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Microwave dielectric properties of $LiNb_3O_8$ ceramics with TiO_2 additions

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Abstract

The microwave dielectric properties of $LiNb_3O_8$ ceramics were investigated as a function of the sintering temperature and the amount of TiO_2 additive. $LiNb_3O_8$ ceramics, which were calcined at 750 °C and sintered at 1075 °C for 2 h, showed a dielectric constant (ε_r) of 34, a quality factor ($Q \times f_0$) of 58,000 GHz and a temperature coefficient of resonance frequency (τ_f) of −96 ppm/°C, respectively. The density of the samples influenced the properties of these properties. As the TiO_2 content increased in the $LiNb_3O_8$–TiO_2 system, ε_r and τ_f of the material were increased due to the mixing effect of TiO_2 phase, which has higher dielectric constant and larger positive τ_f. The 0.65$LiNb_3O_8$–0.35TiO_2 ceramics showed a dielectric constant ε_r of 46.2, a quality factor ($Q \times f_0$) of 5800 GHz and a temperature coefficient of resonance frequency τ_f of near to 0 ppm/°C.

Keywords: Microwave dielectrics; Dielectric properties; TiO_2

1. Introduction

The microwave dielectric materials for applications in wireless communication systems such as cellular phones, broadcasting satellites and global positioning systems have been widely studied in the past decade.[1,2] These materials in the range of microwave frequency require a high dielectric constant (ε_r), a high quality factor ($Q \times f_0$) and a small temperature coefficient of resonance frequency (τ_f). The recent studies have concentrated on the development of low temperature-cofired ceramics (LTCC) with high conductive internal electrode materials such as silver, copper and their alloys, because of the fabrication of a small resonator within the multilayered integrated circuit.[3,4] Most of the commercial dielectric materials have a high sintering temperature over 1300 °C. To reduce sintering temperature, sintering additives having low-melting points have been generally used in the LTCC systems.[5,6] However, the addition of sintering additives results in an abrupt degrading of the dielectric properties due to the formation of secondary phases. Several dielectric compounds including Nb_2O_5 and their solid solution have been investigated and the niobate-based materials are tested for microwave dielectrics due to their lower sintering temperature and high quality factors. [7–9]

The purpose of this work is to examine new niobate dielectric materials combined with lithium oxide that have good microwave dielectric properties and a lower sintering temperature. In order to improve their dielectric constant and temperature coefficient of resonance frequency τ_f, the compound is combined with TiO_2 that has a dielectric constant of 104 and a high positive τ_f of +450 ppm/°C.[10] The microwave dielectric properties of $LiNb_3O_8$–TiO_2 ceramics have been investigated by varying sintering temperatures and the amount of TiO_2.

2. Experimental procedure

$LiNb_3O_8$ compounds were synthesized by the conventional mixed solid oxide method. High purity (99.9%) oxide powders of Li_2CO_3 and Nb_2O_5 were used as the starting materials. The powders were weighed and milled with ZrO_2 balls for 12 h in ethanol. The mixed powders were dried and calcined from 650 to 900 °C at rate of 10 °C/min for 2 h, respectively. The calcined powders were mixed with TiO_2 (0.25 to 0.45 mol) in ethanol for 12 h and then dried. These powders were pressed by uniaxial press into pellets of 15 mm diameter and 10 mm thickness under 1000 kg/cm^2 pressure. The pellets were finally sintered from 1025 to 1175 °C at a rate of 10 °C/min for 2 h under air atmosphere.

