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Microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with glass

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Abstract The effect of the addition of glass on the densification, low temperature sintering, and microwave dielectric properties of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$(CLNT) was investigated. Addition of glass (B_2O_3-ZnO-SiO_2-PbO system) improved the densification and reduced the sintering temperature from 1150°C to 900°C of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}$-$Ti_x]O_{3-\delta}$ microwave dielectric ceramics. As increasing glass contents from 10 wt% to 15 wt%, the dielectric constants (ε_r) and bulk density were increased. The quality factor ($Q{\cdot}f_0$), however, was decreased slightly. The temperature coefficients of the resonant frequency (τ_f) shifted positive value as increasing glass contents over Ti content is 0.2 mol. The dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.75}Ti_{0.25}]O_{3-\delta}$ with 10 wt% glass sintered at 900°C for 3 h were $\varepsilon_r = 40$ $Q{\cdot}f_0 =$ 11500 GHz, $\tau_f = 8$ ppm/°C. The relationship between the microstructure and dielectric properties of ceramics was studied by X-ray diffraction (XRD), and scanning electron microscope (SEM).

Keywords Microwave · Dielectric · LTCC · Addition of glass

1 Introduction

The low temperature co-fired ceramics(LTCC) for microwave applications represents a key position in mobile products. The integration of passive components in LTCC is, therefore, particularly interesting in multilayers technology. RF multilayer device structures have been developed to reduce device size, in which low melting point flux are frequently added so that dielectric ceramics can be co-fired with low resistance conductors such as Ag and Cu instead of Ag-Pd or ternary (Pt:Pd:Au) electrodes at low sintering temperature. The microwave dielectric materials require high dielectric constants (ε_r), high quality factor values($Q{\cdot}f_0$), and stable temperature coefficient of the resonant frequency ($\tau_f \leq |10|$ ppm/°C) generally. The low sintering temperature microwave dielectric materials also require the same properties of them. It is known that microwave dielectric constant between 35 and 40 materials can be used for the band pass filter and below 20 of dielectric constant also used for antennas generally. Now, microwave dielectric materials, $Ba_2Ti_9O_{20}$ [1] and (Zr,Sn)TiO_4 [2] etc, used for filters(duplexer, BPF, LPF etc), but they have high sintering temperature. So, they can not be co-fired with inner electrode (Ag, Cu) at low sintering temperature (<900°C).

In our previous work[3], $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics were already reported. The dielectric properties were that dielectric constant is between 30 and 45 and $Q{\cdot}f_0$ value is over 20,000 GHz at 1150°C. This paper reports the characteristic and microwave dielectric properties on $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0 \leq x \leq 0.3)$ with glass(B_2O_3-ZnO-SiO_2-PbO system) as a sintering flux to decrease the sintering temperature, and the relationship between the physical properties and microwave dielectric properties of ceramics.

2 Experimental procedure

The $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}(0 \leq x \leq 0.3)$ powders compositions were synthesized by the conventional solid-solution

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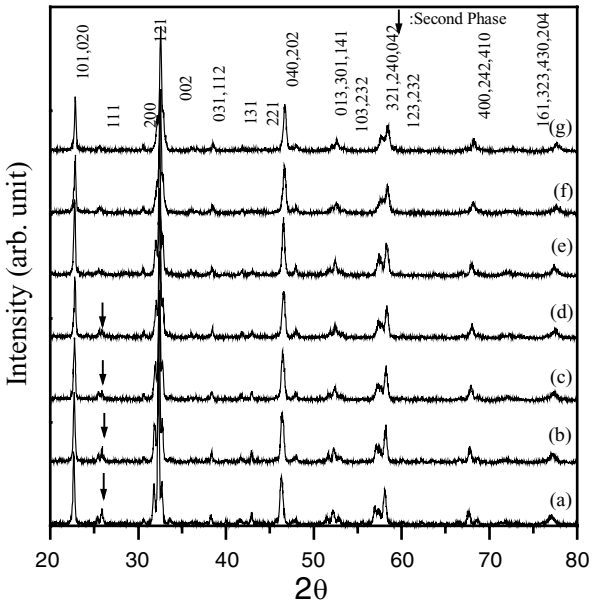

