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Microwave dielectric properties of Bi_2O_3-doped $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics

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Abstract

The effect of the additive 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. Bi_2O_3 addition improved the densification and reduced the sintering temperature from 1150 to 900 °C of CLNT microwave dielectric ceramics. As the Bi_2O_3 content increased, the dielectric constant (ε_r) and bulk density increased. The quality factor ($Q{\cdot}f_0$), however, was decreased slightly. The temperature coefficient of resonant frequency (τ_f) shifted to a positive value with increasing Bi_2O_3 content. The dielectric properties (ε_r, $Q{\cdot}f_0$, τ_f) of $Ca[(Li_{1/3}Nb_{2/3})_{0.95}Ti_{0.05}]O_{3-\delta}$ and $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with 5 wt.% Bi_2O_3 sintered at 900 °C for 3 were 20, 6500 GHz, −4 ppm/°C, and 35, 11,000 GHz, 13 ppm/°, respectively. The relationship between the microstructure and dielectric properties was studied by X-ray diffraction (XRD), and SEM.

Keywords: Bi_2O_3; Dielectric properties; LTCC; Microwave ceramics; Ca(Li,Nb,Ti)O_3

1. Introduction

Recently, RF multilayer device structures have been developed (to reduce device size) in which a low melting point flux is frequently added so that dielectric ceramics can be co-fired with low resistance conductors such as Ag and Cu at low temperature instead of using Ag–Pd or ternary (Pt:Pd:Au) electrodes. Most 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 ($\tau_f \leqslant |10|$ ppm/°C). The low sintering temperature microwave dielectric materials also require the same properties. It is known that microwave dielectric constant materials between 35 and 40 can be used for band pass filters, and materials with ε_r below 20 can also be used for antennas. Now, existing microwave dielectric materials, $Ba_2Ti_9O_{20}$[1] and (Zr,Sn)TiO_4[2] etc., all used for filters (duplexer, BPF, LPF etc), but they have high sintering temperatures. So, they can not be co-fired with an internal electrode (Ag, Cu) at a low sintering temperature (<900 °C).

In our previous work,[3] the properties of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics were reported. Depending upon stoichiometry, the dielectric properties vary between 30 and 45 and the $Q{\cdot}f_0$ value is over 20,000 GHz at 1150 °C. This paper reports: (i) the characteristics and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ doped with Bi_2O_3 as a sintering flux to decrease the sintering temperature, and (ii) the relationship between the physical properties and microwave dielectric properties of the ceramics.

2. Experimental procedure

The $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ powder compositions were synthesized by the conventional solid–solution reaction method using high purity $CaCO_3$, Li_2Co_3, Nb_2O_5, TiO_2, Bi_2O_3 (all Aldrich, 99.9%). The starting materials were mixed for 24 h in a ball mill with zirconia balls according to the desired stoichiometry, $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$, and ground in ethyl alcohol to prevent dissolution of Li_2O_3 in water. The mixtures were dried and calcined in an alumina crucible at 850 °C for 2 h in air. The calcined powder was milled again with the additive, Bi_2O_3 from 5 wt.% to 10 wt.% for 24 h. The dried powders were pressed into rods of 12 mm diameter and 5–6 mm thickness under a pressure of 20,000 psi by cold isostatic pressing (CIP). The sintering temperature

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was 900 °C for 3 h with 5 °C/min 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 a 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 for narrow frequency range was utilized: $Q{\cdot}f_0$ = constant (GHz). The temperature coefficient of resonant frequency (τ_f) at microwave frequencies was measured in the temperature range of 20–80 °C. Sintered pellets were examined by powder X-ray diffraction (XRD, Philips PW 1820) analysis with CuK_α radiation. The microstructures of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ with Bi_2O_3 ceramics were investigated using a scanning electron microscope (SEM, JXA-8600, Jeol).

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with Bi_2O_3 from 5 wt.% to 10 wt.% sintered at 900 °C for 3 h. The diffraction peaks can be indexed according to the $CaTiO_3$-type orthorhombic perovskite structure. The $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ prepared without Bi_2O_3 was single phase.[3] When 5 wt.% Bi_2O_3 was added, a small amount of the second phase was detected. With increasing amount of Bi_2O_3 (m.p. 825 °C), the intensity of the second phase peaks slightly increased. The second phase is found in the specimens, because of the liquid phase in the grain boundaries.

