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Microwave dielectric properties of $Ca(Li_{1/4}Nb_{3/4})O_3$–$CaTiO_3$ ceramic systems

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Abstract

The microwave dielectric properties of $Ca(Li_{1/4}Nb_{3/4})O_3$–$CaTiO_3$ ceramics have been investigated with regard to calcination temperature and the amount of $CaTiO_3$ additive. $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics with an orthorhombic crystal structure can be synthesized by the conventional mixed oxide method by calcining at 750 °C and sintering at 1275 °C. The dielectric constant (ε_r), quality factor ($Q \times f_0$) and temperature coefficient of resonant frequency (τ_f) for $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics are 26, 13,000 GHz and -49 ± 2 ppm/°C, respectively. With increase in the $CaTiO_3$ content, ε_r and τ_f are increased and the quality factor decreased due to the solid-solution formation between $Ca(Li_{1/4}Nb_{3/4})O_3$ and $CaTiO_3$. The $0.7Ca(Li_{1/4}Nb_{3/4})O_3$–$0.3CaTiO_3$ ceramic exhibits ε_r of 44, quality factor ($Q \times f_0$) of 12,000 GHz and τ_f of -9 ± 1 ppm/°C.

Keywords: Microwave dielectrics; Dielectric properties; Calcination

1. Introduction

The applications of the microwave dielectric ceramics such as resonators, filters, antennas, etc. has been rapidly increasing for use in mobile communications.[1] Materials for microwave use should consider three dielectric properties: the dielectric constant (ε_r), the quality factor ($Q \times f_0$) and the stability of temperature coefficient of the resonant frequency (τ_f).[2,3] One of the most important dielectric materials is complex perovskite $A(B_I, B_{II})O_3$ ceramics which have high quality factors ($Q \times f_0$) and small τ_f. However, it is very difficult to fabricate microwave dielectric components due to the high sintering temperatures of above 1400 °C. Recently, lithium-based perovskite $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics possessing good dielectric properties and a low sintering temperature of about 1150 °C have been reported.[4,5] However, during synthesis of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics, volatilisation of lithium occurs producing secondary phases deteriorating the dielectric properties.

The purpose of this work is to examine the microwave dielectric properties of the stoichiometric perovskite $Ca(Li_{1/4}Nb_{3/4})O_3$ compound and to improve the dielectric characteristics by the formation of solid solutions in the range of 0.2–0.4 mol%, using a $CaTiO_3$ which has a dielectric constant (ε_r) of 170 and a high positive τ_f of +800 ppm/°C. Thus, the microwave dielectric properties of $Ca(Li_{1/4}Nb_{3/4})O_3$–$CaTiO_3$ ceramics have been investigated as a function of calcination temperatures and the amount of $CaTiO_3$ additives.

2. Experimental procedure

The starting materials were high-purity (99.9%) $CaCO_3$, Li_2CO_3, Nb_2O_5 and $CaTiO_3$ powders. These powders were weighed according to the stoichiometric composition of $Ca(Li_{1/4}Nb_{3/4})O_3$ compound and then milled using ZrO_2 balls for 12 h in ethanol. The mixed powders were dried and calcined from 650 to 850 °C for 2 h, respectively. The calcined powders were mixed with $CaTiO_3$ (0.2–0.4 mol) in ethanol for 12 h and then dried. These powders were pressed into pellets of 15 mm diameter and 10 mm thickness under 1000 kg/cm^2 pressure. The pellets were finally sintered from 1200 to 1300 °C at a heating rate of 10 °C/min for 2 h under air atmosphere.

The crystalline phase of the calcined powders and sintered specimens were analyzed by the X-ray powder diffraction method (MO3XHF, MAC Science, Japan) radiation for 2θ from 10° to 80°. The microwave dielectric properties of specimens were then measured by the Hakki–Coleman dielectric

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resonator method with the TE_{011} mode. The τ_f of the sample was obtained by the cavity method in the temperature range from 25 to 85 °C.[6,7]

3. Results and discussion

Fig. 1 shows powder X-ray diffraction patterns of $Ca(Li_{1/4}Nb_{3/4})O_3$ compounds calcined in the range 650–850 °C for 2 h. The XRD patterns of powders calcined above 750 °C can be identified as having an orthorhombic perovskite structure. However, the powders calcined below 700 °C display unreacted starting materials. As the calcination temperature increased, the particle size of powder increased due to agglomeration.

The microwave dielectric properties of $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics prepared by calcining and sintering at different temperatures are shown in Fig. 2. With increased sintering temperature the quality factor ($Q \times f_0$) value increased due to the densification of specimens; however, the dielectric constant increased only up to 1275 °C and then decreased slightly. Also, as the calcination temperature increased, the dielectric constant and quality factor ($Q \times f_0$) value increased up to 750 °C and then decreased again. Generally, the microwave dielectric properties depend upon the defects, pore size and second phase in dielectric materials,[8] because they have a very low dielectric constant and produce an anharmonic lattice vibration at the interface boundary. In case of calcination below 700 °C, the unreacted material acted as an inhibitor during sintering and thus, the densification decreased. Above 800 °C, the aggregation of powder could be reduced due to the low surface energy related to density. Therefore, it is confirmed that the optimum calcination temperature for the $Ca(Li_{1/4}Nb_{3/4})O_3$ compound is 750 °C.