Fig. 1 XRD pattern of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with 10 wt% glass addition : (a) 0 (b) 0.05 (c) 0.1 (d) 0.15 (e) 0.2 (f) 0.25 (g) 0.3 [mol]

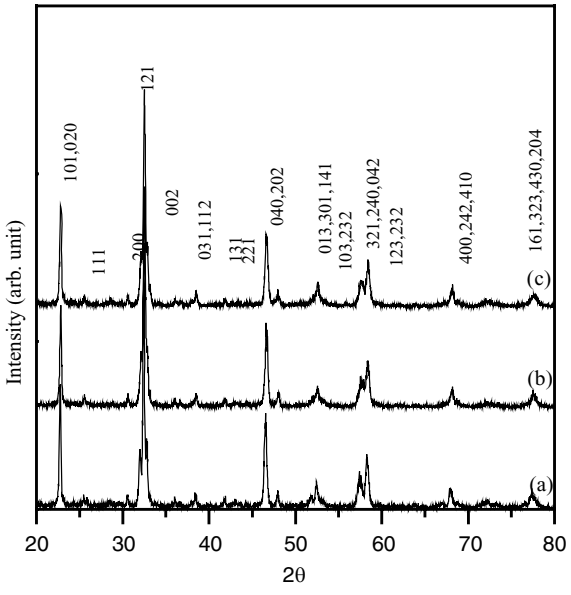

Fig. 2 XRD pattern of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with x wt% glass addition : (a) 10 (b) 12 (c) 15 [wt%]

reaction method using high purity $CaCO_3$, Li_2CO_3, Nb_2O_5, TiO_2 (all Aldrich, 99.9%). All powders were dried at 600°C for 10 h to remove moisture before use. The starting materials were mixed for 24 h in a ball mill with zirconia balls according to the desired stoichiometry, $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0 \leq x \leq 0.3$), and ground in ethyl alcohol to prevent dissolution of Li_2CO_3 in water. The mixtures were dried and calcined in an alumina crucible at 850°C for 2 h in air. The calcined powder milled again with the additives, glass

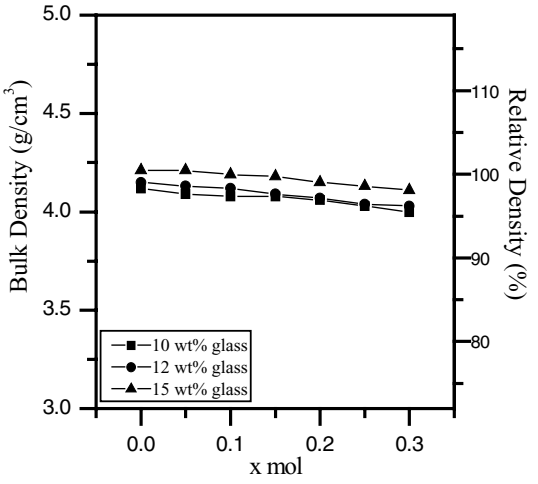

Fig. 3 Bulk Density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with contents of glass

frit(B_2O_3-ZnO-SiO_2-PbO system) from 10 wt% to 15 wt% for 24 h. The dried powder were pressed into rods of 12 mm in diameter and 5–6 mm in thickness under a pressure of 20,000 psi with cold isostatic pressing(CIP). The sintering temperature was 900°C for 3 h with 5°C/min of the heating and cooling rate. The bulk density was measured by the Archimedes method. The microwave dielectric properties were measured by the dielectric rod resonator method [4] using network analyzer (HP8720C). As not all specimens were available in equal size, the properties were measured at different frequencies. For the presentation of loss quality data the following general relation observed in narrow frequency range was utilized: $Q \cdot f_0 = \text{constant(GHz)}$. The temperature coefficient of resonant frequency(τ_f) at microwave frequencies was measured in the temperature range of 20 to 80°C. X-ray diffraction(CuKα radiation, D/MAX 2500, Rigaku) was carried out on powders obtained by crashing the sintered specimens for phase identification. The microstructure of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with glass ceramics were investigated using a scanning electron microscope (SEM, S-4200, Hitachi).

