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Morphology and structure of $LiNb_{0.6}Ti_{0.5}O_3$ particles by molten salt synthesis

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ABSTRACT

M-phase $LiNb_{0.6}Ti_{0.5}O_3$ (LNT) plate-like particles with large anisometric shape were firstly fabricated by molten salt synthesis (MSS) method in LiCl flux. Effects of reaction temperature, holding time and the weight ratio of LiCl salt to the original powders on the phase structure and morphology of the synthesized particles were investigated. The $LiNb_{0.6}Ti_{0.5}O_3$ powders generally showed a multi-layer structure, exhibiting irregular hexagonal or triangle morphology. The reaction temperature showed a strong influence on the particle growth process, and pure LNT particles are obtained at 950 °C. Further increasing the reaction temperature and holding time could increase the average size of the particles. It revealed that the thickness of the plat-like particles was increased as the contents of the chloride salts increased. The synthesis process, the relation between crystal structure and morphology of particles were also discussed.

1. Introduction

$Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ solid-solution, so-called "M-phase" in the Li_2O–Nb_2O_5–TiO_2 system, was discovered by Villafuerte-Castrejón et al. [1]. It is considered to be a promising material in the fabrication of low temperature co-fired ceramic (LTCC) based devices. By altering x and y values in $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ system, the ceramics with high dielectric constant (78–55), $Q \times f$ values up to 9000 GHz (@ 6 GHz), and near zero temperature coefficients in the microwave region could be obtained via sintering at 1100 °C. Its function can be tunable by controlling the microstructure at the lattice level [2]. As a member of M-phase, $LiNb_{0.6}Ti_{0.5}O_3$ ceramics exhibit excellent microwave dielectric properties with high dielectric constant $\varepsilon_r = 64.79$, high quality factor $Q \times f = 6385$ GHz, and a temperature coefficient of resonant frequency $\tau_f = 8$ ppm/°C achievable via sintering at 1100 °C. The crystal structure of $LiNb_{0.6}Ti_{0.5}O_3$ consists of commensurate intergrowth structures with 9 $LiNbO_3$-type (LN) slabs inserted by single $[Ti_2O_3]^{2+}$ corundum-type layers. The Ti atoms are fully accommodated in the octahedra of the $[Ti_2O_3]^{2+}$ layers and are preferentially ordered in the octahedral in adjacent layers. Ti atoms also partially replace Nb atoms in the LN blocks [3]. It is a member of trigonal crystal system, as a low crystal symmetry material, anisotropic physical properties can be obtained by texturing and could be tailored to obtain useful properties such as high $Q \times f$ or near zero τ_f. Templated grain growth (TGG) and reactive templated grain growth (RTGG) technique have been applied to fabricate highly textured ceramics with excellent anisotropic electrical properties. In the TGG and RTGG processes, large oriented anisotropic template particles are distributed in a fine-grained matrix and grow preferentially to produce high-density textured ceramics. Platelet template particles with large shape anisotropy have been widely used to fabricate textured ceramics [4–7].

Molten salt synthesis (MSS) has been widely used to synthesize template particles such as $SrTiO_3$ [8], Bi_3NbTiO_9 [9] and $(K_{0.5}Na_{0.5})NbO_3$ [10], which were used to fabricate textured lead-free piezoelectric ceramics. However, there has been no report on $LiNb_{0.6}Ti_{0.5}O_3$ powders prepared by molten salt method yet. In this work, multi-layer structure $LiNb_{0.6}Ti_{0.5}O_3$ templates were successfully synthesized via molten salt synthesis. The effects of the reaction temperature, weight ratio of salt to reaction powders, and holding time of the reaction on the formation process and morphology of the products are discussed.

In addition, the anisotropic dielectric properties of $LiNb_{0.6}Ti_{0.5}O_3$ microwave ceramics by screen-printing templated grain growth using plate-like $LiNb_{0.6}Ti_{0.5}O_3$ templates prepared by MSS method in this report can be found elsewhere [11].

