Preparation and Dieletrical Properties of Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ Powders by Hydrothermal Method

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A hydrothermal method has been developed and shown to be effective for the preparation of Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ (LNT) nano-particles. Hydrothermal reaction temperature was in the range from 120°C - 200°C. The crystalline structure and morphology of the prepared particles have been characterized by x-ray diffraction and scanning electron microscopy. Results indicate that hydrothermal temperature had a great effect on the phase formation and morphology of the particles. The prepared powders crystallized at 140°C, and the pure LNT phase was formed at 180°C. The size of LNT particles increased with increasing reaction temperature, and plate-like LNT particles with thickness of 15 - 30 mm and a diameter of 80 - 200 mm were obtained at 200°C. It was found that LNT powders synthesized at 180°C gave the LNT ceramics the highest microwave dielectric properties ($\varepsilon_r = 66$, $Q \times f = 8946$ GHz) due to good crystallization and low particle size.

Keywords: Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$, hydrothermal reaction, dielectric properties

1. INTRODUCTION

The rapid growth of the wireless communication industry has created a high demand for microwave ceramic components. The Li$_2$O-Nb$_2$O$_5$-TiO$_2$ system has been extensively studied and a number of researchers have reported on this system, which has many compounds and excellent microwave dielectric properties.$^{[1-3]}$ In particular, Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ (defined as LNT) microwave dielectric ceramics, which were reported by Borisevich and Davies, exhibited good microwave dielectric properties with a high dielectric constant ($\varepsilon_r$) of 65, a high $Q \times f$ of 9000 at 5 GHz and near zero temperature coefficient of resonance frequency ($\tau_f$).$^{[4]}$ Therefore, LNT is known as a potential candidate material for low temperature co-fired ceramics (LTCC) technology. However, in addition to the materials required of high dielectric constant, low dielectric loss, and a zero temperature coefficient of resonant frequency, low cost of individual components and processing are critical requirements for commercial application.

LTCC components are high electrical performance by using highly conductive and inexpensive internal electrode metals, such as silver, copper and their alloys, so co-firing of the ceramic and metal layers is required.$^{[5]}$ Traditionally, LNT powders were synthesized using conventional solid state reaction, which requires a calcination step at high temperatures. For improving the drawbacks of the solid-state reaction, various kinds of solution processes have been investigated. Among the solution processing routes, the hydrothermal process has been proposed to be an effective method for synthesizing fine ceramic powders. In general, the hydrothermal process progresses in a closed system at a high autogenous pressure. By the benefit of the closed system with a high pressure, the required temperature for preparing powders can be greatly reduced because of the enhanced reactivity of reactive species, and fine particles can be obtained.$^{[6-8]}$

In this work, hydrothermal method was used to synthesize LNT powders under different conditions, and then the LNT powders were utilized to fabricate the microwave ceramics using the traditional sintering method. The influence of synthesis conditions and sintering temperatures on the microwave properties of LNT ceramics were investigated.

2. EXPERIMENTAL

Nb$_2$O$_5$ (99.9%), Li$_2$CO$_3$ (97%), Ti(OC$_4$H$_9$)$_4$ (95.0%), HF (40.0%), ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$, 99.5%), citric acid (C$_6$H$_5$O$_7$·H$_2$O, 99.5%), HNO$_3$ (65.0 - 68.0%), and NH$_3$·H$_2$O (25.0 - 28.0%) were used as raw materials. In the typical synthesis of LNT powders, the first stage is to prepare a water-soluble niobate as the niobium source by a chemical chelation method. Nb$_2$O$_5$ was dissolved in HF to
form NbOF$_2^-$ complex by heating for 10 h. (NH$_4$)$_2$C$_2$O$_4$ was added to the solution, keeping the oxalate ions in excess. Then NH$_3$: H$_2$O was added to form a precipitation of hydrous niobium oxide (Nb$_2$O$_5$·nH$_2$O). The precipitation was aged at 80°C for 6 h. The Nb$_2$O$_5$·nH$_2$O was then dissolved in citric acid and heating at 60°C to form a transparent pale yellow Nb-citrate complex. Ti(OC$_4$H$_8$)$_4$ and Li$_2$CO$_3$ were added into the prepared Nb-citrate solution with a molar ratio of [Li]:[Nb]:[Ti] = 1.075:0.625:0.45. HNO$_3$ was employed to turn pH of the mixture solution. The slurry was stirred and then transferred into an autoclave with a Teflon liner. Hydrothermal reaction temperature was varied in the range of 120°C - 200°C. After hydrothermal reaction for 12 h, the obtained powders were washed with distilled water and then dried at 60°C.