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The crystalline phases of calcined powders and sintered specimens were analyzed by X-ray powder diffraction (XRD) method (MO3XHF, MAC Science, Japan) for 2θ in the range 10° to 80°. The microstructure of the specimens was observed using a scanning electron microscope (LEO420, Cambridge, UK) and the sintered density of the samples was measured by the Archimedes method. The microwave dielectric properties of specimens were measured by the Hakki–Coleman dielectric resonator method with the TE_{011} mode.[11] The τ_f of the samples was obtained by the cavity method in the temperature range from 25 to 85 °C.[12]

3. Results and discussion

From the XRD analysis of calcined powders showed that a single phase $LiNb_3O_8$ compound is formed by heat treatment above 700 °C. However, as the calcination temperature increased, the particle size of the calcined powder increased due to the aggregation of particles. The density of $LiNb_3O_8$ ceramics as a function of sintering temperature is shown in Fig. 1. The density increased as the sintering temperature increased up to 1075 °C. The density is decreased slightly above 1100 °C. The density of the specimen sintered at 1075 °C using powder calcined at 75 °C showed the maximum value of 4.84 g/cm^3.

Fig. 2 shows the SEM micrographs of $LiNb_3O_8$ ceramics with various sintering temperatures. The grain size of specimens increases with increasing sintering temperature, but large pores were observed in the specimens sintered above 1125 °C. The large pores may be related to the volatility of lithium ions during the sintering process. The measurements of weight loss during sintering of the specimens showed no change in weight up to 1075 °C, but showed a weight loss of about 0.29 wt.% at 1175 °C. Also, we confirmed that lithium vacancy as a result of its volatility, yields a large abnormal grain growth and changed the grain orientation from the (4 1 0) to the (4 0 0) plane. From the Fig. 1, as the calcination temperature increased, the apparent density of $LiNb_3O_8$ ceramics increased up to 800 °C and then decreased at 900 °C. Thus, it could be considered that the unreacted material and aggregation powder prevented the grain size increasing.

XRD patterns of $LiNb_3O_8$ ceramics with various sintering temperatures are shown in Fig. 3. The peaks of the (2 0 0) and (4 0 0) planes were increased with increasing sintering temperature.

Fig. 4 shows microwave dielectric properties of $LiNb_3O_8$ ceramics with various calcination temperature as a function of sintering temperature. As the sintering temperatures increased, the dielectric constant increased up to 1075 °C and then decreased slightly, and the quality factors increased up to

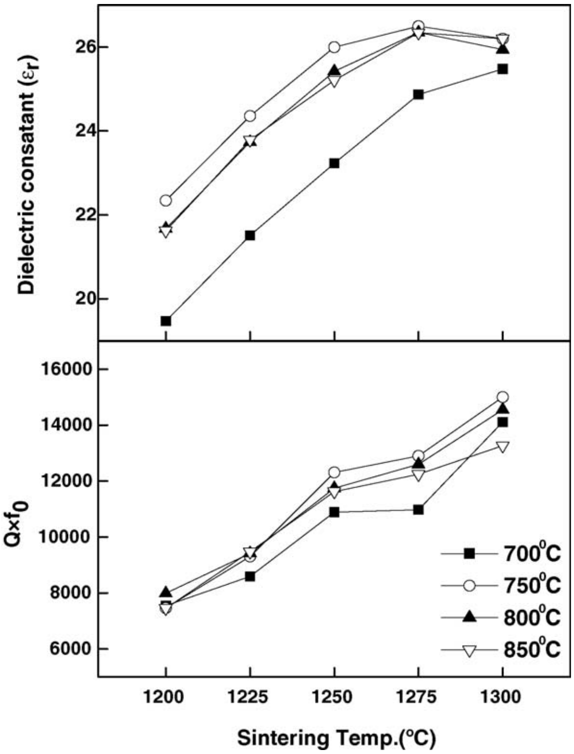

Fig. 2. Dielectric constant and quality factor of $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics as a function of sintering temperature.