2. Experimental

The raw materials used in this experiment are commercial metal oxide powders with high-purity Li_2CO_3 (99.86%), Nb_2O_5 (99.82%) and TiO_2 (99.71%) (Sinopharm Chemical Reagent Co., Shanghai, China). They were weighed according to the molar ratio of the composition of $LiNb_{0.6}Ti_{0.5}O_3$. The starting powders were ball-milled

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in an ethanol medium for 24 h after drying the resource powders mixed with high-purity LiCl (99.5%, Sinopharm Chemical Reagent Co.) with a weight ratio of 1:1, 1:2, 1:3, respectively. The mixture powders were heated at predefined temperatures of 850 °C, 950 °C, 1000 °C and 1050 °C, respectively. Heat treatment was carried out for different holding times (3, 6 and 9 h) in a muffle furnace. After cooling to room temperature the powders were washed with hot de-ionized water for several times to remove the salt until no free Cl^- ions were detected. X-ray diffraction (XRD) analysis was used to determine the crystalline phases (RINT 2000V, Rigaku, Japan). Particle morphology was observed by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Japan).

3. Results and discussion

3.1. Influence of preparing temperature

LiCl was chosen as the solvent in this research as opposed to NaCl and KCl which can react with the Nb_2O_5 and TiO_2 powders and hence could prevent pure LNT from being obtained. The weight ratio of the prepared reactant (Li_2CO_3–Nb_2O_5–TiO_2) to solvent (LiCl) was 1:2. Fig. 1 shows the XRD patterns of the LNT powders obtained by MSS synthesized at different temperatures for 3 h. At temperatures below 850 °C, the products were identified as a mixture of $LiNbO_3$ phase and M-phase LNT powders, with the $LiNbO_3$ phase indexed according to JCPDS card (No. 20-0631). Pure crystalline M-phase particles were obtained after being heated above 950 °C. The X-ray patterns of M-phases bear a strong resemblance to that of $LiNbO_3$ (LN) with the exception of several peak splitting by the insertion of the corundum-type structure $[Ti_2O_3]^{2+}$ layer. The indexing of the M-phase patterns was conducted using fractional l Miller indexes and an incommensurate parameter δ using the schemes proposed by Roth and Davis that utilize rhombohedral extinction rules with a symmetric splitting for $l = 3p$ ($l \pm 3n\delta$), and asymmetric splitting for $l = 3p+1$ $[(l+\delta) \pm 3n\delta]$ and $l = 3p+2$ $[(l-\delta) \pm 3n\delta]$, where δ is defined as $2c_{subcell}/c_{supercell}$. The quantity $c_{supercell}/c_{subcell}$ (=$2/\delta$) in this scheme can be interpreted as the average number of layers $\langle n \rangle$ in the repeating block of each composition [12]. It reveals that at temperatures lower than 850 °C, Nb-rich $LiNbO_3$ and Ti-rich M-phase LNT particles were formed separately,

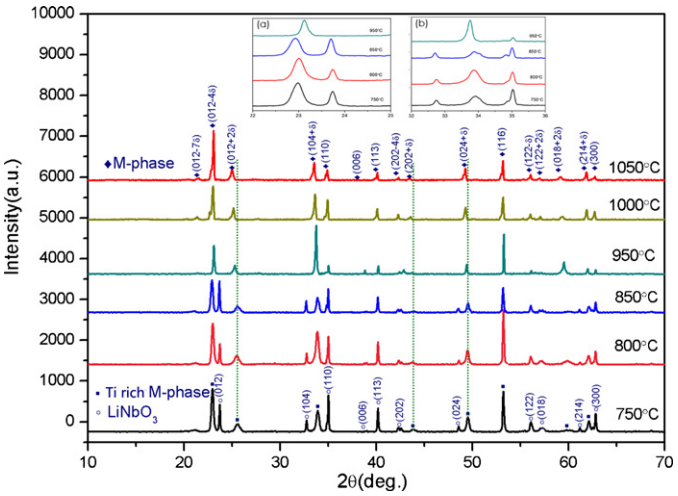

Fig. 1. XRD patterns of LNT powders prepared by molten salt synthesis at various temperatures.

and M-phase begins to exhibit plate-like morphology with a diameter of 2–4 μm at 850 °C (Fig. 2(a)). When synthesized at a higher temperature, Ti atoms become inserted into the $LiNbO_3$ structure as a single corundum-type structure $[Ti_2O_3]^{2+}$ layer and partially replace Nb atoms in LN slabs, and M-phase multilayered structure LNT was formed completely. The particles grew up significantly when the synthesis temperature increased, and at 950 °C the particles' diameter was about 2–10 μm. At 1000 °C the particle diameter was between 5 and 20 μm with a thickness of 0.5–2.0 μm, and at 1050 °C, particles of diameter 10–30 μm can be seen (Fig. 2(b–d)).

