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Low-Temperature Sintering and Microwave Dielectric Properties of Li_2O-3ZnO-5TiO_2 Ceramics Doped with B_2O_3

J. Liu[1], J. Zhu*[1,2], Y. Zeng[2]

[1]College of Optoelectronic Engineering, Shenzhen University, Shenzhen, Guangdong 518060, China
[2]Shenzhen Zhenhua Fu Electronics Co., Ltd., Shenzhen, Guangdong 518109, China

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Abstract

Phase composition, crystal structure as well as microwave dielectric properties of Li_2O-3ZnO-5TiO_2 ceramics (LZT135, for short) with the addition of B_2O_3 and TiO_2 were investigated. X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS) results revealed that the samples with added B_2O_3 and sintered at 900 °C had formed solid solutions with a similar crystal structure to $Zn_2Ti_3O_8$. When 0.25 wt% B_2O_3 was added, LZT135 ceramics could be densified at about 900 °C, while the negative τ_f value of about -31.5 ppm/K restricted its applications. TiO_2 was added for further adjustment of the τ_f value of LZT135 ceramics. Finally, with the addition of 0.25 wt% B_2O_3 and 9 wt% TiO_2, near zero τ_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_2O-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 [1]. 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_2O-Nb_2O_5-TiO_2, $ZnTiO_3$, Zn_2SiO_4, and $ZnNb_2O_6$, have attracted much attention especially owing to their relatively low sintering temperatures, as well as low dielectric loss at microwave frequency [2–9].

Compared with other LTCC materials, $Li_2ATi_3O_8$ (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 [10,11], are very attractive for LTCC applications. Another system, $ZnLi_{2/3}Ti_{4/3}O_4$ (Li_2O-3ZnO-4TiO_2) ceramic with a higher Qf value of 106 700 GHz was reported by Zhou [12], however, its sintering temperature of 1 075 °C and large negative τ_f value of -48 ppm/K are still not suitable for most LTCC applications. A solid solution of Li_2O-3ZnO-5TiO_2 (LZT135, for short) was reported in 2018 [13]. Doping with V_2O_5 reduced the sintering temperature of LZT135 to near 900 °C, combined doping with TiO_2 corrected the negative τ_f value to near zero, however, the toxicity of V_2O_5 still hampered application. B_2O_3 is usually used as the sintering aid because of its low melting point of about 450 °C[14–16], so B_2O_3 replaces V_2O_5 in this research for lower the sintering temperatures of the promising LZT135 ceramics system.

II. Experimental Procedure

Li_2O-3ZnO-5TiO_2 ceramics were synthesized with the conventional solid-state reaction method. Li_2CO_3, TiO_2, ZnO, and B_2O_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_2O_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 [17,18]. The τ_f value was also measured with the same method in the temperature range of 25 ~ 75 °C.

* Corresponding author: julianjianhua@163.com

III. Results and Discussion

Fig. 1 shows the XRD patterns of sintered LZT135 ceramics doped with different amounts of B_2O_3, all the samples were sintered at 900 °C. XRD results showed that the sintered LZT135 ceramics formed a cubic structure similar to $Zn_2Ti_3O_8$ (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)$Li_2Zn_3Ti_4O_{12}$-xTiO_2 (where 0.2≤x≤0.4) ceramics phase previously reported by Liu [19]. Therefore, the B_2O_3 doping does not strongly influence the phase composition of LZT135.