3 Results and discussions

The X-ray diffraction patterns of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with 10 wt.% of glass contents sintered at 900°C for 3 h shown in Fig. 1. The diffraction peaks could be indexed based on the $CaTiO_3$-type orthorhombic perovskite structure with four formula units per cell. When glass contents added 10 wt%, little amount of the second phase were detected below 0.2 mol of Ti content. The stability of the perovskite phase increased with increasing Ti concentration and the single phase specimens were obtained in the range of over 0.2 mol [3]. Figure 2 shows powder x-ray diffraction

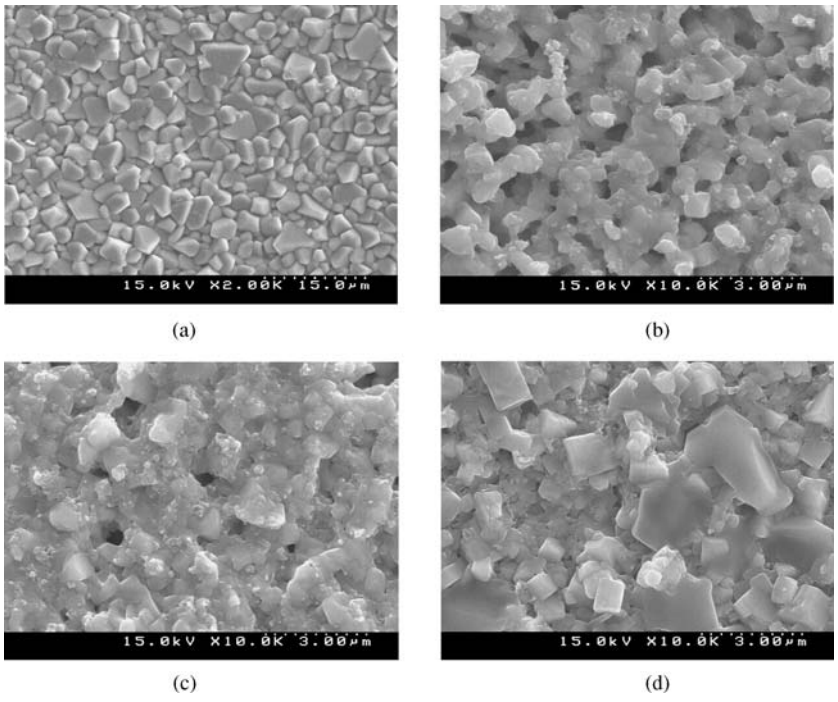

Fig. 4 Microstructure of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with contents of glass (a) 0 [wt% at 1150°C 3 h] (b) 5 (c) 7 (d) 10 [wt%]

