal structured ferroelectric ceramics were carried out. In this study, phase development, sintering behavior and dielectric characteristics of the composites of tungsten bronze structured ferroelectric $K_3Li_2Nb_5O_{15}$ (KLN) and perovskite structured $PbTiO_3$ (PT) were examined as a function of molar ratio $x$ in $(1-x)$ $K_3Li_2Nb_5O_{15}$–$x$$PbTiO_3$. A wide range of solid solution of PT in KLN was observed and the lattice constants of KLN decreased with PT contents. However, the solubility of KLN in PT was very narrow. X-ray analysis revealed that both KLN and PT phases coexisted in the samples from $x=0.4$ to $x=0.9$. Therefore, two dielectric relaxation peaks were observed in the samples with $x=0.4$–$0.8$, each of which is originated from KLN and PT phase, respectively. The addition of PT to KLN increased the maximum dielectric constant at $T_C$ and shifted the $T_C$ to lower temperature. While $T_C$ of PT rich samples were not changed significantly with KLN.


*Keywords:* Tungsten bronze structure; Perovskite structure; Ferroelectrics; KLN; PT

## 1. Introduction

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 $[(A1)_2(A2)_4C_4][(B1)_2(B2)_8]O_{30}$ [1]. $K_3Li_2Nb_5O_{15}$ (KLN), $Sr_xBa_{1-x}Nb_2O_6$ (SBN), $Ba_2NaNb_5O_{15}$ (BNN) are the typical materials of tungsten bronze structured ceramics. Because of the excellent ferroelectric properties of tungsten bronze structured ceramics, their dielectric [2–11], electro-optic [12], pyroelectric [13,14] and piezoelectric [15] characteristics have been studied. Among various tungsten–bronze-structured materials, potassium lithium niobate $K_3Li_2Nb_5O_{15}$ (KLN) is well known to have excellent ferroelectric, piezoelectric, and optical properties [16,17].

Another representative crystal structure among various ferroelectric materials is the perovskite structure. $PbTiO_3$ (PT), $BaTiO_3$ (BT), $Pb(Zr_xTi_{1-x})O_3$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) have the typical perovskite structure of $ABO_3$. Among them, PT single crystals have shown that the dielectric constant obeys the Curie–Weiss law above the Curie temperature ($T_C$=about 495 °C) with a maximum dielectric constant close to 10,000 [18]. Since ferroelectric PT has a high tetragonality ($c/a$) at room temperature, a polycrystalline sintered body easily breaks during the cooling process due to the destructive stress.

There has been some research on the composite materials composed of two different crystal structures [19,20], but it has been limited to dielectric device applications by making flat dielectric curves with respect to temperature such as the case of X7R compositions. When composites composed of two different crystal structures are made, transfer of matters between the two structures will occur. In the case of a composite between the tungsten bronze structured BNN and the perovskite structured BT, a wide range of solid solution was observed which can affect the microstructure, Curie temperature and dielectric characteristics of the composites [21].

In this study, the ferroelectric composites of tungsten bronze structured ferroelectric $K_3Li_2Nb_5O_{15}$ (KLN) and perovskite structured ferroelectric $PbTiO_3$ (PT) were considered as a model

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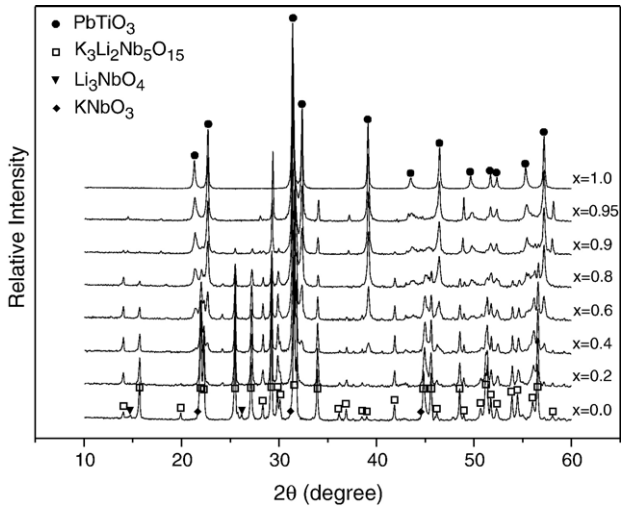


Fig. 1. X-ray diffraction patterns of KLN–PT samples sintered at optimum sintering temperatures for 2 h with different $x$ in $(1-x)$KLN–$x$PT.