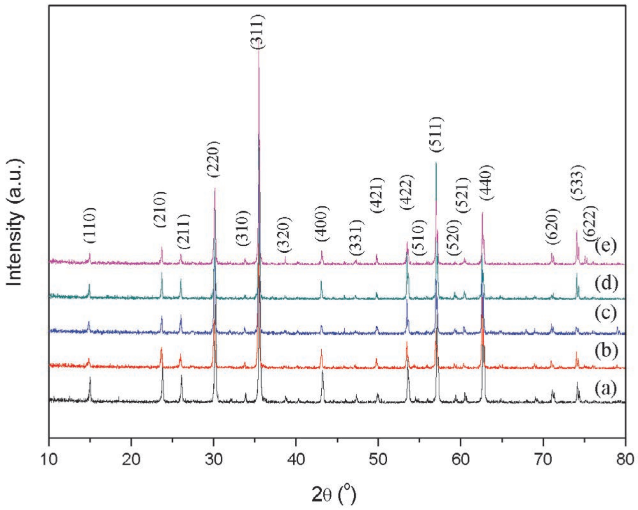

Fig. 1: XRD patterns of the sintered LZT135 ceramics doped with different amounts of B_2O_3 and sintered at 900 °C, where (a) 0 wt% (b) 0.25 wt%, (c) 0.5 wt%, (d) 0.75 wt% and (e) 1 wt%.

Fig. 2 shows the bulk densities of LZT135 ceramics sintered at different temperatures and different B_2O_3 doping levels. It is clear that B_2O_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_2O_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_2O_3 addition and after sintering at 900 °C. Doping beyond these levels did not improve densification.

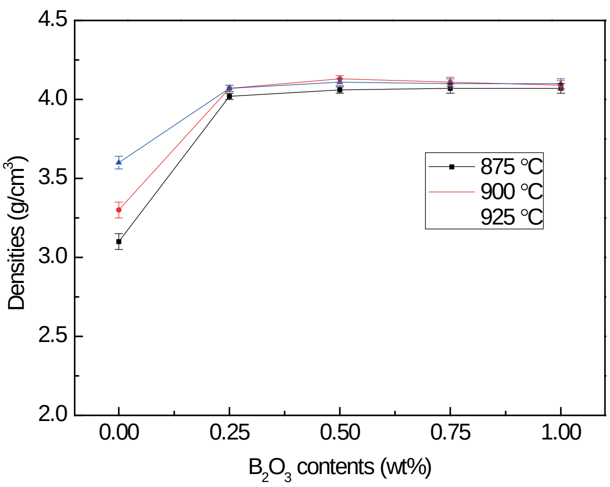

Fig. 2: Densities of LZT135 ceramics as a function of the B_2O_3 addition content and sintering temperatures.

The SEM micrographs in Fig. 3 show sintered LZT135 with different levels of B_2O_3 doping. When B_2O_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_2O_3 and sintering at about 900 °C, LZT135 ceramics can form solid solutions.

The microwave dielectric properties of B_2O_3-doped LZT135 are shown in Fig. 5. For samples doped with 0.25 wt% B_2O_3 and sintered at 900 °C, the ε_r of LZT135 reaches a relatively high value of 20.5, while again further additions of B_2O_3 have almost no influence on ε_r values as found earlier for density values. With increasing amounts of B_2O_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_2O_3 does not impact the τ_f values of LZT135 with 0.25 wt% B_2O_3 exhibiting -30 ppm/K, which is unacceptable in application. TiO_2 has an unusually high positive τ_f value of +465 ppm/K, and therefore, TiO_2 doping was used to significantly reduce the negative τ_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_2O_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 1 300 °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 [23]. 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, τ_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 τ_f value. The optimal doping levels of 0.25 wt% B_2O_3 and 9 wt% TiO_2 in LZT135 sintered at 900 °C led to excellent dielectric properties of ε_r = 24.9, Qf = 48 300 GHz and τ_f = -0.5 ppm/K.

