Rapid synthesis and structural analysis of Li–Nb–Ti–O solid solutions with superstructure by millimeter-wave heating

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We have succeeded in synthesizing \( \text{Li}_{1+x+y} \text{Nb}_{1-x-y} \text{Ti}_{1+y} \text{O}_{3} \) solid solutions \((0.11 \leq x \leq 0.18, 0 \leq y \leq 0.09)\) having a superstructure by millimeter-wave heating for only 1 h. Synthesizing temperatures were attempted in the range from 873 to 1273 K. A homogeneous LNT solid solution with a superstructure was formed above 1173 K. Such LNT solid solutions were characterized using X-ray diffraction, a scanning electron microscope, and a transmission electron microscope (TEM) from micro-scale to nano-scale. Element analysis revealed that the superstructure was formed by periodical insertion of intergrowth layers with a high concentration of Ti ions. The structural stability of the LNT solid solution was estimated by a first-principles calculation. The results revealed that the structure was stable due to the formation of the superstructure, which is composed through an anisotropic arrangement of the Ti ions.

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1. Introduction

In the \( \text{Li}_2\text{O}–\text{Nb}_2\text{O}_5–\text{TiO}_2 \) system, \( \text{Li}_{1+x+y} \text{Nb}_{1-x-y} \text{Ti}_{1+y} \text{O}_3 \) \((0.11 \leq x \leq 0.33, 0 \leq y \leq 0.09)\) (LNT) forms with a superstructure, and this is known as the M-phase. Since the discovery of the M-phase by Castrejon et al., it has been investigated. The superstructure of the M-phase is formed by periodical insertion of an intergrowth layer in a matrix having a trigonal structure. The relationship between the dielectric properties and the period of the M-phase’s intergrowth layer has been studied. Yamamoto et al. synthesized an anisotropy structure of an M-phase solid solution in which rod-precipitates were arranged regularly by a crystal growth method. Recently, an Eu-doped LNT solid solution has been developed as a new photoluminescence material. The synthesis of a homogeneous M-phase, however, required treatment at 1373 K for 24 h, after calcination at 1273 K for 3 h, in an electric furnace. Accordingly, a fast synthesizing technique that uses lower energy is required for practical application of this material.

Heating by millimeter-wave radiation has certain advantages in industrial processes or applications from the viewpoints of the homogeneity of large materials, control of grain growth, and densification at low temperature. Millimeter-wave frequency is typically over 30 GHz (<10 mm), but in this paper, a frequency of 24 GHz is considered. High-density Si₃N₄ or AlN ceramics, which are not easily sintered ceramics, could be synthesized using suitable additives by millimeter-wave heating at lower temperatures and shorter times than with a conventional sintering method. Recently, we have characterized the relationship between the microstructure and bending strength of alumina ceramics synthesized by millimeter-wave heating. The results revealed that a higher boundary velocity \( (V_b) \) than pore velocity \( (V_p) \) caused nanometer-sized pores to remain in the grains, where rapid diffusion of atoms occurred in the electromagnetic field.

In the present study, we were the first to succeed in synthesizing M-phase \( \text{Li}_{1+x+y} \text{Nb}_{1-x-y} \text{Ti}_{1+y} \text{O}_3 \) solid solutions \((0.11 \leq x \leq 0.18, 0 \leq y \leq 0.09)\) by millimeter-wave heating for only 1 h. Synthesizing temperatures were attempted in the range from 873 to 1273 K. Structural analysis of the LNT solid solutions was performed carefully using X-ray diffraction, a scanning electron microscope, and a transmission electron microscope (TEM) from micro-scale to nano-scale. The structural stability of the LNT solid solution was estimated by a first-principles calculation. As discussed below, this was done because a stable M-phase could be synthesized quickly and homogeneously by the millimeter-wave radiation.

