Int. J. Appl. Ceram. Technol., 5 [4] 341–346 (2008)
DOI:10.1111/j.1744-7402.2008.02219.x

International Journal of Applied Ceramic Technology
Ceramic Product Development and Commercialization

Low-Temperature Firing and Microwave Dielectric Properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ Ceramics with ZnB_2O_4 Glass Addition

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Low-temperature sintered $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ microwave dielectric ceramics with ZnB_2O_4 glass (ZBG) addition were prepared by the conventional solid state reaction method. The sintering behavior, microstructure, and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with ZBG addition were investigated. The ZBG addition lowered the densified temperature of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics from 1150°C to 940°C. The dielectric constants of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics decreased from 40 to 34 and the temperature coefficient of resonant frequency (τ_f) changed gradually from +12.7 to −25.7 ppm/°C as ZBG addition increased from 0 to 8 wt%. The Q_f values increased greatly from 20,500 GHz of pure $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ to 26,900 GHz when 5 wt% ZBG was added. $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 8 wt% ZBG addition sintered at 940°C show good microwave dielectric properties with $\varepsilon_r \sim 32.5$, $Q_f \sim 20{,}600$ GHz, and $\tau_f \sim -25.7$ ppm/°C. The relationship between dielectric properties and microstructure was also discussed.

Introduction

Recently, with the development of advanced communication systems, including mobile communications and satellite communications, multilayer microwave devices have been widely used in microwave circuits to miniaturize related components.[1] As an efficient method to fabricate multilayer microwave devices, low-temperature co-fired ceramics technology (LTCC) has received much attention as dielectric materials of potential capability for co-firing with low-loss conductors such as Ag and Cu.[2,3] Low-firing microwave dielectric materials also need to possess high dielectric constant values (ε_r), high quality factor values (Q_f), and near zero temperature coefficients of resonant frequency (τ_f).[2]

The commercial microwave dielectric ceramics available are divided into three groups: (i) ceramics with low dielectric constant ($\varepsilon_r < 20$); (ii) ceramics with middle dielectric constant (20–40), which are mainly used for dielectric resonators (DRs); and (iii) ceramics with high dielectric constant (60–80), which are mainly

This work was supported by National 973-project of China (2002CB613302), National 863-project of China (2006AA03Z0429), NSFC project of China (50572085), and NCET-05-0840.

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used for dielectric filters. Several microwave dielectric ceramic systems with middle dielectric constants, such as $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$, $ZnO–Nb_2O_5–TiO_2$, $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$, and $BiNbO_4$ sintered at low sintering temperature, have been developed over the years.[4–7] 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] However, during the synthesis of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics, volatilization of lithium occurs producing secondary phases and deteriorating dielectric properties. With the substitution of the smaller Ti^{4+} (0.605 Å) into the larger $[Li_{1/3}Nb_{2/3}]^{3.67+}$ (0.660 Å) site, volatilization of lithium was restrained and a single $CaTiO_3$-type orthorhombic perovskite phase was obtained when the substitution content of Ti^{4+} was 20%.[4] However, the sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ is still too high to use Ag or Cu as an internal electrode in multilayer devices. Several low-melting-point sintering aids and their composites, such as B_2O_3, Bi_2O_3, $B_2O_3–Bi_2O_3$, $B_2O_3–ZnO–SiO_2–PbO$ glass, LiF, and xLiF+yZnO–$B_2O_3–SiO_2$ glass,[8–13] have been introduced to lower the sintering temperature of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ system. ZnB_2O_4 glass (ZBG) has a low softening temperature (T_s) = 587°C and begins to melt above T_s.[14] It showed microwave dielectric properties with $\varepsilon_r \sim 6.88$, $Q_f \sim 1733$ GHz, and $\tau_f \sim -10$ ppm/°C.[15] ZBG has successfully lowered the sintering temperature of $Ba_5Nb_4O_{15}$ ceramics from 1400°C to 900°C.[14]

In the present work, $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics was synthesized using traditional solid state reaction method, and the influence of the addition of ZBG on sintering behavior, microstructure, and microwave dielectric properties was investigated.