Fig. 3 shows powder X-ray diffraction patterns of $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics sintered from 1200 to 1300 °C. All specimens have an orthorhombic perovskite crystal structure and their lattice constants are $a = 5.646$ Å, $b = 7.822$ Å and $c = 5.460$ Å, respectively. The $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics sintered well at 1275 °C and showed the dielectric constant (ε_r) of 26, a quality factor ($Q \times f_0$) of 13,000 GHz and a τ_f of -49 ± 2 ppm/°C. The microwave dielectric properties of $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics having a high negative τ_f can be improved through solid-solution formation with $CaTiO_3$ ceramics which have the same orthorhombic perovskite structure and a high positive τ_f.

From the XRD results of the $(1-x)$ $Ca(Li_{1/4}Nb_{3/4})O_3$–$x$$CaTiO_3$ systems in the range of $x = 0.2$–0.4 mol, a single

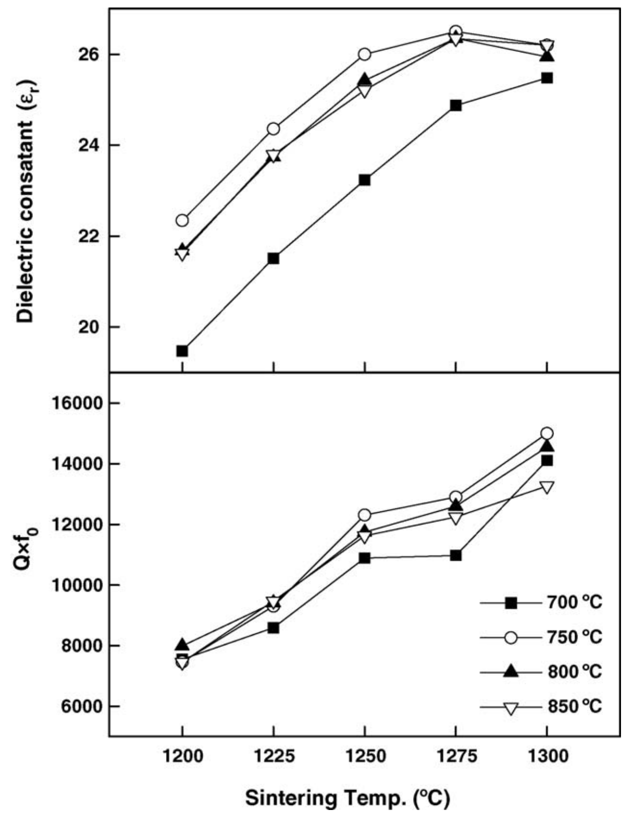

Fig. 2. Dielectric constant and quality factor of $Ca(Li_{1/4}Nb_{3/4})O_3$ ceramics as a function of sintering temperature.

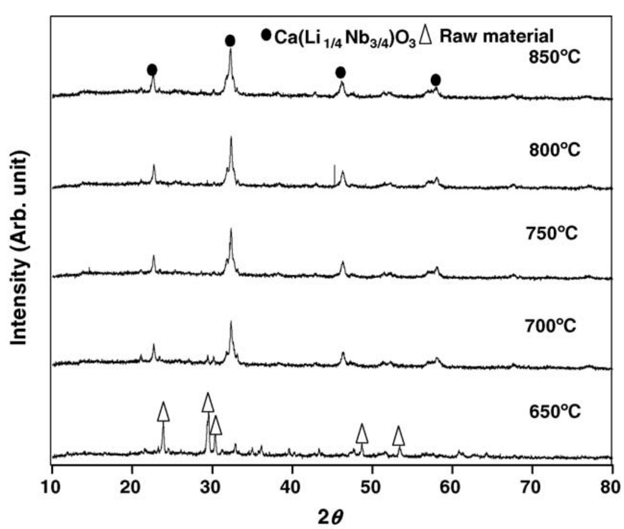

Fig. 1. XRD patterns of $Ca(Li_{1/4}Nb_{3/4})O_3$ calcined specimens with various temperature.

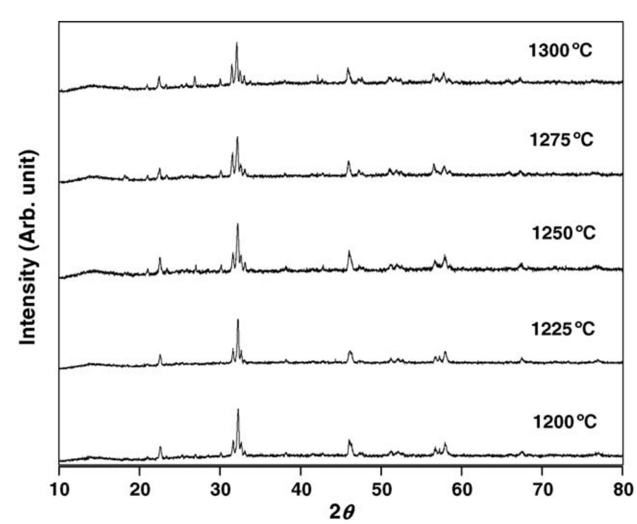

Fig. 3. XRD patterns of $Ca(Li_{1/4}Nb_{3/4})O_3$ specimens with various sintering temperature.