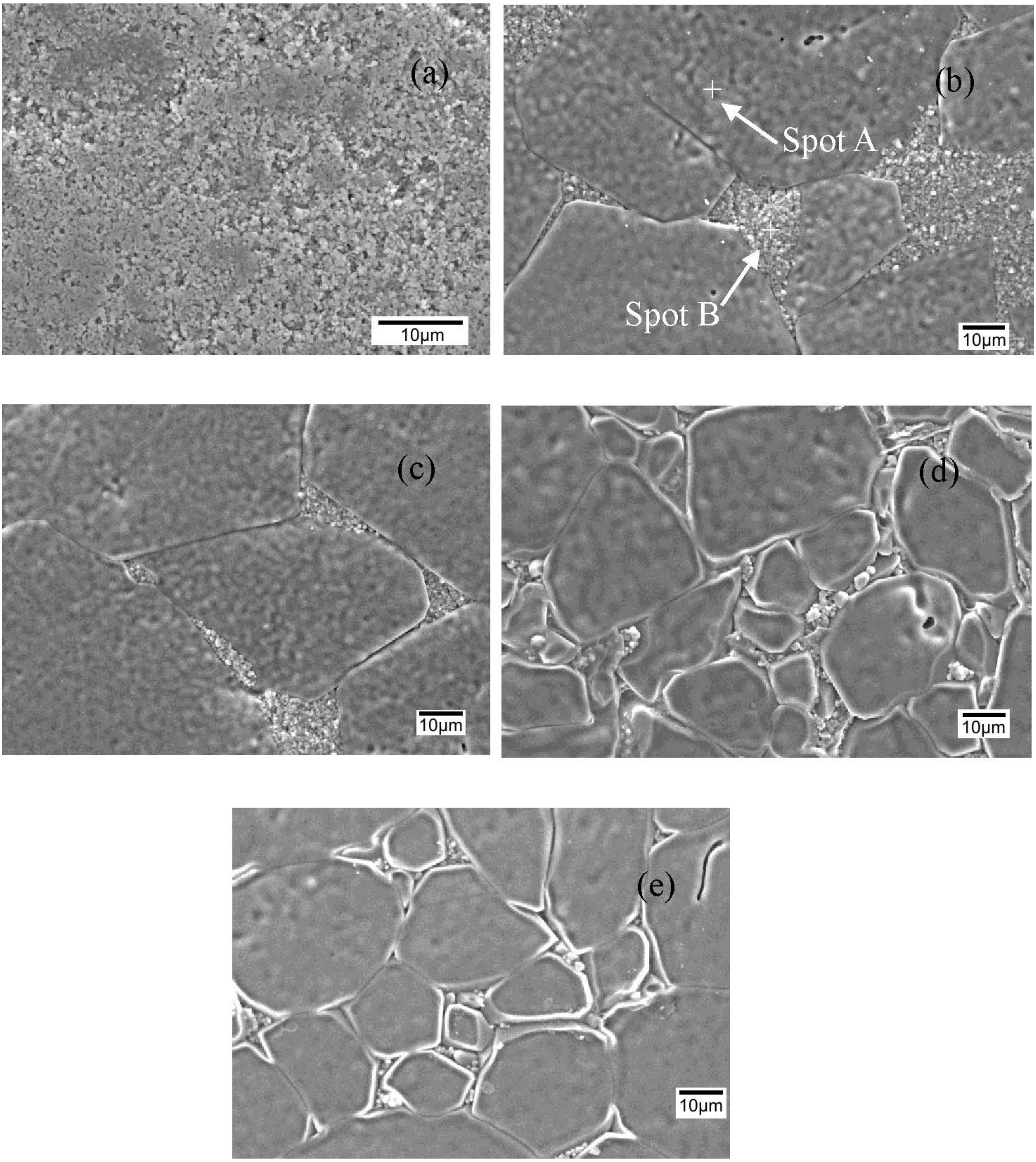

Fig. 3: SEM micrographs of LZT135 ceramics doped with different amounts of B_2O_3 and sintered at 900 °C for 3 h.