Experimental Procedure

High-purity oxide (>99%) powders of $CaCO_3$, Li_2CO_3, Nb_2O_5, and TiO_2 (anatase phase) were used as the starting powders. The powders were weighed according to the composition of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ and then milled with ZrO_2 balls (2 mm in diameter) for 4 h in ethanol. Mixtures were dried and calcined at 1000°C for 2 h. The calcined powders with $x$wt% (x = 0, 1, 3, 5, 8) self-made ZBG addition were then milled again for 5 h with ZrO_2 balls in ethanol. After drying, the powder was uniaxially pressed into disks of 8 mm diameter and 4 mm thickness. The disks were sintered in air at 920–1180°C for 3 h. The crystal structures of the samples were investigated using X-ray diffractometry with Cu$K\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The microstructure was studied using scanning electron microscopy (SEM) (JEOL JSM-6460, Tokyo, Japan). Densities of the sintered specimens, as a function of sintering temperature, were measured by the Archimedes method. The volatilization of Li^+ during the sintering process was investigated on the calcined ceramic powder in air by thermogravimetry (TG) analysis using a thermoanalyzer system (STA-449C, Netzsch, Selb, Germany). Dielectric behaviors at microwave frequency were measured at a frequency of 6–9 GHz by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a DELTA 9023 temperature chamber (Delta Design, Poway, CA). The temperature coefficient of resonant frequency τ_f was calculated from the following equation:

$$\tau_f = \frac{f_T - f_{T_0}}{f_{T_0}(T - T_0)} = \frac{f_{85°C} - f_{25°C}}{f_{25°C} \times 60} \quad (1)$$

where f_T is the resonant frequency of the dielectric resonator at temperature T (°C) and T_0 is room temperature (25°C).

Results and Discussion

Densification Behaviors

Figure 1 shows the bulk density of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 0–8 wt% ZBG addition as a function of sintering temperature. The bulk density of pure $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics increased as sintering temperature increased and reached a maximum value at 1150°C, and then decreased slightly as sintering temperature increased further. Similarly, the bulk density of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 1–5 wt% ZBG addition firstly increased sharply with sintering temperature increasing and reached maximum values at 1000°C, and then decreased slightly, as shown in Fig. 1. This result was consistent with that reported by Liu *et al.*[10] The bulk densities of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 3–5 wt% ZBG addition sintered at 970–1060°C were in the range of 4.03–4.10 g/cm^3 and those of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 8 wt% ZBG addition sintered at 940–970°C were in the range of 4.03–4.05 g/cm^3. It

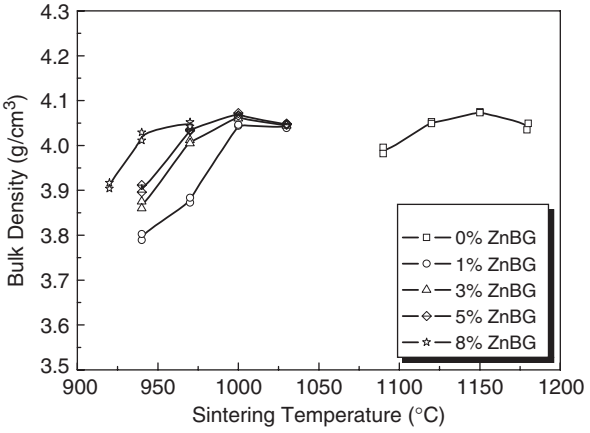

Fig. 1. Bulk densities of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 0–8 wt% ZBG addition as a function of sintering temperature.

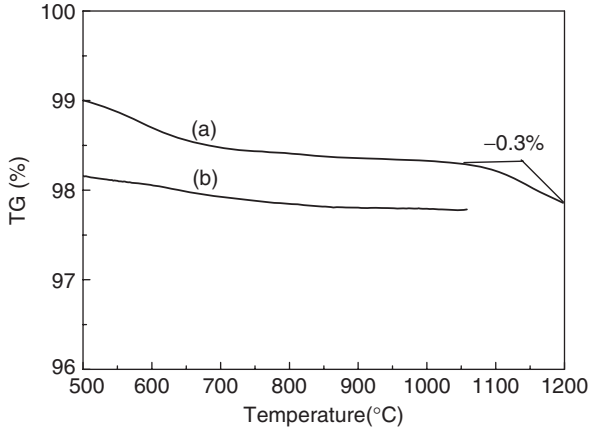

Fig. 2. Thermogravimetry (TG) curves of calcined $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramic powder with (a) 0 wt% and (b) 8 wt% ZnB_2O_4 glass addition.

was considered that $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 3–5 wt% and 8 wt% ZBG addition have been well densified at 970–1060°C and 940–970°C, respectively. Thus, the sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with ZBG addition had been lowered from 1150°C to 940°C.