2. Experimental procedure

The starting materials used were \( \text{Li}_2\text{CO}_3, \text{Nb}_2\text{O}_5 \) and \( \text{TiO}_2 \) (>99.9% grade) to prepare the solid solution of LNT. The compositions of the LNT solid solutions prepared in this work followed the general formula \( \text{Li}_{1+x+y} \text{Nb}_{1-x-y} \text{Ti}_{1+y} \text{O}_3 \), with \( 0.11 \leq x \leq 0.18, 0 \leq y \leq 0.09 \). The TiO₂ content of the specimens was varied from 15 to 35 mol %. The powders were mixed and pressed in air at various temperatures from 873 to 1273 K for 1 h by millimeter-wave heating. The millimeter-wave heating equipment consists of a 24-GHz gyrotron millimeter-wave generator and a multi-mode chamber (MSP Corp., Japan). The heating rate was approximately 30 K/min, and the specimen was cooled down in the chamber after sintering.

Structural analysis was carried out by X-ray diffraction (XRD) using a RINT 2500 (Rigaku Co., Ltd., Japan) operating at 40 kV and 200 mA. The angles were corrected by an external standard method for calculation of the lattice parameters. Microstructure images were observed with a scanning electron microscope (SEM) (SU8000, Hitachi Co., Ltd., Japan) operating at 3 kV. High-resolution TEM (HRTEM) images and selected area...
electron diffraction (SAED) patterns were also observed by a device (2100 F, JEOL Co., Ltd., Japan) operating at 200 kV and equipped with energy-dispersed spectroscopy (EDS).

First-principles calculations were carried out in the Cambridge Serial Total Energy Package (CASTEP), which uses the density functional theory with a plane wave basis set. The exchange–correlation interactions were treated using the spin-polarized version of the generalized gradient approximation within the scheme of Perdew–Burke–Ernzerhof. The ultrasoft pseudopotentials represented in reciprocal space were used for all elements in the calculations. The wave functions were expanded to the plane wave basis set with an energy cutoff of 400 eV. The Brillouin zone was sampled using a Monkhorst-Pack 5×2×1 k-point mesh. All atomic positions were fully relaxed until the Hellmann–Feynman force on each atom was reduced to within 0.01 eV/Å.

3. Results and discussion

Two types of LNT solid solutions were prepared, one with calcination at 1073 K for 5 h in an electric furnace and the other without calcination. Then, these specimens were synthesized at 1273 K for 1 h by millimeter-wave heating. These structures were analyzed by XRD, and no secondary phases were observed in either of them. Figure 1 shows XRD patterns of LNT solid solutions with various Ti content at 1273 K for 1 h without calcination. Satellite reflections were detected around 012, 202 and 132 reflections of the LiNbO3 cell, which were caused by the superstructure formed by the LNT solid solution. The periods of the satellite reflections in the XRD pattern increased with increasing Ti content. To confirm the effect of the millimeter-wave heating, the LNT solid solutions were also synthesized in the electric furnace at 1273 K for 1 h. Figure 2 shows XRD patterns and SEM images of LNT solid solution with Ti 20 mol% by millimeter-wave heating and by heating with an electric furnace. In the case of using the electric furnace for heating, the intensities of satellite reflections were lower and the peaks were broader than those found for millimeter-wave heating; the SEM image shows that the grain size is clearly 1/10 the size of that obtained by millimeter-wave heating. The changes in the lattice constants of the LNT solid solutions were calculated as shown in Fig. 3. In Fig. 3(a), the lattice constants were in good agreement between LNT solid solutions with calcination and those without calcination. The results show that the LNT solid solution with a superstructure was formed quickly and homogeneously by millimeter-wave heating even without calcination. On the other hand, Fig. 3(c) shows the lattice constants of the specimens...
synthesized in the electric furnace. The slope of the change in the $c$-parameters in Fig. 3(c) was in agreement with that of millimeter-wave heating in Fig. 3(a), but the trends of the $a$-parameters varied widely. This means that the solid solution was synthesized for a short time even in the electric furnace, but it is expected that the superstructure would be formed during the grain growth process for a longer time. The grain shapes clearly changed from spherical to plate-like, as seen in Fig. 2(b).