Generally, during the development of the particles two processes in molten salts synthesis are observed, these being the nucleation and grain growth [13,14]. During the nucleation process at lower temperature, the composition and morphology of the particle depends on the difference in dissolution rates

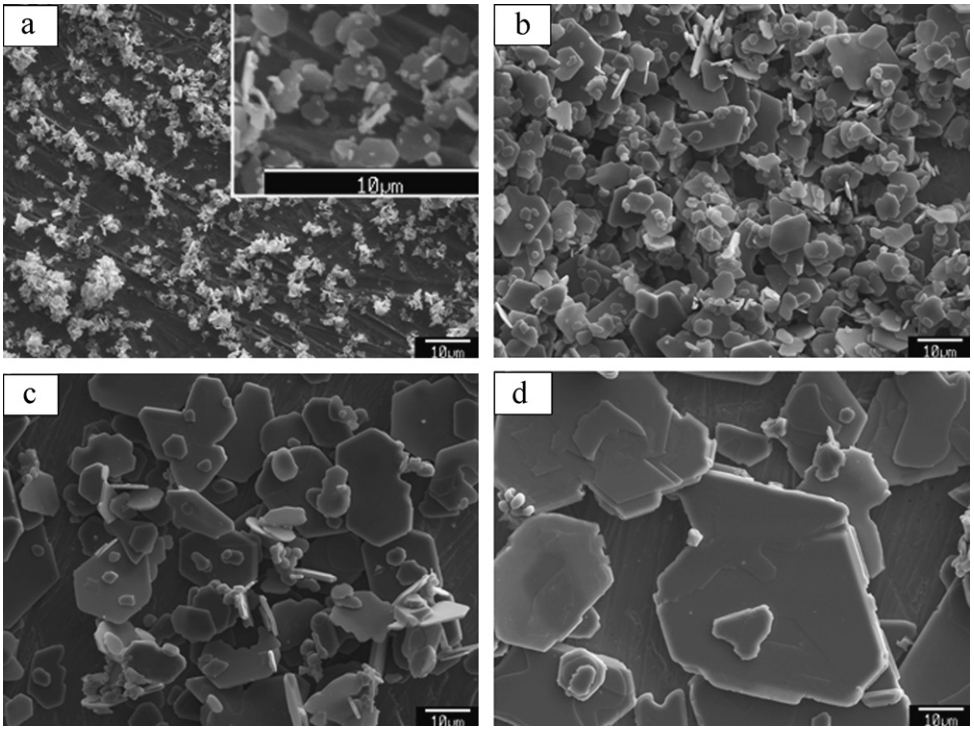

Fig. 2. SEM micrographs of LNT powders prepared by molten salt synthesis at various temperatures. (a) 850 °C, (b) 950 °C, (c) 1000 °C, (d) 1050 °C.

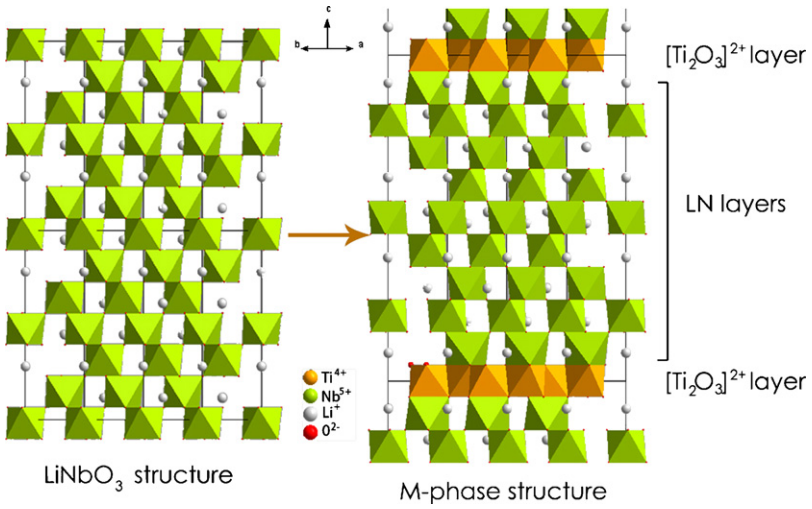

Fig. 3. Polyhedral representation of the $LiNbO_3$ and M-phase 10-layer structure projected along [1 1 0] and the structure change occurred at 850–950 °C.

