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Fabrication and anisotropic electronic property for oriented $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ solid solution by slip casting in a high magnetic field

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ABSTRACT

The $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($0.06 \leq x \leq 0.33$, $0 \leq y \leq 0.09$) (hereafter LNT), forms a unique and periodical structure in the Li_2O-Nb_2O_5-TiO_2 ternary system. In this work, toward application of the unique qualities of an electro-ceramic, we fabricated oriented LNT bulk ceramics by slip casting in a strong magnetic field of 12 T using various sizes of particles. The *c*-axis of the LNT powders was aligned parallel to the magnetic field. As a result, we found anisotropic- and unique- electric properties which were caused by a superstructure with intergrowth layers of corundum-type $[Ti_2O_3]^{2+}$. The *Qf* value parallel to the *c*-axis was about five times greater than that of perpendicular to the *c*-axis. We first clarified the mechanism showing that the anisotropic *Qf* value was caused by the anisotropic electron conductivity and the anisotropic bonding strength in the superstructure.

1. Introduction

In the Li_2O-Nb_2O_5-TiO_2 system, $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($0.06 \leq x \leq 0.33$, $0 \leq y \leq 0.09$) (LNT) forms with a superstructure, and this is referred to as the M-phase. The superstructure of the M-phase is formed by periodical insertion of an intergrowth layer of corundum-type $[Ti_2O_3]^{2+}$ in a matrix having a trigonal structure. Since the discovery of the M-phase by Castrejon et al. [1,2], related structures have been investigated [3–6]. The relationship between its dielectric property and the period of the intergrowth layer of the M-phase has also been studied [7,8]. To enable the application of this unique structure as a host material of phosphor, new phosphors were investigated based on LNT or related compounds fabricated by conventional solid state reaction [9–11].

The controlled development of texture has recently become a topic of interest in ceramic processing, since it allows for improved tailoring of the materials' properties. The anisotropy structure of an M-phase solid solution was synthesized, in which rod-precipitates were arranged regularly by a crystal growth method [12]. An oriented thin film of $Li_{1.18}Nb_{0.82}Ti_{0.18}O_3$ on the Al_2O_3 (0001) substrate was prepared by a sol-gel and spin-coating process, however the orientation degree of the thin film was reported to be low [13]. A strong magnetic field has been used to control the development of texture, even in feeble magnetic ceramics such as Al_2O_3, ZnO, AlN, SiC, and TiO_2 [14–18].

In this paper, we fabricated oriented LNT bulk ceramics by slip casting in a strong magnetic field of 12 T and clarified the relationship between the unique qualities and the crystal structure. We will discuss here the important mechanism analyzed for appearance of the anisotropic and its unique properties.

2. Experimental procedure

2.1. Fabrication of materials

The starting materials used were Li_2CO_3, Nb_2O_5 and TiO_2 (>99.99% grade) to prepare solid solutions of LNT. The four compositions, in which $Li_{1.03}Nb_{0.97}Ti_{0.03}O_3$, $Li_{1.11}Nb_{0.89}Ti_{0.11}O_3$, $Li_{1.25}Nb_{0.75}Ti_{0.25}O_3$, $Li_{1.14}Nb_{0.78}Ti_{0.24}O_3$, followed the general formula $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$. The Ti content (mol%) of the specimens are 3%, 10% and 20%, as shown in Fig. 1. The LNT powders were mixed and calcined at 1273 K for 5 h and continuously at 1393 K for 24 h by an electric furnace in air. The sintering at 1373 K was

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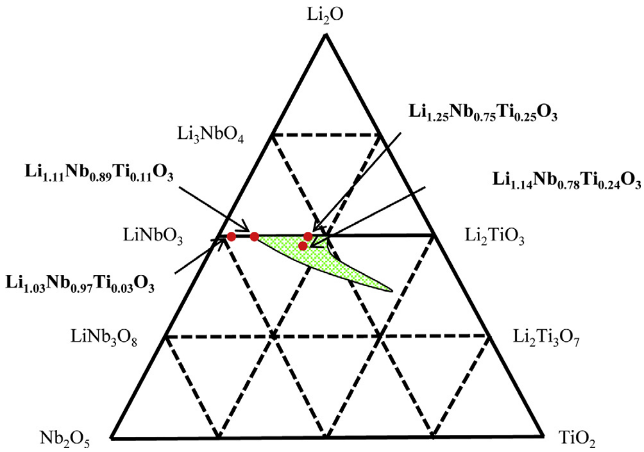

Fig. 1. LNT compositions in ternary phase system.

repeated until the X-ray diffraction (XRD) patterns of resultant powders were free of impurity peaks. The LNT ceramic powders were pulverized to be various grain sizes by planetary ball-milling (P-6, Fritsch Japan Co., Ltd.) and then used to prepare slurries. The particle distribution was measured by using particle sizer (Analysette 22, Fritsch Japan Co., Ltd.). Aqueous slurries containing 15.0 vol% solids were prepared with added polyelectrolyte (poly ammonium acrylate A-6114, Toaghosei, Co., Japan) to ensure dispersion. A strong magnetic field of 12 T was applied to the slurries during slip casting. The direction of the magnetic field was parallel or perpendicular to the casting direction. The specimen was formed with the diameter of 11 mm and the height (d) of about 22 mm (h) by a slip casting process because the measurement of the electrical properties is needed to d/h = 1.8–2.3. The green compact was densified by cold isostatic pressing at 392 MPa and then sintered at 1373 K for 15 h.