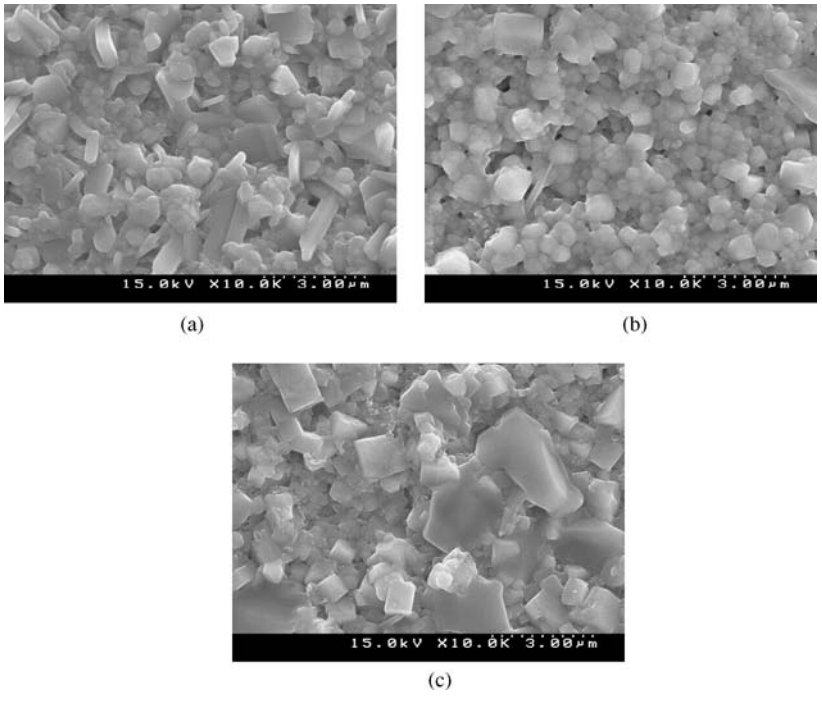

Fig. 5 Microstructure of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with contents of 15 wt% glass (a) 0 (b) 0.05 (c) 0.2 [mol]

patterns of the $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ glass 10 wt% to 15 wt% of glass contents sintered at 900°C for 3 h. The second phase was not detected as shown in Fig. 2. The glass frit in this system did not affect forming of the second phase in sintered specimens.

The bulk density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with glass specimens sintered at 900°C for 3 h were increasing when glass contents increase from 10 wt% to 15 wt%. The reason of this result was that the microstructure of specimen was densified by glass frit (Fig. 4). However, the bulk density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}(0 \leq x \leq 0.3)$ specimens slightly decreased from 4.12 to 4 g/cm^3 with 10 wt% of glass contents (Fig. 3). The XRD density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}(0 \leq x \leq 0.3)$ specimens also slightly decreased from 4.21 to 4.16 g/cm^3 with increasing Ti concentration. By adding glass frit in

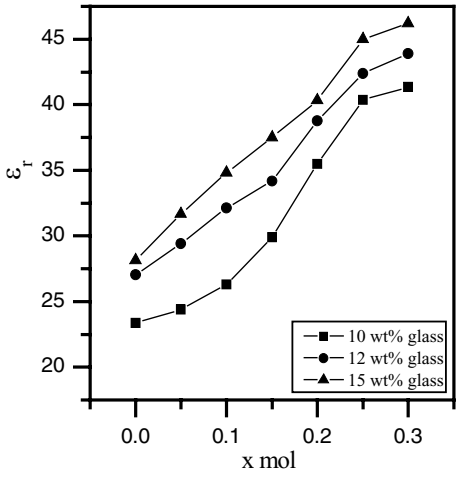

Fig. 6 Dielectric constant of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with contents of glass

$Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics, it can be obtained at over 95% relative density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics at 900°C for 3 h.

The microstructure of the $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with glass frit from 10 wt% to 15 wt% sintered at 900°C for 3 h and without addition sintered at 1150°C for 3 h is shown in Fig. 4. The undoped $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramic was dense and homogeneously fine microstructure at 1150°C. As increasing glass frit contents, porosities were reduced and grain size was slightly increased. The abnormal grain growth was found at addition of 15 wt% glass frit. Figure 5 shows the microstructure of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with 15 wt% contents of glass frit sintered at 900°C for 3 h. The $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramic with 15 wt% contents of glass frit showed dense and a little abnormal grain microstructures at 900°C.

Figure 6 shows the dielectric constant (ε_r) of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with different amounts of glass frit sintered at 900°C for 3 h. The relationship between ε_r value and amounts of glass revealed the same trend with those between the bulk density and glass contents. The reason of increased dielectric constant of specimen as increasing glass contents was reduction of porosity [5]. However, the dielectric constant of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with glass contents increased as increasing Ti concentration from 0 to 0.3 mol because a small Ti^{4+} ion (0.56 Å) was incorporated to a B-site $[Li_{1/3}Nb_{2/3}]^{3.67+}$ with larger ionic radius (0.66 Å) hence, it was easily displaced under an electrical field [3, 6].