Next, we analyzed the superstructure of the LNT solid solutions by an electron diffraction method. Figure 4 shows the SAED patterns of LNT solid solutions synthesized by millimeter-wave heating at 1273 K with various Ti content taken from the [100] or [100] zone axis. The super-lattice reflections were detected between fundamental reflections along the $c$-direction. Our results showed that the number of satellite reflections decreased by 31, 23, 19, 13, and 11 times, relative to the (006) spacing, for Ti contents of 15, 20, 25, 30, and 35 mol%, respectively; accordingly, the change in the layers’ spacing decreased as the Ti content increased. The periodicities were in good agreement with that of the LNT solid solution synthesized in the electric furnace at 1373 K for 24 h.\textsuperscript{21} The periodicities hardly increased with increasing Ti content above 40 mol% in the previous examinations.\textsuperscript{21} Figure 5 shows an HRTEM image of the LNT solid solution with Ti 35 mol% synthesized by
millimeter-wave heating. The intergrowth layer inserted periodically in the LiNbO$_3$-like sub-cell showed a value 11 times that of (006) spacing. The intergrowth layer seemed to be composed of a single atomic layer with different contrast, as seen in the HRTEM image of a 10-layer M-phase composition.\textsuperscript{6)}

We compared atomic-scale Ti concentration between sites at the intergrowth layer and at the matrix by EDS analysis. Figure 6 shows a STEM image of the LNT solid solution with Ti 15 mol\% in (a), Ti mapping image in (b), and Nb mapping image in (c). In Fig. 6(a), dark contrasts were observed between intergrowth layers, which might be caused by the strain due to insertion of the intergrowth layer. Mapping images were successfully obtained, and these showed that Ti ions were distributed with higher concentration at the intergrowth layers. In other words, the superstructure of the LNT solid solution was composed through an anisotropic arrangement of the Ti ions of rock-salt-type Li$_2$TiO$_3$.\textsuperscript{6)}

In order to understand the effect of the millimeter-wave irradiation, synthesizing temperatures were attempted in the range from 873 to 1273 K. Figure 7 shows XRD patterns in (a) and lattice constants in (b) of the LNT solid solutions with Ti 30 mol\% at various temperatures. The satellite reflections were detected even at 973 K, but the intensity of the satellite reflections became lower with decreasing temperature. This means that the period of the superstructure was not formed homogeneously. At 873 K, the LNT solid solution did not form because the secondary phase was detected as a TiO$_2$ phase around 28 degrees and the lattice constants were nearly equal to that of LiNbO$_3$. The period of the superstructure was confirmed precisely by the SAED pattern and HRTEM image. The results show that homogeneous M-phases were formed with a superstructure above 1173 K. Figure 8 shows an HRTEM image and SAED pattern of the LNT solid solution with Ti 30 mol\% at 1073 K for 1 h. The image

![STEM image](image1)

**Fig. 6.** (Color online) STEM image of LNT solid solution with 15 mol\% in (a), Ti mapping image in (b), and Nb mapping image in (c).

![XRD pattern](image2)

**Fig. 7.** (Color online) XRD patterns of LNT solid solution with Ti content of 30 mol\% in (a) and changes in lattice constants in (b) at various temperatures for 1 h.

![TEM image](image3)

**Fig. 8.** TEM image and SAED pattern of LNT solid solution with Ti content of 30 mol\% at 1073 K for 1 h.
shows that the period of the intergrowth layer had various periodicities with slightly different width along the c-direction. In the SAED pattern, weak streaks along the c-axis were also observed, indicating an inhomogeneous period of the intergrowth layer. At 873 K, almost all grains have no superstructure, but a few grains have a superstructure in which their periods are inhomogeneous.