2.2. Characterization and simulation

Structure analysis was carried out by X-ray diffraction (XRD) using a RINT 2500 (Rigaku Co., Ltd. Japan) operating at 40 kV and 200 mA. Microstructure images were observed by scanning electron microscope (SEM) using an SU8000 (Hitachi, Tokyo, Japan) operating at 3 kV. High-resolution transmission electron microscope TEM images and selected area electron diffraction (SAED) patterns were observed by 2100 F (JEOL, Tokyo, Japan) operating at 200 kV equipped with energy-dispersed spectroscopy (EDS).

The ratio of Ti^{4+}/Ti^{3+} was measured by X-ray absorption fine structure spectroscopy (XAFS) at beam line BL5S1 in the Aichi Synchrotron Center with fluorescence mode at room temperature. The simulation of the XAFS was undertaken using Artemis software [19].

The microwave dielectric properties were measured using a pair of parallel conducting Cu plates in the TE011 Mode, using Hakki and Coleman's method (JIS R 1627-1996).

First-principles calculations were carried out using the Cambridge Serial Total Energy Package (CASTEP) [20], in which density functional theory [21,22] was used with a plane wave basis set. The plane-wave energy cutoff was set to 400 eV with a Gaussian smearing of 0.1 eV. The exchange-correlation interactions were treated using the spin-polarized version of the generalized gradient approximation within the scheme of Perdew-Burke-Ernzerhof [23]. The ultrasoft pseudopotentials [24] represented in reciprocal space were used for all elements. The Brillouin zone was sampled using a Monkhorst-Pack $5 \times 5 \times 2$, and $5 \times 2 \times 1$ k-point mesh according to the cell size. In the structural optimization, all atomic positions were fully relaxed until the Hellmann-Feynman force on each atom was reduced to within 0.01 eV/Å.

3. Results

3.1. Effect of particle sizes on the orientation for slip casting

In order to fabricate high oriented LNT bulk ceramics by slip casting in a magnetic field, the effect of particle sizes on the orientation was investigated. The particle sizes, dispersibility and sedimentation velocity are the important factors for the slip casting method. The $Li_{1.03}Nb_{0.97}Ti_{0.03}O_3$ ceramic powders were pulverized into small particles by ball-milling, which was repeated several times. Fig. 2 shows XRD patterns of top-plane in oriented $Li_{1.03}Nb_{0.97}Ti_{0.03}O_3$ ceramics by slip casting using crushed powders with several grain sizes. The top-plane is the perpendicular to the magnetic direction, as indicated by picture. The $Li_{1.03}Nb_{0.97}Ti_{0.03}O_3$ ceramic has a basic $LiNbO_3$ type structure without a superstructure. Consequently, single peaks of (006) and $(00\underline{12})$ were detected with very small intensities in the random specimen. On the other hand, strong peaks of $(00l)$ were observed in the top-plane of the oriented specimens. As a result, the *c*-axis of the LNT powders was aligned parallel to the magnetic field. The samples prepared from the powders of 3.56 and 0.46 µm showed low orientation degrees. The sample prepared from the powder of 2.65 µm showed the highest orientation degree in the various grain sizes.

3.2. Fabrication and characterization of oriented LNT ceramics

3.2.1. Magnetic direction parallel to the casting direction

The oriented LNT ceramics were fabricated with various compositions of $Li_{1.03}Nb_{0.97}Ti_{0.03}O_3$, $Li_{1.11}Nb_{0.89}Ti_{0.11}O_3$, $Li_{1.25}Nb_{0.75}Ti_{0.25}O_3$ and $Li_{1.14}Nb_{0.78}Ti_{0.24}O_3$ using slurries including the particles with a size of 2–3 µm and the direction of the magnetic field was parallel to the casting direction. Fig. 3 shows XRD patterns of top-plane in the oriented LNT ceramics. The *c*-axis of the LNT with various compositions was also aligned parallel to the magnetic field. The peak shifted to a high angle with increasing Ti content, because the lattice constant of the *c*-axis became shorter with increasing Ti content [25]. Interestingly, the satellite peaks were detected around the peaks of (006) and $(00\underline{12})$ in the oriented specimens, although these satellite peaks around $(00l)$ have never been observed in the random specimens (in Fig. 2). The spacing of the satellite reflections became wider with increasing the Ti content, as indicated by the arrows. The periodical structures of the LNT ceramics can be seen in the TEM images. Fig. 4 shows TEM images and SAED patterns of oriented LNT ceramics taken from [010] axis. TEM data showed that the period was formed by insertion of the intergrowth layers by the doping of Ti ions. The periods of the intergrowth layers are 14.3 nm in $Li_{1.11}Nb_{0.89}Ti_{0.11}O_3$ and 5.8 nm in $Li_{1.11}Nb_{0.89}Ti_{0.11}O_3$. The period became narrower with increasing Ti content. Accordingly, the period of the satellite peaks in the XRD patterns became wider in the reciprocal lattice with increasing Ti content. The period of $Li_{1.25}Nb_{0.75}Ti_{0.25}O_3$ and $Li_{1.14}Nb_{0.78}Ti_{0.24}O_3$ were almost the same because Ti content is 20 mol% (Fig. 1) [25].

The orientation degrees of each grain can be calculated from the tilting data in the SAED patterns as following equation [26].

$$\varphi = \cos^{-1}(\cos x \cdot \cos y) \tag{1}$$

$$\theta = \tan^{-1}(\tan y / \sin x) \tag{2}$$

Here, *x* and *y* are measured angle *x*-axis and *y*-axis, respectively in the TEM device. φ is the degree of tilting angle from the basis [001] axis. θ is the direction of tilting on the two-dimensional plane.

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