Low-Temperature Sintering and Microwave Dielectric Properties of Li$_2$O-3ZnO-5TiO$_2$ Ceramics Doped with B$_2$O$_3$

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Abstract

Phase composition, crystal structure as well as microwave dielectric properties of Li$_2$O-3ZnO-5TiO$_2$ ceramics (LZT135, for short) with the addition of B$_2$O$_3$ and TiO$_2$ were investigated. X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS) results revealed that the samples with added B$_2$O$_3$ and sintered at 900 °C had formed solid solutions with a similar crystal structure to Zn$_2$Ti$_3$O$_8$. When 0.25 wt% B$_2$O$_3$ was added, LZT135 ceramics could be densified at about 900 °C, while the negative $\tau_f$ value of about -31.5 ppm/K restricted its applications. TiO$_2$ was added for further adjustment of the $\tau_f$ value of LZT135 ceramics. Finally, with the addition of 0.25 wt% B$_2$O$_3$ and 9 wt% TiO$_2$, near zero $\tau_f$ values of about -0.5 ppm/K can be achieved for LZT135 ceramics, and at the same time, high Qf values of about 48 300 GHz are attractive for low-temperature co-firing ceramics technology.

Keywords: Microwave dielectric properties, LTCC, Li$_2$O-3ZnO-5TiO$_2$

I. Introduction

Low-temperature co-fired ceramic (LTCC, for short) technologies are widely used in RF wireless communication, electronic packaging, automotive electronics, radar, and space navigation, etc. Since silver is usually used as the inner circuit patterns electrode for LTCC technologies, the sintering temperatures of these ceramics need to be lower than the melting point of silver, ordinarily 900 °C or even lower. Lots of ceramic materials with low sintering temperature have been developed to meet the demands of LTCC technologies. Zn-containing compounds and Li-containing compounds, such as Li$_2$O-Nb$_2$O$_5$-TiO$_2$, Zn$_2$SiO$_4$, and ZnNb$_2$O$_6$, have attracted much attention especially owing to their relatively low sintering temperatures, as well as low dielectric loss at microwave frequency.

Compared with other LTCC materials, Li$_2$ATi$_3$O$_8$ (A=Mg, Zn) ceramics with a sintering temperature of about 1 075 °C and a high Qf value of 72 000 GHz, as reported by S. George and M.T. Sebastian in 2010, are very attractive for LTCC applications. Another system, ZnLi$_2$Ti$_4$O$_7$ (Li$_2$O-ZnO-TiO$_2$) ceramic with a higher Qf value of 106 700 GHz was reported by Zhou, however, its sintering temperature of 1 075 °C and large negative $\tau_f$ value of -48 ppm/K are still not suitable for most LTCC applications. A solid solution of Li$_2$O-3ZnO-5TiO$_2$ (LZT135, for short) was reported in 2018. Doping with V$_2$O$_5$ reduced the sintering temperature of LZT135 to near 900 °C, combined doping with TiO$_2$ corrected the negative $\tau_f$ value to near zero, however, the toxicity of V$_2$O$_5$ still hampered application. B$_2$O$_3$ is usually used as the sintering aid because of its low melting point of about 450 °C, so B$_2$O$_3$ replaces V$_2$O$_5$ in this research for lower the sintering temperatures of the promising LZT135 ceramics system.

II. Experimental Procedure

Li$_2$O-3ZnO-5TiO$_2$ ceramics were synthesized with the conventional solid-state reaction method. Li$_2$CO$_3$, TiO$_2$, ZnO, and B$_2$O$_3$ powder (reagent grade, over 99 wt%) were mixed and milled using deionized water and zirconia balls as milling media. After drying, the mixtures were calcined at 900 °C for 3 h. Different amounts of B$_2$O$_3$ and TiO$_2$ were then added and the mixture was remilled and dried. The resulting powder was pressed into disks under a pressure of 100 MPa with a size of 14 mm in diameter and 6 – 8 mm in thickness. Finally, samples were sintered at 875 – 925 °C for 3 h in an air atmosphere.