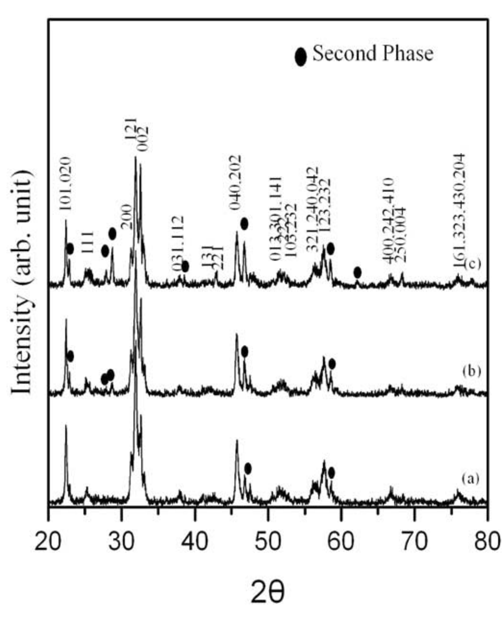

Fig. 1. XRD spectra of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ specimens sintered at 900 °C for 3 h with Bi_2O_3 contents of: (a) 5 (wt.%), (b) 7 (wt.%), (c) 10 (wt.%).

The bulk density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ plus Bi_2O_3 specimens sintered at 900 °C for 3 h increased when the Bi_2O_3 content increased from 5 to 10 wt.%. However, the bulk density slightly decreased, as the Ti concentration increased from 0.05 to 0.3 mol as shown in Fig. 2. By preparing $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with Bi_2O_3 additions, densities over 92% theoretical can be obtained by sintering at 900 °C for 3 h.

Fig. 3 shows the microstructure of the $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ prepared with 5–10 wt.% Bi_2O_3 from sintered at 900 °C for 3h and sintered without Bi_2O_3 sintered at 1150 °C for 3 h. It is evident that the grains typically exhibited platelet morphology.[5] Abnormal grain growth

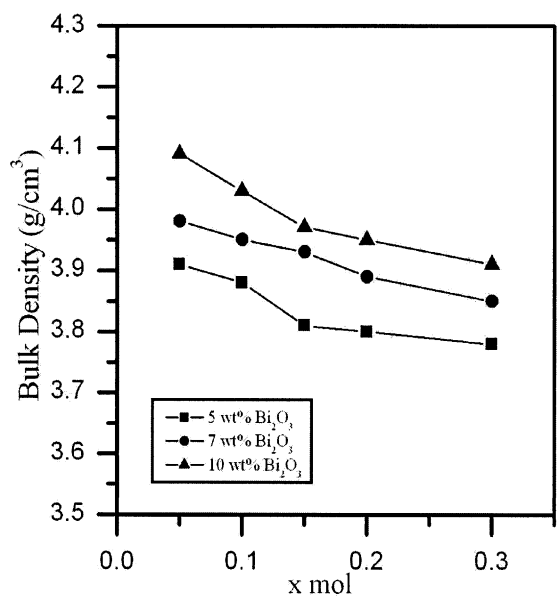

Fig. 2. Bulk density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900 °C for 3 h as function y of Bi_2O_3 content in starting mixture.