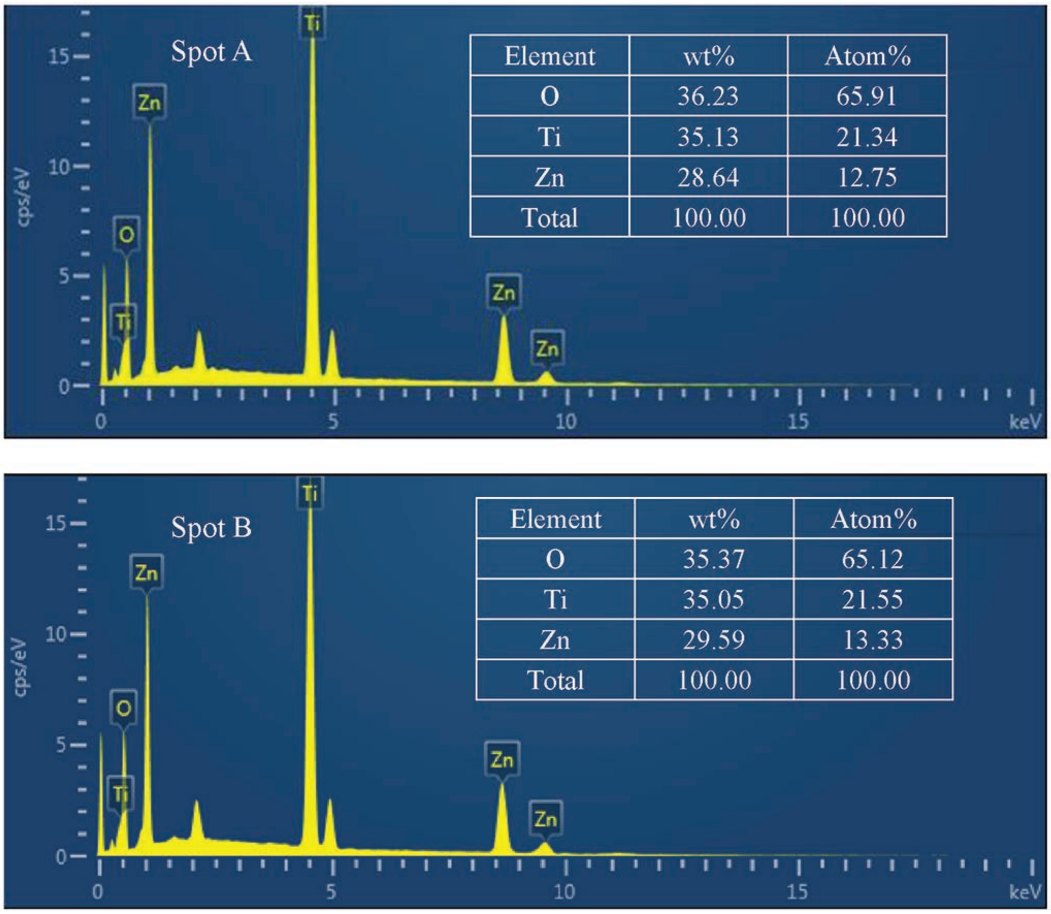

Fig. 4: EDS analysis of $Li_2ZnTi_3O_8$ ceramic with 0.25 wt% B_2O_3 added and sintered at 900 °C for 3 h.