The bulk density of the sintered samples was measured with the Archimedes’ method. The microstructure of the specimens was examined by means of X-ray diffraction (XRD, model Shimadzu XRD-7000) and a scanning electron microscope (SEM, model JEOL JSM-64). Element composition analysis was performed using an energy-dispersive spectrometer (EDS, model Oxford X-max N50). The microwave dielectric properties were measured with Hakki and Coleman’s method. The $\tau_f$ value was also measured with the same method in the temperature range of 25 - 75 °C.
III. Results and Discussion

Fig. 1 shows the XRD patterns of sintered LZT135 ceramics doped with different amounts of B$_2$O$_3$, all the samples were sintered at 900 °C. XRD results showed that the sintered LZT135 ceramics formed a cubic structure similar to Zn$_2$Ti$_3$O$_8$ (JCPDS087 – 1781) with lattice parameters of $a = 8.382$ Å, $V = 588.9$ Å$^3$. The 2θ positions of all of the peaks closely match the $(1-x)Li_2Zn_3Ti_4O_{12-x}TiO_2$ (where $0.25\leq x\leq0.4$) ceramics phase previously reported by Liu 19. Therefore, the B$_2$O$_3$ doping does not strongly influence the phase composition of LZT135.

![Image](42x437 to 282x629)

**Fig. 1:** XRD patterns of the sintered LZT135 ceramics doped with different amounts of B$_2$O$_3$ and sintered at 900 °C, where (a) 0 wt%, (b) 0.25 wt%, (c) 0.5 wt%, (d) 0.75 wt% and (e) 1 wt%.

Fig. 2 shows the bulk densities of LZT135 ceramics sintered at different temperatures and different B$_2$O$_3$ doping levels. It is clear that B$_2$O$_3$ increases the density of LZT135 ceramics in the temperature range of 875 – 925 °C. This can be explained by the low melting point of B$_2$O$_3$ at 450 °C, which forms liquid phases that can enhance the grain rearrangement and densification of LZT135 ceramics. LZT135 ceramic reaches a density of 4.07 g/cm$^3$ with 0.25 wt% B$_2$O$_3$ addition and after sintering at 900 °C. Doping beyond these levels did not improve densification.

![Image](42x437 to 282x629)

**Fig. 2:** Densities of LZT135 ceramics as a function of the B$_2$O$_3$ addition content and sintering temperatures.

The SEM micrographs in Fig. 3 show sintered LZT135 with different levels of B$_2$O$_3$ doping. When B$_2$O$_3$ was added, LZT135 exhibited two types of grains: bigger grains of about 40 μm (marked A), and smaller grains about 1 μm (marked B). EDS results, in Fig. 4, showed that these two types of grains mainly contained Zn, Ti, and O elements, with nearly the same atomic ratio of Zn : Ti = 3 : 5. According to the XRD analysis results and EDS analysis, with the addition of B$_2$O$_3$ and sintering at about 900 °C, LZT135 ceramics can form solid solutions.

The microwave dielectric properties of B$_2$O$_3$-doped LZT135 are shown in Fig. 5. For samples doped with 0.25 wt% B$_2$O$_3$ and sintered at 900 °C, the $e_r$ of LZT135 reaches a relatively high value of 20.5, while again further additions of B$_2$O$_3$ have almost no influence on $e_r$ values as found earlier for density values. With increasing amounts of B$_2$O$_3$, the Qf values of LZT135 decreased markedly regardless of sintering temperatures, which could be explained by high dielectric losses coming from the liquid phase. Doping with B$_2$O$_3$ does not impact the $\tau_f$ values of LZT135 with 0.25 wt% B$_2$O$_3$ exhibiting ~30 ppm/K, which is unacceptable in application. TiO$_2$ has an unusually high positive $\tau_f$ value of +465 ppm/K, and therefore, TiO$_2$ doping was used to significantly reduce the negative $\tau_f$ values of some ceramics 20–22.

The XRD patterns for different TiO$_2$ levels are shown in Fig. 6. The major crystal phase of all the samples is LZT135 solid solution as mentioned above, however, a secondary phase, rutile TiO$_2$, was detected. Fig. 7 illustrates the microstructure of the as-sintered surface of LZT135 ceramics doped with B$_2$O$_3$ and TiO$_2$, which is still well-densified with low porosity. The grain size of LZT135 is smaller and more uniform with increased TiO$_2$, and this might stem from the high sintering temperature of TiO$_2$ ceramic (above 1300 °C).