Lithium is very volatile. Previous work considers that the volatilization of lithium was restrained in $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics because of the substitution of the smaller Ti^{4+} (0.605 Å) into the larger $[Li_{1/3}Nb_{2/3}]^{3.67+}$ (0.660 Å) site.[4] But a thermal analysis on $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ has not been carried out. In the present work, the volatilization of lithium during the sintering process was investigated by TG analysis. As shown in Fig. 2, there was only 0.3 wt% mass loss detected in pure $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ during the sintering process (from 1100°C to 1200°C), whereas there was little mass loss in $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with 8 wt% ZBG addition. The reason was that the volatilization of lithium in the $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ system occurred at temperatures above 1100°C, and the sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ with 8 wt% ZBG addition was lower than 1100°C.

Microstructures

There are two kinds of B-site order in the CaO–Li_2O–Nb_2O_5–TiO_2 system, 1:2 order and 1:3 order ($Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ and $Ca[(Li_{1/4}Nb_{3/4})_{1-x}Ti_x]O_3$). The lattice volume of stoichiometric $Ca[(Li_{1/4}Nb_{3/4})_{1-x}Ti_x]O_3$ is smaller than that of nonstoichiometric $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ because the radius of Nb^{5+} (0.64 Å, coordination number(CN) = 6) is smaller than that of Li^+ (0.76 Å, CN = 6).[13] When $xLiF+yZnO–B_2O_3–SiO_2$ glass[13] or B_2O_3[16] was added to $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$, a phase transformation from nonstoichiometric $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ to stoichiometric $Ca[(Li_{1/4}Nb_{3/4})_{1-x}Ti_x]O_3$ occurred, and the main diffraction peaks split in XRD patterns due to the coexistence of two $CaTiO_3$-type perovskite phases. Figure 3 illustrates the XRD patterns of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 0–8 wt% ZBG addition. All the XRD patterns can be identified as a $CaTiO_3$-type orthorhombic structure and no secondary phase is observed. There were no main diffraction peaks splitting in all the XRD patterns. This means that there was no phase transformation from nonstoichiometric $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ to stoichiometric $Ca[(Li_{1/4}Nb_{3/4})_{1-x}Ti_x]O_3$ in the $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 0–8 wt% ZBG addition.

The SEM micrographs of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with ZBG addition are shown in Fig. 4. Well-packed uniformly distributed grains were observed. The average grain size of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 3 wt% ZBG addition sintered at 970°C and that of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 8 wt% ZBG addition sintered at 940°C were 1.5 and 1 μm (Fig. 4b and c), smaller than that of pure $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$

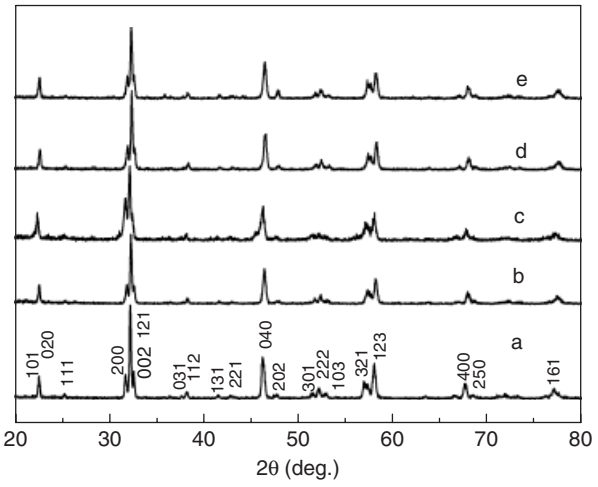

Fig. 3. XRD patterns of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics: (a) sintered at 1180°C for 3 h with no ZnB_2O_4 glass (ZBG) addition; sintered at 1030°C for 3 h (b) with 1 wt% ZBG addition; (c) with 3 wt% ZBG addition; (d) with 5 wt% ZBG addition; and (e) sintered at 970°C for 3 h with 8 wt% ZBG addition.

ceramics sintered at 1150°C (about 2.5 μm, as shown in Fig. 4a). This may be due to the much lower sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with ZBG addition. Besides, uniform microstructures with grains densely connected were found in Fig. 4d–f, which it indicates that all the specimens have been densified well at the sintering temperatures. The results were consistent with that from the bulk densities of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics.