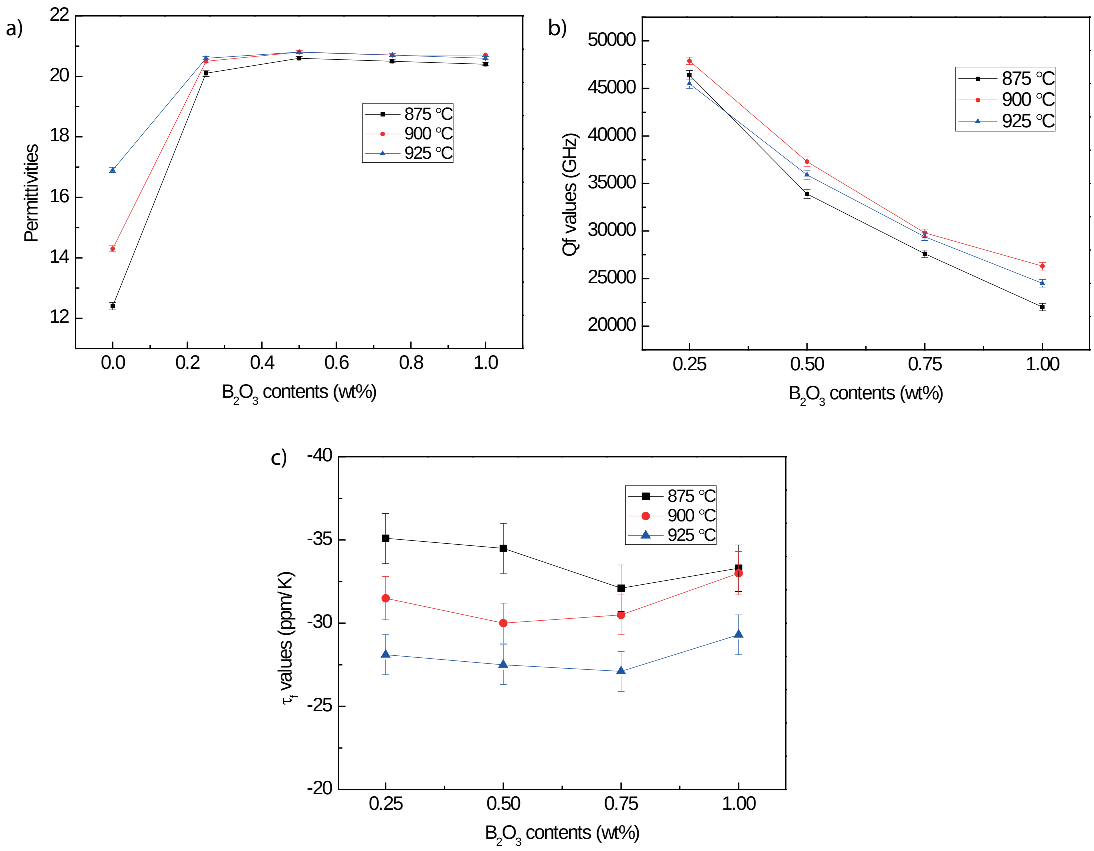

Fig. 5: Microwave dielectric properties of LZT135 ceramics as a function of the B_2O_3 addition contents and sintering temperature; (a) Permittivities; (b) Qf values; (c) τ_f values.

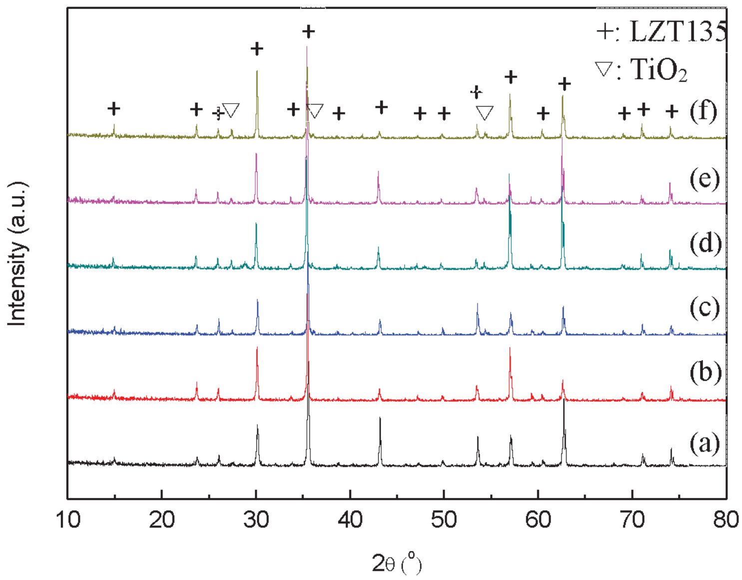

Fig. 6: XRD patterns of LZT135 ceramics doped with 0.25 wt% $B_2O_3$and different amounts of TiO_2, where (a) 0 wt%, (b) 2.5 wt%, (c) 5.0 wt%, (d) 7.5 wt%, (e) 9.0 wt% and (f) 10.0 wt%.