among reacting oxides in the molten salt. Li_2O with relatively higher solubility in LiCl liquids is transported to the outer surface of the slow-dissolving components Nb_2O_5 and TiO_2, reacted with the latter, and then formed Nb-rich $LiNbO_3$ and Ti-rich M-phase LNT particles (as shown in Fig. 1, 750 °C sample). M-phase particles with hexagonal plate-like shape are initially formed as shown in Fig. 2(a). At higher temperatures, the increase of Li_2O solubility accelerated the formation reactions, and the size and shape of the particles were changed gradually (Fig. 2(b–d)).

The grain growth process was initiated by a diffusion mechanism (or template formation mechanism), and then by an interfacial controlled mechanism (or dissolution–precipitation mechanism) [15]. At 850–950 °C, the growth is similar to two-dimensional nucleation and controlled by a diffusion mechanism. During this process, Ti atoms in the Ti-rich M-phase diffuse to the $LiNbO_3$ structure, and become inserted as a corundum $[Ti_2O_3]^{2+}$ layer and partially replace Nb in the LN layers, after which stoichiometric $LiNb_{0.6}Ti_{0.5}O_3$ M-phase particles are formed. This process is confirmed by the XRD patterns (Fig. 1). From 850 °C to 950 °C, a slight peak shift to lower angle in M-phase and merging of several peaks of $LiNbO_3$ and Ti-rich M-phase is observed. The phase transformation from $LiNbO_3$ to M-phase LNT was illustrated in (Fig. 3). When the synthesis temperature increased, the particles are formed by an interfacial reaction controlled mechanism. LNT particles grow up by consuming the smaller particles in accordance with the Ostwald ripening mechanism [16], so the size of particles becomes larger and larger, and the composition remains unchanged. Compared to the conventional solid-state reaction that the LNT precursor cannot fully synthesized until 1100 °C, the molten salt synthesis could accelerated the kinetics of the reaction at a lower temperature, which attributed to the short diffusion distance and the high mobility of species in the liquid state [17]. It is obvious that the synthesis temperature plays a key role for the formation of LNT particles.

3.2. Influence of the salt contents

The weight ratios of 1:1, 2:1, 3:1 (chloride salt to precursor powders) were chosen to reveal the influence of salt content upon LNT powders formation. The raw powders were calcined with different amounts of chlorides at 1000 °C for 6 h. Fig. 4 showed the XRD patterns of the powders synthesized under different conditions. All the products were pure LNT M-phase particles, which means that the salt content bears little influence on the synthesis of M-phase when the ratio varies from 1:1 to 3:1 at this temperature.

Fig. 5 shows the SEM micrographs of the LNT powders synthesized under different conditions. The particles were uniformly dispersed, exhibiting a plate-like shape and a high aspect ratio with diameters of 5–30 μm and a thickness of 0.5–2.0 μm. The diameter of the particles shows little dependence to the salt content, but the average thickness became larger as weight ratio increase. When the weight ratio reached 3:1, a small amount of platelets agglomerated and aligned along the *c*-axis, and the shape became irregular along with an increase in the surface roughness (Fig. 5(c)).

3.3. Influence of holding time

As the kinetics of the solid-phase synthesis reaction depends on both synthesis temperature and holding time [9], the impact of holding time to particle morphology in MSS was studied. LNT precursor mixed with double weight of LiCl salts was heated at 1000 °C for different holding times, e.g. 3, 6 and 9 h, respectively. The XRD patterns reveal that pure LNT powders were obtained as shown in Fig. 6. Fig. 7 shows the SEM photographs of the powders. As the reaction time prolonged, the large particles grew in diameter and thickness at the consumption of smaller ones which means the particle growth occurred both along *c*-axis and *a*/*b*-axis. The particles have a diameter of 5–20 μm and a thickness of 0.5–2.0 μm when