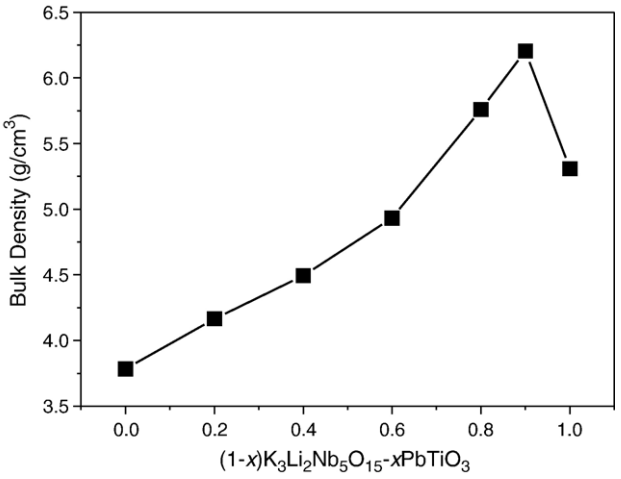


Fig. 3. Bulk density of KLN–PT samples sintered at 1000 °C for 2 h as a function of $x$ in $(1-x)$KLN–$x$PT.

system. Perovskite and tungsten bronze structures are similar in that their structural framework is composed of oxygen octahedron. In perovskites, only tetragonal tunnels, which are called A sites, are formed in the structure. In the tungsten bronze structure, various kinds of tetragonal, pentagonal and trigonal tunnels are formed, which are called A1, A2 and C site, respectively. In the case of stoichiometric KLN, K occupies both the A1 and A2 sites, Li occupies the C site, and Nb occupies the B site. Therefore, KLN is a completely filled tungsten bronze structure because all A, B and C sites are completely filled [22].

In the current study, ferroelectric ceramic composites of KLN and PT were prepared. The phase development and sintering behavior as well as dielectric characteristics of obtained materials were examined as a function of the molar ratio $x$ in $(1-x)K_3Li_2Nb_5O_{15}$–$x$PbTiO$_3$.

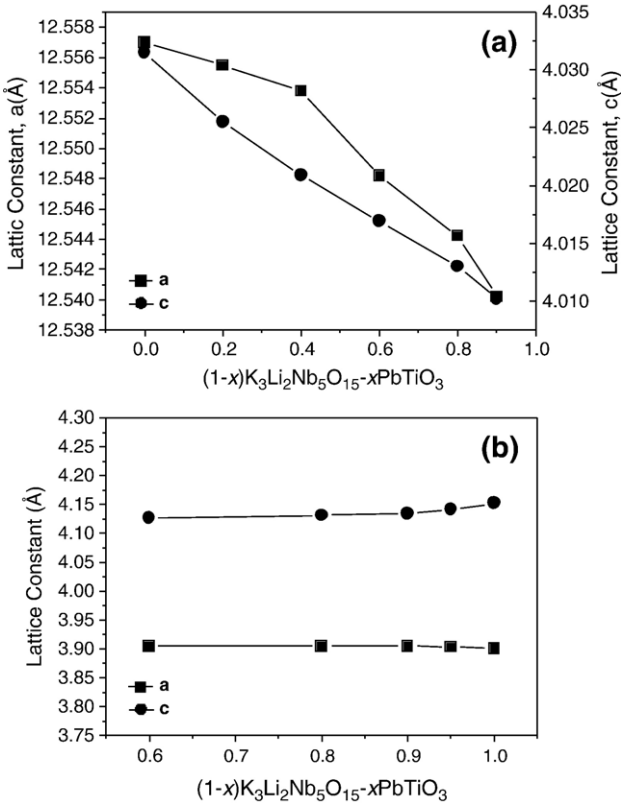


Fig. 2. Variation of lattice constants of (a) tungsten bronze structured KLN and (b) perovskite PT for the KLN–PT composite samples sintered at optimum sintering temperatures for 2 h as a function of $x$ in $(1-x)$KLN–$x$PT.

## 2. Experimental procedure

Starting powders of $(1-x)K_3Li_2Nb_5O_{15}$–$x$PbTiO$_3$, where $x=0.0$–$1.0$, were prepared using high purity raw materials of $K_2CO_3$ (99.9%), $Li_2CO_3$ (99.8%), $Nb_2O_5$ (99.9%), PbO (99%) and $TiO_2$ (99.9%) using the general solid state reaction process. KLN and PT were synthesized separately and mixed together before sintering. The weighted powders for the synthesis of KLN and PT were wet-mixed separately for 24 h in plastic jars with zirconia balls and ethanol. After drying, both mixtures were calcined separately at 800 °C for 2 h. The proper amount of KLN and PT starting powders corresponding to the designated compositions in $(1-x)$KLN–$x$PT was weighed and wet-mixed for 24 h in a plastic jar with zirconia balls and ethanol. After drying, the powders were ground in an alumina mortar and sieved to form granules. Green pellets of 10 mm diameter disks were cold isostatically pressed at a pressure of 100 MPa for 3 min. Samples were sintered at a temperature range between 850 and 1100 °C for 2 h at a heating rate of 5 °C/min. The crystal structure and phase evolution were identified by an X-ray diffractometer (M03XHF, Mac Science, Japan) using Cu–$K_\alpha$ radiation. The density of the sintered samples was determined by the Archimedes' method and the microstructure of the polished samples was observed using a scanning electron microscope (SEM; JEOL, JML5400, Tokyo, Japan). The average grain size of the sample was determined by the linear intercept method [23] using the SEM photographs. An Ag electrode was screen-printed on the both surfaces of sintered specimens, and fired at 600 °C for 10 min. The dielectric properties were analyzed by an