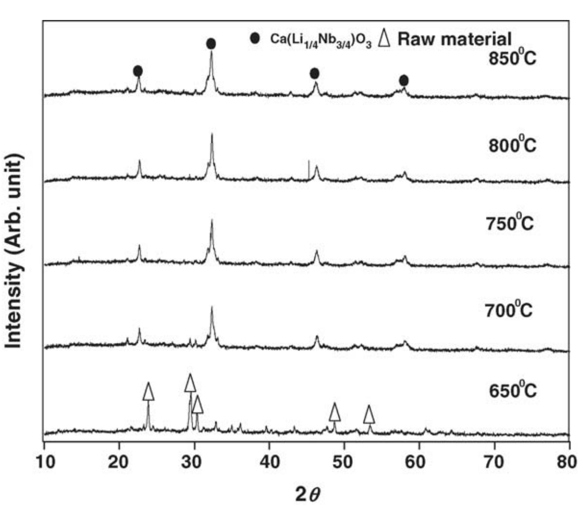

Fig. 1. XRD patterns of $Ca(Li_{1/4}Nb_{3/4})O_3$ calcined specimens with various temperature.

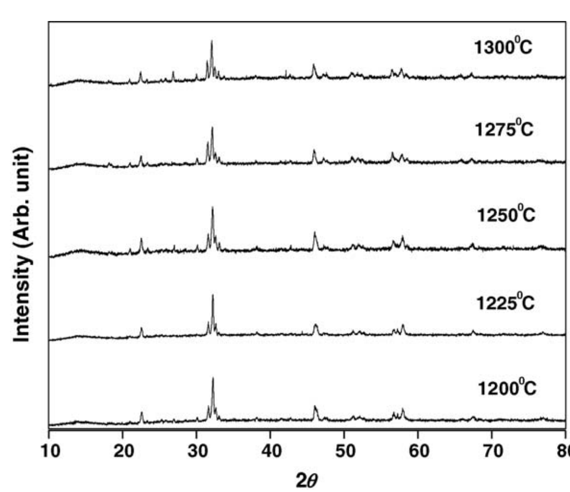

Fig. 3. XRD patterns of $Ca(Li_{1/4}Nb_{3/4})O_3$ specimens with various sintering temperature.

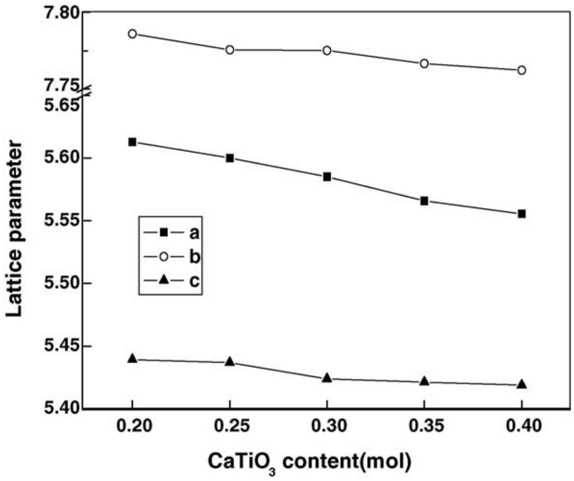

Fig. 4. Lattice parameters of $(1-x)Ca(Li_{1/4}Nb_{3/4})O_3$–$xCaTiO_3$ system as a function of x mol.