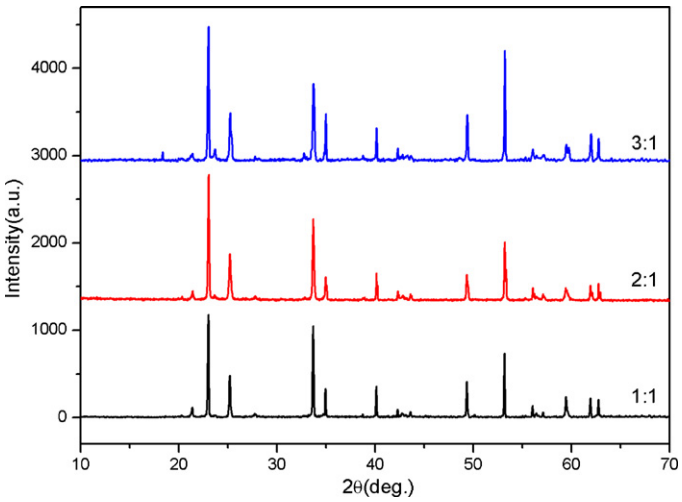

Fig. 4. XRD patterns of LNT powders by molten salt synthesis with different salt contents.

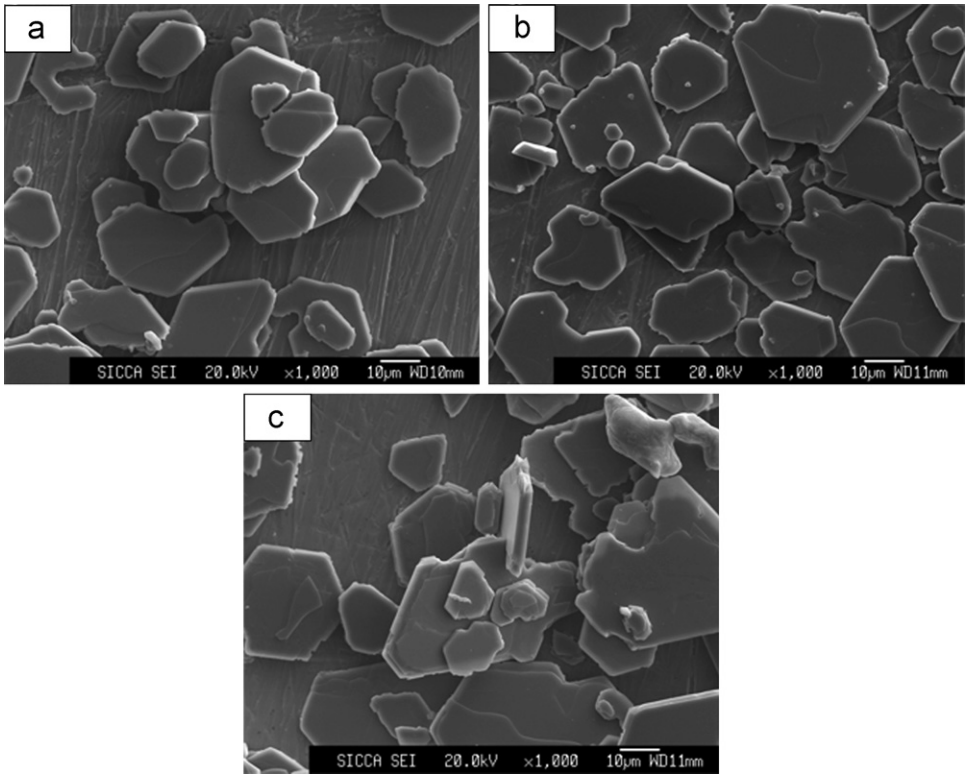

Fig. 5. SEM micrographs of LNT powders by molten salt synthesis with different salt contents: (a) 1:1, (b) 2:1, (c) 3:1.

reacted for 3 h (Fig. 7(a)); a diameter of 10–30 μm and a thickness of 1–3.0 μm for 6 h (Fig. 7(b)); and some particles with a diameter of 40–50 μm and a thickness of 5–6 μm for 9 h (Fig. 7(c)). It is considered that the particle growth behavior with temperature and different reaction time is in accordance with the following equation [15]:

$$D^2 - D_0^2 = k(t - t_0)\exp\left(\frac{-E}{RT}\right) \quad (1)$$

where D is the average particle size at time t, D_0 is the initial particle size at initial time t_0, k is a rate constant, E is the activation energy for particle growth, R is the gas constant, and T is the growth temperature.

