Crystal structure and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}-xTiO_2$ ceramics

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Abstract. The effects of B_2O_3 on the sinterability and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ ceramics were investigated. B_2O_3 doping can effectively reduce sintering temperatue by 150~200ºC. The temperature coefficient of resonator frequency τf increased with an increase of B_2O_3 content and sintering temperatue. When B_2O_3 of 2wt% were added, the optimum microwave dielectric properties: ε_r =28.5,Qf =13560GHz and τ_f = − 7.6×10−6/ºC were obtained at the sintering temperatue of 950ºC.

1 Introduction

Recently multiplayer microwave filters were widely focused and developed in microwave circuits to meet the rapid development of advanced telecommunication. Microwave dielectric ceramics to be employed in multiplayer devices require low sintering temperature to cofired with the inner low less conductors and low melting point electrode such as Cu and Ag. Among those low-temperature-cofired ceramics(LTCC) $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics have been newly developed and widely investigated because of its excellent microwave dielectric properties and low sintering temperature of about 1150 ºC [1,2]. For the applications of LTCC, the complex perovskite should be further adjust to lower its sintering temperature. In our preliminary work, we found the $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ceramics having the superior dielectric properties: ε_r =28.6,Qf =23880GHz and τ_f = − 14.9×10^{-6}/ºC after sintering at 1170 ºC for 4h. P.Liu et al. [3,4] have reported the addition of B_2O_3 were effectively in reducing the firing temperature of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$-based ceramics. So in this paper we employed B_2O_3 additive as a sintering flux to decrease the sintering temperature of the ceramics. The microwave dielectric properties was also investigated with the discussion of its relationships with the phase formation in the present system.her.

2 Experimental

The $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ powder compositions were synthesized by the conventional solid-state reaction method. High purity (≥99.9%) oxide powders of $CaCO_3$, Li_2CO_3, Zr O_2, Nb_2O_5, TiO_2, were weighed according to the desired stoichiometry, and ground in an agate pot with distilled water for 4h in a planetary mill. The prepared powders calcined at 900ºC for 2h in a closed Al_2O_3 crucible. The calcined powders were milled for 3h again with addition of B_2O_3, and then pressed into disks under a pressure of 150Mpa. The disks were palced in a closed Al_2O_3 crucible to prevent the volatility of Li and sintered from 930ºC to 1100ºC for 4h in air. The bulk densities of sintered specimens were measured by Archimedes method. Phase formation and microstructure were examined by X-ray diffractometer (X'Pert PRO) using CuKα radiaiton. The measurement of microwave dielectric properties were performed on TE_{011} mode at the resonant frequency from 4 to 7GHz by the Hakki-Coleman's dielectric resonator method using a network analyer (ADVANTEST R3767C). The temperature coefficient of resonator frequency (τ_f) was calculated at the range between 20ºC and 80ºC

3 Results and Discussion

Fig. 1 show X-ray diffraction patterns of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ with B_2O_3 specimens sintered at 950ºC for 4h.The diffraction peaks can be indexed according to the $CaTiO_3$ -type orthorhombic perovskite structure. Pure $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens sintered at 1170ºC for 4h was single phase. With B_2O_3 content increases, the peaks of superlattice diffractions of specimen 1:2 decreases until disappear, the degree of B-site 1:2 ordering will decrease, second phase appearence.**Figure 1.** Caption of the Figure 1. Below the figure.

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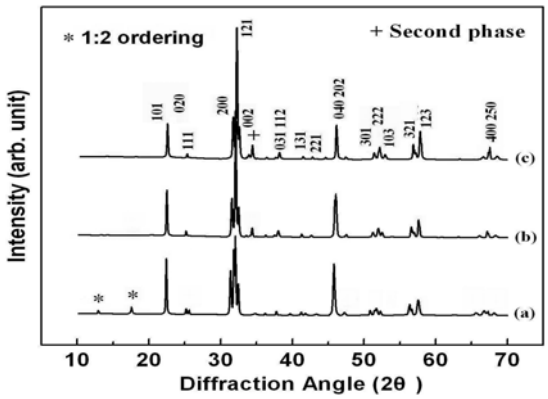

Figure 1. XRD spectra of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens sintered at 950ºC for 4h with content of B_2O_3.

Fig. 2 shows the relationship between the dielectric constant and the B_2O_3 content in $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ sintered at 950ºC for 4h. The ε_r value increased with increasing B_2O_3 content from 0.5 to 1.5wt%, which could be contributed to the increased apparent density. However, as B_2O_3 content became greater than 1.5wt%, ε_r began to decrease because of the increasing of the secondary phase as confirmed in Fig. 1..