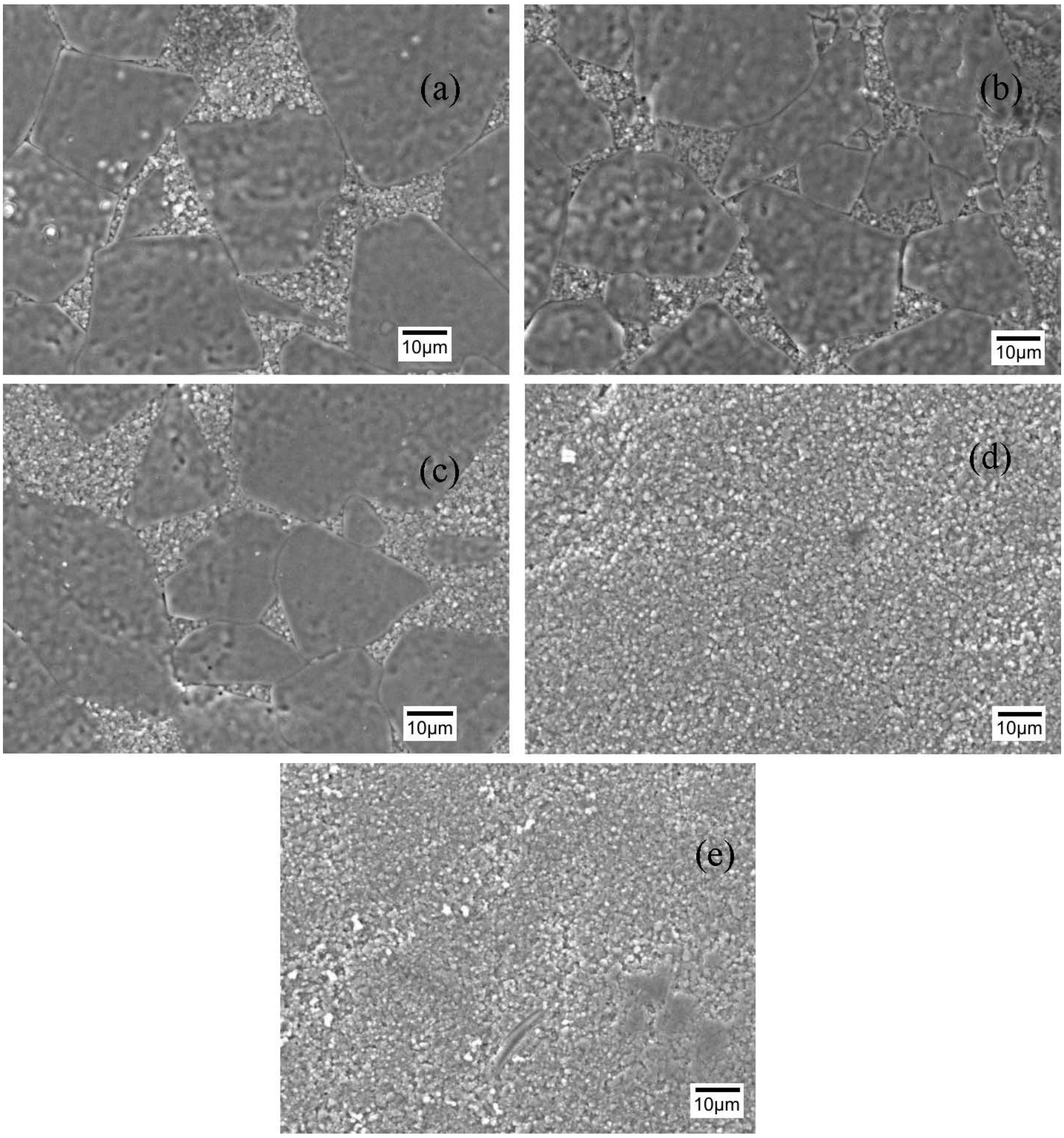

Fig. 7: SEM micrographs of LZT135 ceramics doped with 0.25 wt% B_2O_3 and different amounts of TiO_2, where (a) 2.5 wt%, (b) 5.0 wt%, (c) 7.5 wt%, (d) 9.0 wt% and (e) 10.0 wt%.