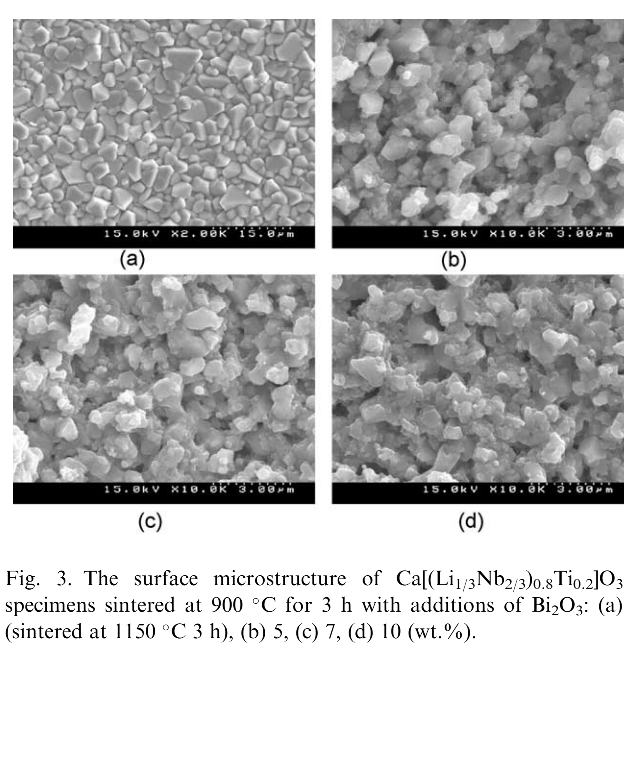

Fig. 3. The surface microstructure of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ specimens sintered at 900 °C for 3 h with additions of Bi_2O_3: (a) 0 (sintered at 1150 °C 3 h), (b) 5, (c) 7, (d) 10 (wt.%).

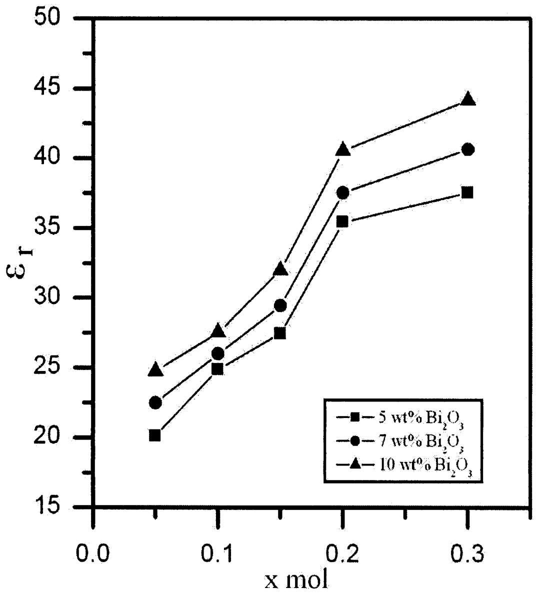

Fig. 4. Dielectric constant of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900 °C for 3 h as a function TiO_2 content and Bi_2O_3 content of starting mixture.

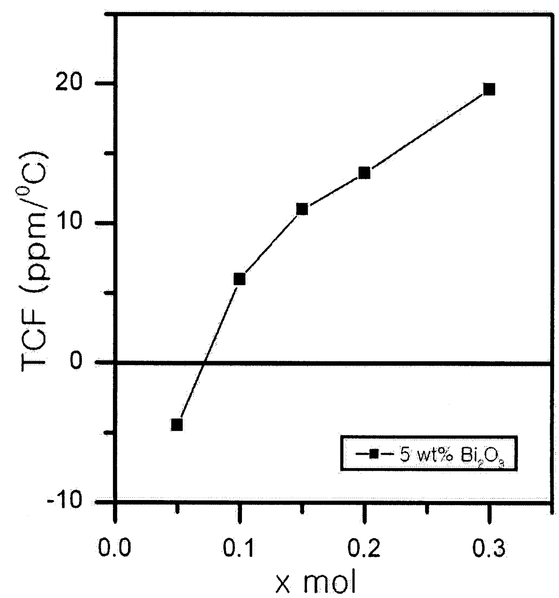

Fig. 6. τ_f of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900 °C for 3 h with 5 wt.% Bi_2O_3 as a function y TiO_2 content.

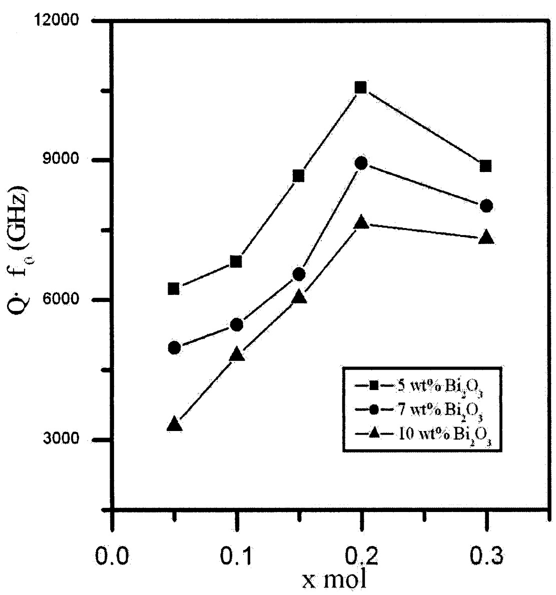

Fig. 5. $Q{\cdot}f_0$ of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ specimens sintered at 900 °C for 3 h as a function y TiO_2 content and Bi_2O_3 content of starting mixture.

does not occur because the limited liquid phase in grain boundary inhibited grain growth. So the grains are very small (average grain size 0.5 μm) and homogeneous with few pores.