The as-prepared powders mixed with polyvinyl alcohol were formed into a cylinder with 18 mm in diameter and 9 mm in thickness by die pressing at a pressure of 135 MPa. The pellets were subsequently sintered at 800°C - 1100°C for 2 h with a heating rate of 5°C /min and then cooled to room temperature.

The crystalline phases of the ceramic powders were identified by x-ray diffraction (XRD, Bruker D8) using Cu K$_\alpha$ radiation. Microstructure observations of the ceramic powders were performed by scanning electron microscopy (SEM, S-3500N). Microwave dielectric constants $\varepsilon_r$ and the quality values $Q\times f$ at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using an Agilent 8719ET (50 MHz to 13.5 GHz) Network Analyzer.

3. RESULTS AND DISCUSSION

The XRD patterns of the prepared powders synthesized at different hydrothermal temperatures for 16 h are shown in Fig. 1. The powders were treated below 120°C exhibits a typical amorphous pattern, showing a broad peak around 25°. When the hydrothermal temperature reaches 160°C, only the characteristic diffraction peaks of LiNbO$_3$ crystals could be detected. No diffraction peaks of LNT can be seen in the patterns, which indicated the titanium dioxide is in an amorphous state. After heat treatment above 180°C, the peak splits due to the formation of LNT (M-phase) and no impurity peaks can be detected. According to the initial studies, M-phase bears a strong resemblance to that of LiNbO$_3$ with the exception of several peak splitting and additional satellite reflections. The obtained results confirm the structural analysis by Farber,[9] the LNT field actually contains a homologous series of commensurate intergrowth structures comprised of LiNbO$_3$-typed slabs of thickness L separated by single [Ti$_3$O$_5$]$^{2+}$ layers with a corundum-type structure. The layer distance between each intergrowth was found to depend on Ti content and resultant balances of Li and Nb.

Figure 2 show the SEM photographs of the prepared powders synthesized at different temperatures. An overview image illustrates that the obtained samples are quite uniform in shape and have a spherical morphology below 180°C. It can be observed that the particles treated at 140°C are composed of nanocrystals and the average crystalline size is about 40 nm. Meanwhile, powders synthesized at 160°C have particles that are essentially uniform in size and shape, although forming agglomerates with the diameter of approximately 60 nm. With increasing the hydrothermal temperature to 180°C, the SEM image shown in Fig. 2(c) displays that the particles have similar morphology and size to the particles obtained at 160°C, except that the spheres are assembled by some aggregates. When the hydrothermal temperature was increased to 200°C, fine particles are coarsening into relatively big aggregates, which is a normal phenomenon in polycrystalline materials during the synthesis process because of the large surface area and greater strain energy of these fine particles. A closer examination of Fig. 2(d) indicates that the LNT particles were plate-like with thickness of 15 - 30 nm and a diameter of 80 - 200 nm. According to the study of Yamamoto,[10,11] a minor axis of the plate-like grains corresponded to the $c$-axis of the LiNbO$_3$ subcell.

The dielectric constants ($\varepsilon_r$) of the specimens sintered at different temperatures from different powders are reported in Fig. 3. The maximum value was observed in the specimen sintered at 900°C from the LNT powder synthesized at 180°C, and it amounts to 66. It indicates that the LNT powders can be sintered completely at 900°C.