Fig. 8 shows the improved sintered densities and microwave dielectric properties of LZT135 as a function of TiO$_2$ doping. The sintered densities and dielectric constants of LZT135 ceramics increased with the amounts of TiO$_2$ added. These increases mostly occur owing to the presence of the TiO$_2$ phase, which has a higher sintered density and dielectric constant. The Qf values of the LZT135 increased slightly with TiO$_2$ doping and reached a maximum value of about 50 000 GHz at 5 wt% TiO$_2$. Dielectric loss in ceramics can be divided into intrinsic loss and extrinsic loss. Intrinsic loss is mainly determined by the crystal structure, while extrinsic loss is determined by factors such as density, grain size, porosity, and second phases. When TiO$_2$ doping at less than 5 wt% increased density and decreased grain size to effect higher Qf values. This is balanced by the continued increase of rutile TiO$_2$ phase, which has a lower Qf value, which affects the LZT135 Qf overall. Within the sintering temperature range 875 – 925 °C, $\tau_f$ values of LZT135 ceramics shifted from negative to positive values with the doping of TiO$_2$ because of the rutile phase, effecting a near zero $\tau_f$ value. The optimal doping levels of 0.25 wt% B$_2$O$_3$ and 9 wt% TiO$_2$ in LZT135 sintered at 900 °C led to excellent dielectric properties of $e_r = 24.9$, Qf = 48 300 GHz and $\tau_f$ = -0.5 ppm/K.
Fig. 3: SEM micrographs of LZT135 ceramics doped with different amounts of B$_2$O$_3$ and sintered at 900 °C for 3 h.
Fig. 4: EDS analysis of Li$_2$ZnTi$_3$O$_8$ ceramic with 0.25 wt% B$_2$O$_3$ added and sintered at 900 °C for 3 h.

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Fig. 5: Microwave dielectric properties of LZT135 ceramics as a function of the B$_2$O$_3$ addition contents and sintering temperature; (a) Permittivities; (b) Qf values; (c) $\tau_f$ values.
Fig. 6: XRD patterns of LZT135 ceramics doped with 0.25 wt% B$_2$O$_3$ and different amounts of TiO$_2$, where (a) 0 wt%, (b) 2.5 wt%, (c) 5.0 wt%, (d) 7.5 wt%, (e) 9.0 wt% and (f) 10.0 wt%.

Fig. 7: SEM micrographs of LZT135 ceramics doped with 0.25 wt% B$_2$O$_3$ and different amounts of TiO$_2$, where (a) 2.5 wt%, (b) 5.0 wt%, (c) 7.5 wt%, (d) 9.0 wt% and (e) 10.0 wt%.
IV. Conclusions

The addition of B$_2$O$_3$ can effectively decrease the sintering temperature of LZT135 ceramics to about 900 °C. XRD and EDS results showed that the LZT135 ceramics formed a solid solution with a similar crystal structure to Zn$_2$Ti$_3$O$_8$. When 0.25 wt% B$_2$O$_3$ was added, dielectric properties of $\varepsilon_r = 20.5$, $Qf = 47,900$ GHz and $\tau_f = -31.5$ ppm/K could be obtained. The addition of TiO$_2$ formed a secondary phase of rutile TiO$_2$ in LZT135 ceramics, and can thus adjust the $\tau_f$ values for LZT135 ceramics. With the addition of 0.25 wt% B$_2$O$_3$ and 9 wt% TiO$_2$, LZT135 ceramics exhibited excellent microwave dielectric properties with $\varepsilon_r = 24.9$, $Qf = 48,300$ GHz and $\tau_f = -0.5$ ppm/K when sintered at 900 °C.

References


Fig. 8: Densities and microwave dielectric properties of LZT135 ceramics as a function of the TiO$_2$ addition contents and sintering temperature; (a) Sintered densities; (b) Permittivities; (c) Qf values; (d) $\tau_f$ values.