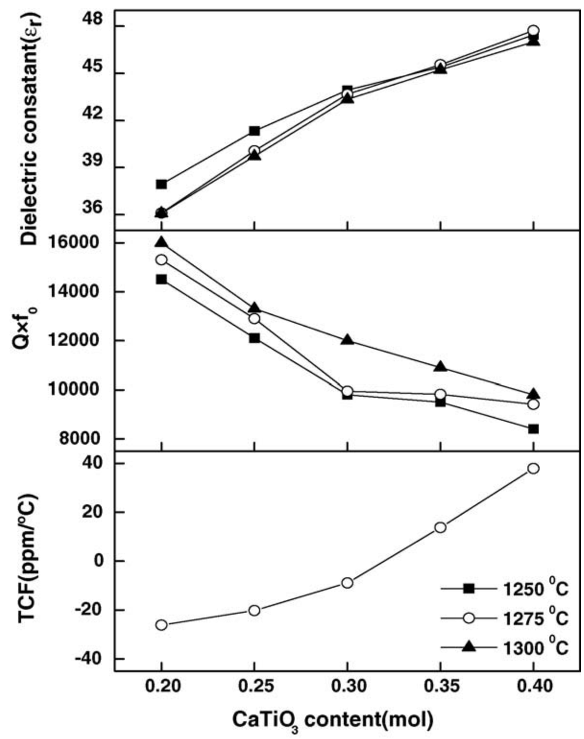

Fig. 5. Dielectric constant, quality factor and TCF of $(1-x)Ca(Li_{1/4}Nb_{3/4})O_3$–$xCaTiO_3$ system as a function of x mol.

1100 °C and then decreased. These results are very similar to the changes of apparent densities with varying calcination and sintering temperatures. As shown in Fig. 4, the $LiNb_3O_8$ ceramics, which were calcined at 750 °C and sintered at 1075 °C for 2 h, showed a ε_r of 34, a quality factor ($Q \times f_0$) of 58,000 GHZ and a τ_f of −96ppm/°C. In order to improve the dielectric properties of $LiNb_3O_8$ ceramics to make a good candidate for microwave dielectrics, it is essential to improve the τ_f through the addition of TiO_2 that has a high positive τ_f and a high dielectric constant.[11]

X-ray diffraction patterns of $(1-x)LiNb_3O_8$–$xTiO_2$ ceramics sintered at 1100 °C for 2 h with various TiO_2 concentrations as shown in Fig. 5. XRD patterns could be indexed as two phase mixtures that are composed of the main $LiNb_3O_8$ compound and the added TiO_2 compound. With the increase of the TiO_2 concentration in the range of 0.25–0.45 mol, the peak intensity for TiO_2 compound increased steadily. However, the peak positions according to $LiNb_3O_8$ were constant due to the absence of solid solutions.

Fig. 5 shows microwave dielectric properties of $(1-x)LiNb_3O_8$–$xTiO_2$ ceramics sintered at 1100 °C for 2 h as a function of x concentration. As the TiO_2 concentration increase from 0.25 to 0.45 mol, the dielectric constant and temperature coefficient of resonance frequency τ_f increased from 40.5 to 55.8 and from −52 to 43 ppm/°C, respectively. This can be explained by the logarithmic mixing rule of properties in mixture ceramics between $LiNb_3O_8$ having a dielectric constant of 34, a τ_f of −96 ppm/°C and by TiO_2 having a dielectric constant of 104 and a τ_f of +450 ppm/°C. These results are well agreed with the results related to rutile and its compounds by Haga K. et al.[10] However, the quality factor ($Q \times f_0$) values decrease with an increasing TiO_2 concentration. This could be considered due to the fact that the phase boundary in mixture ceramics was affected by an increase of interface loss resulting from the generation of anharmonic vibration that decreases the quality factor.[13]

In conclusion, $0.65LiNb_3O_8$–$0.35TiO_2$ ceramics sintered at 110 °C have good microwave dielectric properties with a dielectric constant of 46.2, quality factor ($Q \times f_0$) values of 5800 GHz and a τ_f of near to 0 ppm/°C.

4. Conclusion

$LiNb_3O_8$ ceramics, which were calcined at 750 °C and sintered at 1075 °C for 2 h, showed a ε_r of 34, a $Q \times f_0$ of 58,000 GHz and a τ_f of −96 ppm/°C. These properties were influenced by changes in sintered densities due to the calcination temperature and lithium evaporation.

As the TiO_2 content increases in $LiNb_3O_8$–TiO_2 systems, the dielectric constant and τ_f increased due to the mixing effect of the TiO_2 phase. The ε_r of 46.2, a quality factor of 5800 GHz and a τ_f of near 0 ppm/°C were obtained for the $0.65LiNb_3O_8$–$0.35TiO_2$ ceramics sintered at 1100 °C.

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