Figure 7 shows the $Q{\cdot}f_0$ values of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with glass frit contents from 10 wt% to 15 wt% sintered at 900°C for 3 h. The $Q{\cdot}f_0$ values were decreased as increasing glass contents. The reason of decreased $Q{\cdot}f_0$ values was due to be increased the abnormal grain growth in specimen as mentioned above. It was reported by

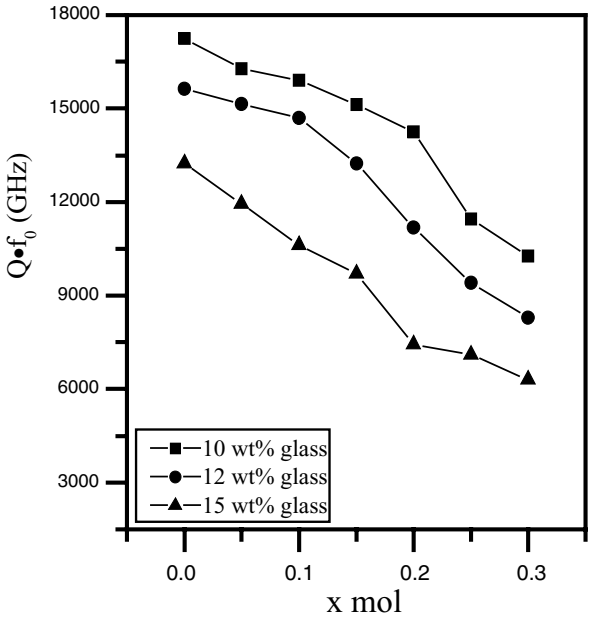

Fig. 7 $Q{\cdot}f_0$ of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with contents of glass

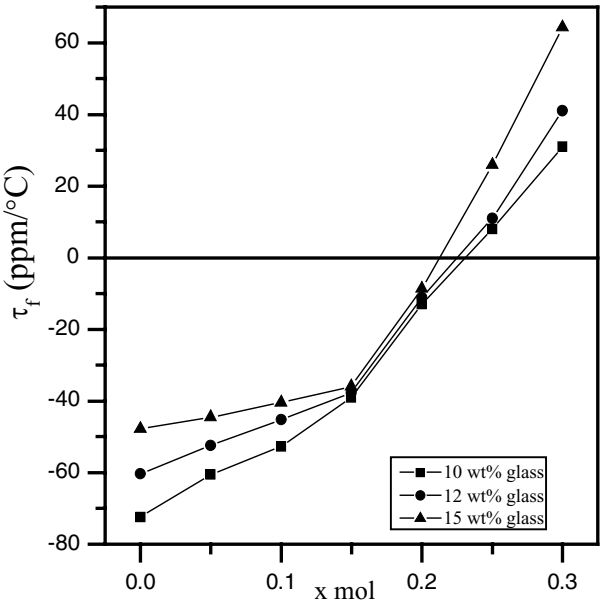

Fig. 8 τ_f of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900°C for 3 hrs with contents of glass

Iddles et al. [7] that the abnormal grain growth was more important factor than the pore to reduce the $Q{\cdot}f_0$ values of microwave dielectric ceramics over 90% of relative density.

Figure 8 shows temperature coefficient of resonant frequency (τ_f) of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with various glass frit contents. The τ_f value abruptly shifted positive from −72.4 to 64.3 ppm/°C with an increase of Ti concentration. As increasing glass contents, the τ_f value

shifts positive direction. The τ_f value was controlled between –10 and 10 ppm/°C to apply microwave device, BPF and antenna etc. The optimized microwave properties for multi-chip filter, $\varepsilon_r = 40$, $Q{\cdot}f_0 = 11500$ GHz, and $\tau_f = 8$ ppm/°C on $Ca[(Li_{1/3}Nb_{2/3})_{0.75}Ti_{0.25}]O_{3-\delta}$ with 10 wt% glass.

4 Conclusions

The microwave dielectric properties of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ added glass frit was investigated. Glass addition improved the densification and reduced the sintering temperature from 1150°C to 900°C of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ microwave dielectric ceramics. As increasing glass contents, the dielectric constants and bulk density were increased. The quality factor, however, was decreased slightly. The temperature coefficients of the resonant frequency shifts positive value as increasing glass frit contents and also increased from −72.4 to 64.3 ppm/°C with an increase of Ti concentration. The dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.75}Ti_{0.25}]O_{3-\delta}$ with 10 wt% glass frit sintered at 900°C for 3 h were $\varepsilon_r = 40$ $Q{\cdot}f_0 = 11500$ GHz, $\tau_f = 8$ ppm/°C.

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