Why did the anisotropic structure form quickly by millimeter-wave heating? We focused the distribution of Ti ions in the LNT solid solutions because Ti ions were distributed with higher concentration at the intergrowth layer, as shown in the mapping data (Fig. 6). In order to investigate the structural stability, two types of their cells were used and compared: One involved an anisotropic distribution of Ti ions in the cell, in other words, a rich distribution of Ti ions at the intergrowth layer (Ti-rich model), and the other had a poor distribution of Ti ions at the intergrowth layer (Ti-poor model). The structural stability of the LNT solid solution was estimated by a first-principles calculation. The simulation cells were constructed based on the crystallographic data for a 10-layer LNT solid solution with a lattice constant of \( a = b = 0.510 \text{nm} \) and \( c = 2.319 \text{nm} \). The initial cell size was \( 0.510 \times 1.531 \times 2.319 \text{nm}^3 \) to fulfill stoichiometry. Periodic boundary conditions were applied in all three directions. The stabilities of the LNT solid solutions are discussed in terms of the cohesive energy, \( E_{\text{coh}} \), defined by Eq. (1):

\[
E_{\text{coh}} = \left( E_{\text{tot}} - \sum_{\beta} n_{\beta} E_{\beta} \right) / \sum_{\beta} n_{\beta}
\]

where \( E_{\text{tot}} \) is total energy of the cell of the LNT solid solution model, \( E_{\beta} \) is the energy of isolated \( \beta \) atoms (or ions) (\( \beta = \text{Li}, \text{Nb}, \text{Ti}, \text{O} \)) in the cell, and \( n_{\beta} \) is the number of \( \beta \) atoms. The values of the cohesive energy calculated from the isolated atoms were \(-6.60 \text{eV/atom} \) for the Ti-poor model and \(-6.65 \text{eV/atom} \) for the Ti-rich model. In cases where the cohesive energy was calculated from the ions, the values were \(-178.41 \text{eV/atom} \) for the Ti-poor model and \(-178.47 \text{eV/atom} \) for the Ti-rich model. Therefore, the structural stability of the Ti-rich model was higher regardless of the calculation method used for the cohesive energy, and the difference between these cohesive energies was significant for the structural stability. The results reveal that the structure is stable due to the formation of the superstructure, which is composed through an anisotropic arrangement of the Ti ions. At the experimental stage, the relationship between the structural stability and the effect of the millimeter-wave irradiation is not clear. Actually, a stable M-phase could be synthesized during grain growth even for a short heating time by using millimeter-wave heating.

4. Conclusions

We aimed to synthesize the Li–Nb–Ti–O solid solution having a superstructure, known as the M-phase, quickly and homogeneously by millimeter-wave heating. Synthesizing temperatures were attempted in the range from 873 to 1273 K. As a result, we were the first to successfully synthesize \( \text{Li}_{2+x}, \text{Nb}_{1-x-y}, \text{Ti}_{1+y}, \text{O}_{3} \) solid solutions (0.11 \( \leq x \leq 0.18 \), 0 \( \leq y \leq 0.09 \)) with a superstructure for only 1 h above 1173 K. The LNT solid solutions were characterized, from micro-scale to nano-scale, using X-ray diffraction, a scanning electron microscope, and a transmission electron microscope (TEM). The changes in the lattice constants revealed that the LNT solid solution began to form even in an electric furnace at 1273 K for 1 h. However, it is expected that the superstructure would be formed during the grain growth process over a long time. On the other hand, the LNT solid solution synthesized by millimeter-wave heating had a homogeneous superstructure after only 1 h, and the grain sizes became significantly larger. Element analysis revealed that the superstructure was formed by periodical insertion of intergrowth layers with higher concentration of Ti ions than at the matrix. The structural stability of the LNT solid solution was estimated by a first-principles calculation. The results revealed that the structure was stable due to the formation of the superstructure, which is composed through an anisotropic arrangement of the Ti ions.

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