The $LiNb_{0.6}Ti_{0.5}O_3$ crystal growth was controlled by an interfacial reaction mechanism at 1000 °C. Based on the theory of anionic coordination polyhedron model, as each growth unit came into the interface from the liquid environment, it always took the most favorable position where it formed most bonding with adjacent units in the crystal to lower the energy and stabilized the crystal structure. This means that the prior position for the growth unit to occupy was the kinked position, and the second prior was step position on the surface. Due to thermal motion of the atoms, the initial growth unit [NbO_6] or [TiO_6] octahedrons come to the particle surface. The steps and kinks in the surface of the particles could significantly lower the energy for crystal growth and accelerate kinetics. Later the growth units filled the layer and the outline of the steps extended outside, forming the multilayer structure, as can be seen in Fig. 8. After 9 overlays of LN slabs, a corundum-type [Ti_2O_3] layer connected LN layers with [TiO_6] octahedrons sharing faces with [NbO_6] octahedrons in adjacent LN layers like in corundum structure. At last, after a series of repetitions of the growth process described above, M-phase particles with large size were formed.

Another interesting result observed was the triangle or hexagonal plate-like morphology of the M-phase particles obtained by sintering at 1000 °C. Although the length of the edge was not equal and hexagon was irregular, the angle between adjacent edges was 60° or 120°. This was because the crystal growth process was controlled by the crystal structure. M-phase LNT belongs to a trigonal crystal system and $P\bar{3}c1$ space group, and it preferentially formed triangle or hexagonal pattern on the surface. The crystal grew fastest on the (0 1 0) and (1 0 0) plane but lowest on the (1 0 0) plane. As a result, (0 1 0) and (1 0 0) faces tend to disappear and the particle edges along the a-axis and b-axis with angle of 60° or 120°

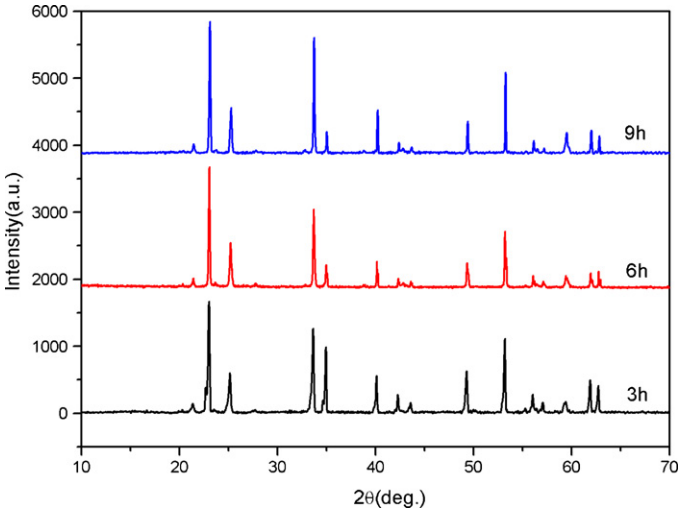

Fig. 6. XRD patterns of LNT powders by molten salt synthesis calcined at 1000 °C for different durations.