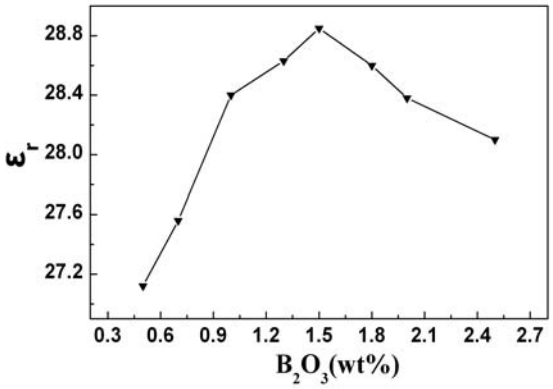

Figure 2. ε_r values of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens sintered at 950ºC for 4h with content of B_2O_3.

Fig. 3 shows the Qf value of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens with B_2O_3 sintered at 950ºC for 4h. The addition of B_2O_3 greatly reduced the Qf value of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens. This is expected since B_2O_3 addition inhibited the degree of 1:2 ordering in $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ ceramics and thus cause the decreases of the quality factor[5,6].As increasing B_2O_3 content, the $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens were dense graducally, and the Qf values of specimens firstly increased and then decreased. The reason for this is the appearance of the second phase in the specimen as mentioned above. It was reported that the Qf value relates to relative density and second phase[7].

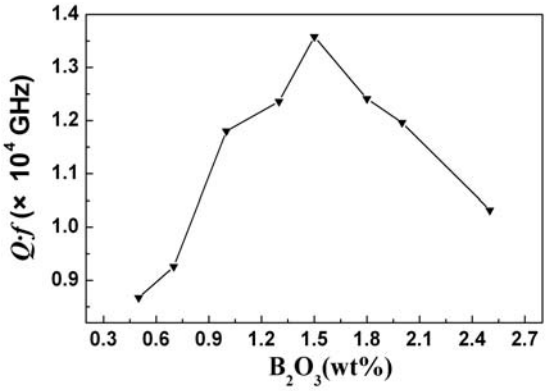

Figure 3. Qf values of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens sintered at 950ºC for 4h with content of B_2O_3.

Fig. 4 shows temperature coefficient of resonant frequency of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ with B_2O_3 specimens sintered at 950ºC temperatures.The τ_f value ranged from negative value of –13.8ppm/ºC to negative value of –7.8ppm/ºC when B_2O_3 content increased from 0.5 to 1.5 wt%,and then decreased. By doping 1.5wt% B_2O_3, the $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ ceramics show the optimized microwave dielectric properties: ε_r =28.4,Qf =13560GHz and $\tau_f = -7.8\times10^{-6}$/ºC after sintering at 950ºC, indicating that the sintering temperatue of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ could be reduced to 950ºC without degraduation of dielectric properties.

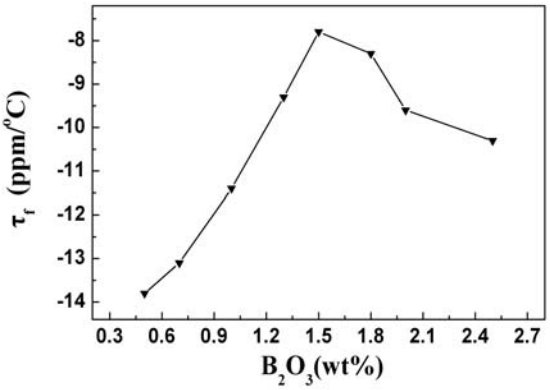

Figure 4. τ_f values of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ specimens sintered at 950ºC for 4h with content of B_2O_3.

4 Summary

Doping of B_2O_3 improves the microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.92}Zr_{0.08}]O_{3-\delta}$ ceramics sintered at 950 ºC.As increasing B_2O_3 additive content, the ε_r and the Qf value firstly increased then decreased from 28.6.8 and 12410GHz to 2.5 and 10320 GHz , respectively with further doping content of B_2O_3 from 1.8wt% to 2.5wt%.The τ_f value gradually moved to a positive direction with the increase of B_2O_3 content. When B_2O_3 of 1.5wt% were added, the optimum microwave dielectric properties: ε_r = 28.5,Qf =13560GHz and $\tau_f = -7.6\times10^{-6}$/ºC were obtained at the sintering temperature of 950ºC.

Acknowledgements

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