Fig. 4 shows the dielectric constant (ε_r) of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics prepared with different amounts of Bi_2O_3 and sintered at 900 °C for 3 h. The relationship between ε_r value and the amounts of Bi_2O_3 exhibits the same trend as that between the bulk densities and Bi_2O_3 content. The reason for the increased dielectric constant as the Bi_2O_3 content increased is the reduction of porosity.[6] However, the dielectric constant of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ prepared with constant amount of Bi_2O_3 increased with increasing Ti concentration from 0.05 to 0.3 mol because the small Ti^{4+} ion (0.605 Å) is incorporated into the B-site $[Li_{1/3}Nb_{2/3}]^{3.67+}$ having larger ionic radius (0.66 Å); hence there is an increase in the rattling effect from the substitution of the smaller Ti^{4+} into the larger $[Li_{1/3}Nb_{2/3}]^{3.67+}$ site.[3,7]

Fig. 5 shows the $Q{\cdot}f_0$ values of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics prepared with Bi_2O_3 contents from 5 to 10 wt.% sintered at 900 °C for 3 h. The $Q{\cdot}f_0$ values decreased with increasing Bi_2O_3 content. The reason for the decrease in $Q{\cdot}f_0$ values is the increased the second phase in the specimen as mentioned earlier. It was reported by Iddles et al.[8] that a second phase was a more important factor than porosity to reduce the $Q{\cdot}f_0$ values of microwave dielectric ceramics having over 90% of relative density. The maximum $Q{\cdot}f_0$ values occur for Ti concentration of 0.2 mol irrespective of Bi_2O_3 content.

Fig. 6 shows temperature coefficient of resonant frequency (τ_f) of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ prepared with 5 wt.% Bi_2O_3. The τ_f value became more positive from −4.5 to 19.6 ppm/°C with an increase of Ti concentration. As Bi_2O_3 content is increased, the τ_f value shifts negative abruptly from −4 to −34 ppm/°C for $Ca[(Li_{1/3}Nb_{2/3})_{0.95}Ti_{0.05}]O_{3-\delta}$ with 5 to 10 wt.% Bi_2O_3. The τ_f value should be controlled between −10 and 10 ppm/°C for applications in band pass filters (BPF) and antenna etc. The optimized microwave properties for multi-chip antenna, are, $\varepsilon_r = 20$, $Q{\cdot}f_0 = 6500$ GHz, and $\tau_f = -4$ ppm/°C for $Ca[(Li_{1/3}Nb_{2/3})_{0.95}Ti_{0.05}]O_{3-\delta}$ with 5 wt.%

Bi_2O_3, and $\varepsilon_r = 35$, $Q{\cdot}f_0 = 11{,}000$ GHz, and $\tau_f = 13$ ppm/°C, and for multi-chip filters based on $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with 5 wt.% Bi_2O_3.

4. Conclusions

The microwave dielectric properties of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ doped with Bi_2O_3 additive was investigated. Bi_2O_3 additions improved the densification and reduced the sintering temperature from 1150 to 900 °C. With increasing Bi_2O_3 content, the dielectric constant and bulk density increased. The quality factor, however, decreased slightly. The temperature coefficients of the resonant frequency shifted slightly positive with increasing Bi_2O_3 content and increased from −4.5 to 19.6 ppm/°C with an increase of Ti concentration. The dielectric properties (ε_r, Qf_0, τ_f) of $Ca[(Li_{1/3}Nb_{2/3})_{0.95}Ti_{0.05}]O_{3-\delta}$ and $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with 5 wt.% Bi_2O_3 sintered at 900 °C for 3 h were 20, 6500 GHz, −4 ppm/°C, and 35, 11,000 GHz, 13 ppm/°C, respectively.

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