Crystal structure and microwave dielectric properties of Ca[(Li\(_{1/3}\)Nb\(_{2/3}\))\(_{0.92}\)Zr\(_{0.08}\)]O\(_{3-δ}\)−xTiO\(_2\) ceramics

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Abstract. The effects of B\(_2\)O\(_3\) on the sinterability and microwave dielectric properties of Ca[(Li\(_{1/3}\)Nb\(_{2/3}\))\(_{0.92}\)Zr\(_{0.08}\)]O\(_{3-δ}\) ceramics were investigated. B\(_2\)O\(_3\) doping can effectively reduce sintering temperature by 150~200ºC. The temperature coefficient of resonator frequency \(τ_f\) increased with an increase of B\(_2\)O\(_3\) content and sintering temperature. When B\(_2\)O\(_3\) of 2wt% were added, the optimum microwave dielectric properties: \(ε_r = 28.5, Q_f = 13560\)GHz and \(τ_f = -7.6\times10^{-6}/ºC\) were obtained at the sintering temperature 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 cofire 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\(_{3-δ}\) 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\(_{3-δ}\) having the superior dielectric properties: \(ε_r = 28.5, Q_f = 23880\)GHz and \(τ_f = -14.9\times10^{-6}/ºC\) after sintering at 1170 ºC for 4h. P.Liu et al. [3,4] have reported the addition of B\(_2\)O\(_3\) were effectively in reducing the firing temperature of Ca(Li\(_{1/3}\)Nb\(_{2/3}\))O\(_{3-δ}\)-based ceramics. So in this paper we employed B\(_2\)O\(_3\) 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.

2 Experimental

The Ca[(Li\(_{1/3}\)Nb\(_{2/3}\))\(_{0.92}\)Zr\(_{0.08}\)]O\(_{3-δ}\) powder compositions were synthesized by the conventional solid-state reaction method. High purity (≥99.9%) oxide powders of CaCO\(_3\), Li\(_2\)CO\(_3\), ZrO\(_2\), 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\(_2\)O\(_3\) crucible. The calcined powders were milled for 3h again with addition of B\(_2\)O\(_3\), and then pressed into disks under a pressure of 150Mpa. The disks were sintered at 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 CuK\(_α\) radiation. 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 analyser (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\(_{3-δ}\) with B\(_2\)O\(_3\) 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\(_{3-δ}\) specimens sintered at 1170ºC for 4h was single phase. With B\(_2\)O\(_3\) 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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Fig. 1. XRD spectra of Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ specimens sintered at 950°C for 4h with content of B2O3.

Fig. 2 shows the relationship between the dielectric constant and B2O3 content in Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ sintered at 950°C for 4h. The εr value increased with increasing B2O3 content from 0.5 to 1.5wt%, which could be contributed to the increased apparent density. However, as B2O3 content became greater than 1.5wt%, εr began to decrease because of the increasing of the secondary phase as confirmed in Fig. 1.

Fig. 3 shows the Qf value of Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ specimens sintered at 950°C. The addition of B2O3 greatly reduced the Qf value of Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ ceramics. This is expected since B2O3 addition inhibited the degree of 1:2 ordering in Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ ceramics and thus cause the decreases of the quality factor[5,6]. As increasing B2O3 content, the Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ specimens were dense gradually, 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].

Fig. 4 shows the temperature coefficient of resonant frequency of Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ with B2O3 specimens sintered at 950°C temperatures. The τf value ranged from negative value of –13.8ppm/°C to negative value of –7.8ppm/°C when B2O3 content increased from 0.5 to 1.5 wt%, and then decreased. By doping 1.5wt% B2O3, the Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ ceramics show the optimized microwave dielectric properties: εr = 28.4, Qf = 13560GHz and τf = – 7.6×10^{-6}/°C after sintering at 950°C, indicating that the sintering temperature of Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ could be reduced to 950°C without degradation of dielectric properties.

4 Summary

Doping of B2O3 improves the microwave dielectric properties of Ca[(Li1/3Nb2/3)0.92Zr0.08]O3−δ ceramics sintered at 950°C. As increasing B2O3 additive content, the εr 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 B2O3 from 1.8wt% to 2.5wt%. The τf value gradually moved to a positive direction with the increase of B2O3 content. When B2O3 of 1.5wt% were added, the optimum microwave dielectric properties: εr = 28.5, Qf = 13560GHz and τf = – 7.6×10^{-6}/°C were obtained at the sintering temperature of 950°C.
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References