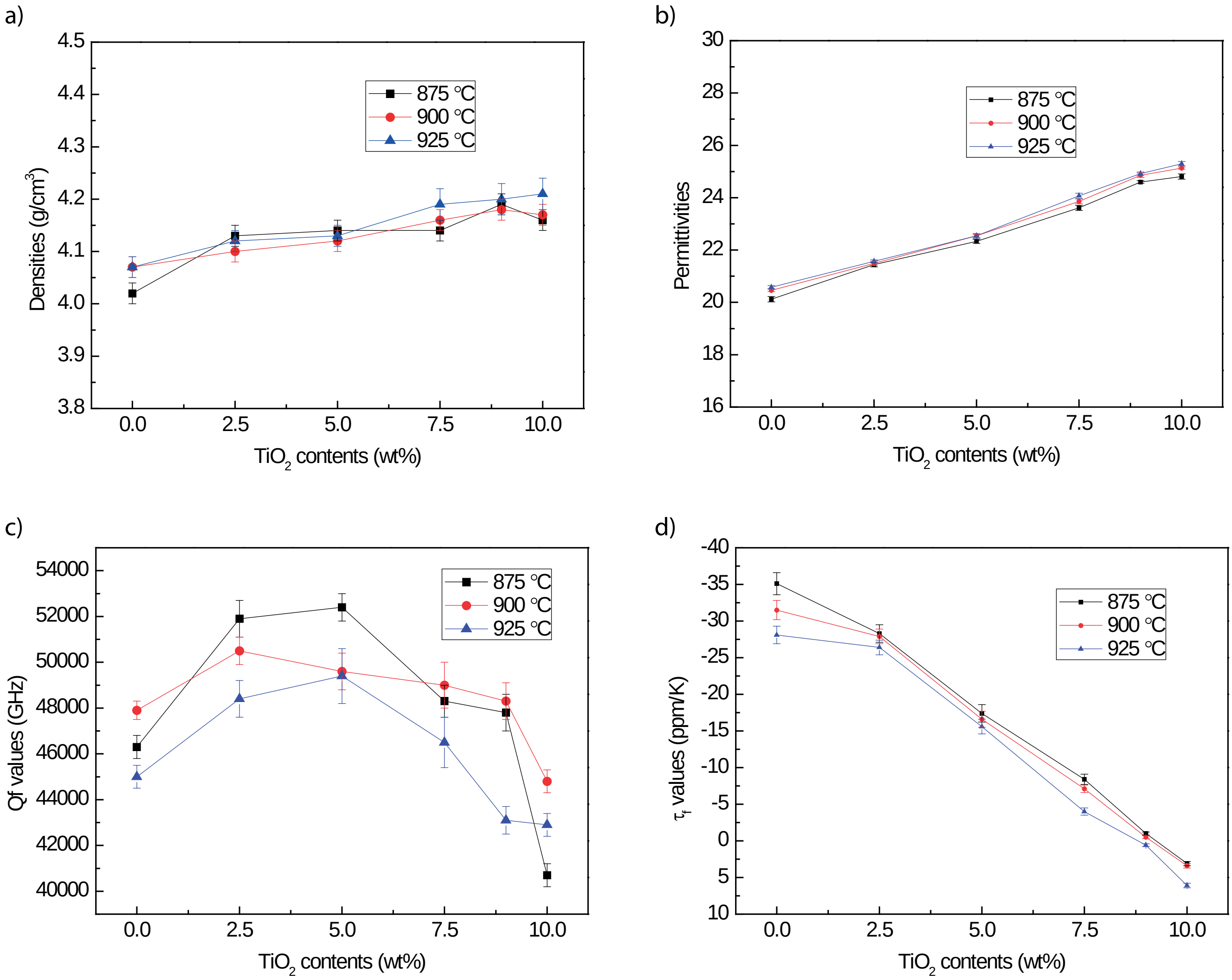

Fig. 8: Densities and microwave dielectric properties of LZT135 ceramics as a function of the TiO_2 addition contents and sintering temperature; (a) Sintered densities; (b) Permittivities; (c) Qf values; (d) τ_f values.

IV. Conclusions

The addition of B_2O_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 $Zn_2Ti_3O_8$. When 0.25 wt% B_2O_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 τ_f values for LZT135 ceramics. With the addition of 0.25 wt% B_2O_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.

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