Microwave Dielectric Properties

Figure 5 presents the microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 0–8 wt% ZBG addition as a function of sintering temperature. In the present work, $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics without ZBG addition sintered at 1150°C showed microwave dielectric properties with $\varepsilon_r \sim 40$, $Q_f \sim 20{,}500$ GHz, and $\tau_f \sim 12.7$ ppm/°C. As shown in Fig. 5, the dielectric constant of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 1–3 wt% ZBG addition increased linearly with increase in sintering temperature, although the bulk density decreased slightly when sintering temperature was higher than 1000°C, as shown in Fig. 1. This means that the decrease of bulk density caused by elevated sintering temperature had no adverse effect on the dielectric constant. The dielectric constant of well-densified $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics decreased as the amount of ZBG added increased, because the dielectric constant of ZBG is much

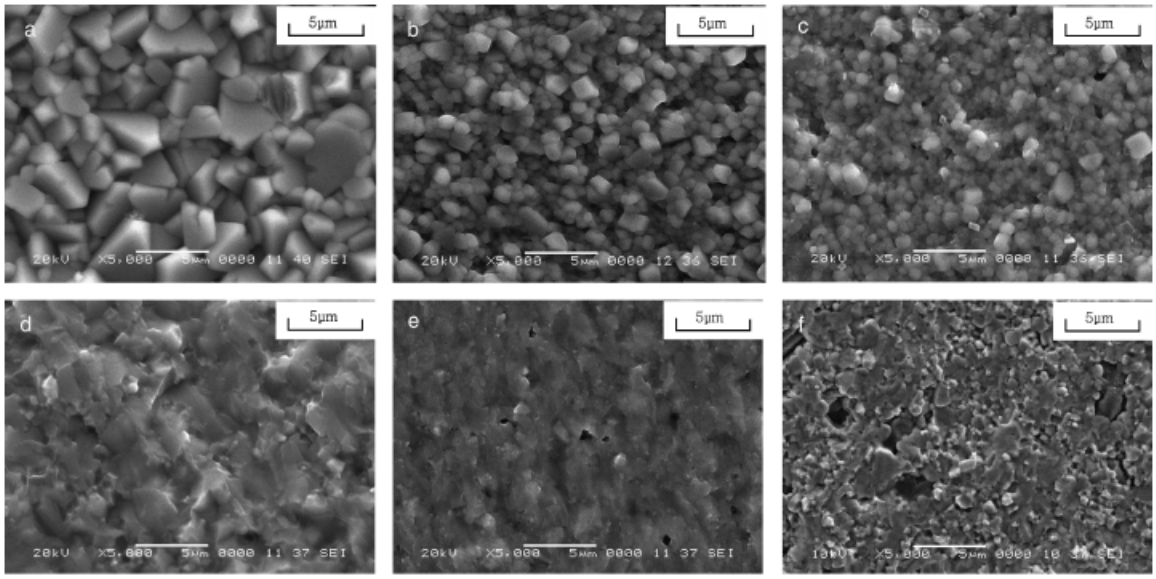

Fig. 4. SEM micrographs of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with x wt% ZnB_2O_4 glass addition: surface of (a) x = 0 sintered at 1150°C; (b) x = 3 sintered at 970°C; (c) x = 8 sintered at 940°C; and fractured section of (d) x = 0 sintered at 1150°C; (e) x = 3 sintered at 970°C; and (f) x = 8 sintered at 940°C.