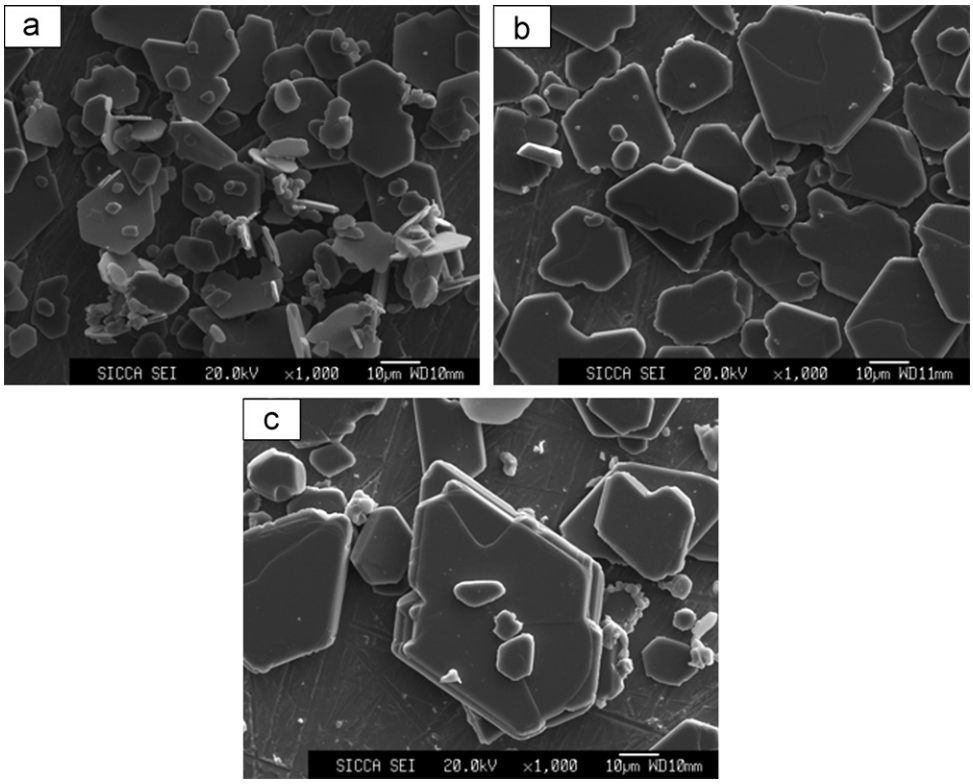

Fig. 7. SEM micrographs of LNT powders by molten salt synthesis calcined at 1000 °C for different durations. (a) 3 h; (b) 6 h; (c) 9 h.

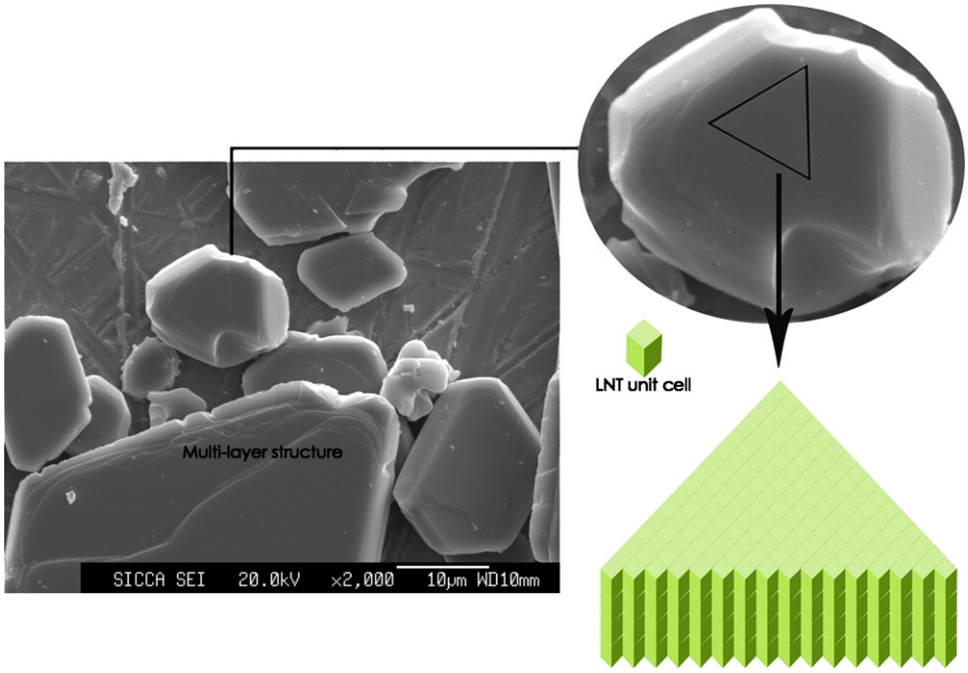

Fig. 8. SEM photographs LNT particles of multi-layer morphology with triangle surface pattern and illustration of the arrangement of the unit cells.

present. On the other hand, (1 0 0) plane grew large and particles exhibit plate-like shape. Multi-layer particles with triangle surface pattern were illustrated in Fig. 8

4. Conclusions

M-phase $LiNb_{0.6}Ti_{0.5}O_3$ hexagonal plate-like particles were fabricated by molten salt synthesis (MSS). Using LiCl as solvent, pure M-phase $LiNb_{0.6}Ti_{0.5}O_3$ could be synthesized at 950 °C without other intermediate phases, which is about 150 °C lower than that of conventional solid-state reaction. Further increasing temperature led to an increase in the size of the particles. The weight ratio of the chloride salt (LiCl) to LNT precursor powders showed an impact to the average thickness of the powders. Prolonged holding time could also increase the particle size significantly. The particles with a diameter of 5–20 μm and a thickness of 0.5–2.0 μm

synthesized at 1000 °C exhibited the largest dimensions, and such large anisometric particles can be used as templates for TGG and RTGG techniques.

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