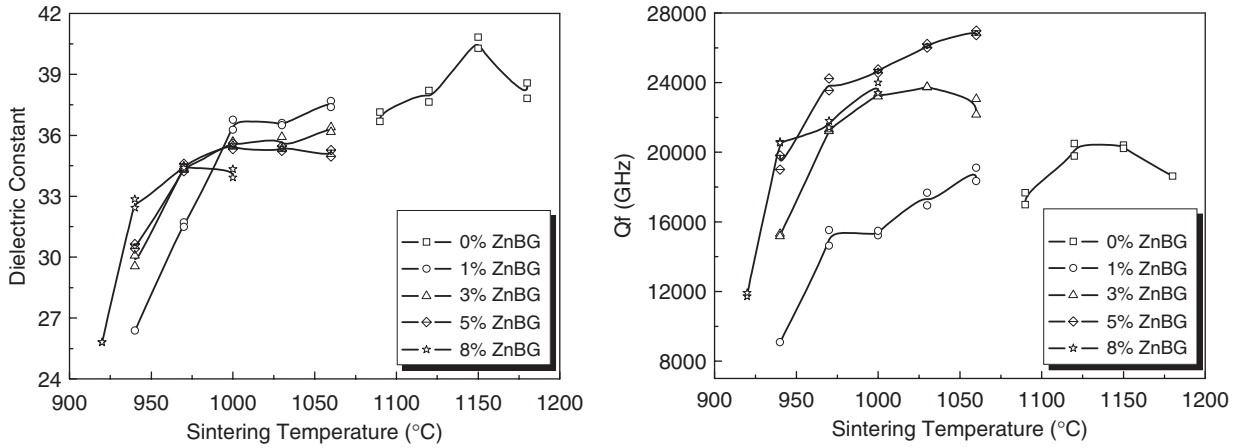

Fig. 5. Microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 0–8 wt% ZnB_2O_4 glass addition as a function of sintering temperature.

smaller (about 6.88).[15] It was interesting that the Q_f values of well-densified $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics increased greatly from 20,500 to 26,900 GHz as ZBG addition increased from 0 to 5 wt%, as shown in Fig. 5. The grain of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with ZBG addition was uniform and much smaller than that of pure $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics, as shown in Fig. 4. This may be partially responsible for the increase of Q_f value.

The temperature coefficient of resonant frequency τ_f value of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics as a function of content of ZBG addition is shown in Fig. 6. The τ_f value of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics changed gradually from +12.7 to −25.7 ppm/°C as the content of ZBG addition increased from 0 to 8 wt%. ZBG has a negative τ_f,[15] and this may be the reason for lowering the τ_f value of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics. The $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 3 wt% ZBG addition possessed a near-zero τ_f value (−3.9 ppm/°C).

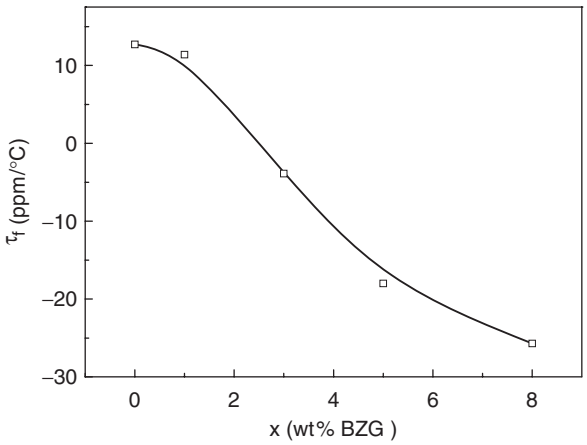

Fig. 6. τ_f values of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics as a function of content of ZnB_2O_4 glass addition.

Conclusions

It was found that ZBG addition lowered the sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics from 1150°C to 940°C. The crystalline phase of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics was the orthorhombic perovskite structure with 1:2 ordering of Li^+ and Nb^{5+} on B-site and no second phase was detected. The dielectric constant of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics decreased from 40 to 34 and the τ_f value changed gradually from +12.7 to −25.7 ppm/°C as ZBG addition increased from 0 to 8 wt%. The Q_f value of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics increased greatly from 20,500 to 26,900 GHz as ZBG addition increased from 0 to 5 wt%. The microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$ ceramics with 8 wt% ZBG addition sintered at 940°C were $\varepsilon_r \sim 32.5$, $Q_f \sim 20{,}600$ GHz, and $\tau_f \sim -25.7$ ppm/°C. It could be a good candidate for LTCC application.

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