New Journal of Glass and Ceramics, 2019, 9, 25-32
http://www.scirp.org/journal/njgc
ISSN Online: 2161-7562
ISSN Print: 2161-7554

Effects of V_2O_5 Addition on Microwave Dielectric Properties of $Li_2ZnTi_3O_8$ Ceramics for LTCC Applications

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How to cite this paper: Zhu, J.H., Liu, J.Y., Lu, S.J. and Zeng, Y. (2019) Effects of V_2O_5 Addition on Microwave Dielectric Properties of $Li_2ZnTi_3O_8$ Ceramics for LTCC Applications. *New Journal of Glass and Ceramics*, **9**, 25-32.
https://doi.org/10.4236/njgc.2019.93003

Received: April 6, 2019
Accepted: June 3, 2019
Published: June 6, 2019

Abstract

The sintering temperature of $Li_2ZnTi_3O_8$ ceramics is still high for LTCC-based applications. In this work, V_2O_5 was doped as the sintering aid. The sintered density, phase composition, grain size, as well as microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics with the addition of V_2O_5 were investigated. Based on our research, V_2O_5 doping effectively promoted the densification of $Li_2ZnTi_3O_8$ ceramics at about 900˚C, without affecting the main crystal phase of the ceramics. $Li_2ZnTi_3O_8$ ceramics with 0.5 wt% V_2O_5 doping (sintered at 900˚C) exhibited the best microwave dielectric properties (Qf = 22,400 GHz at about 6 GHz, ε_r = 25.5, and τ_f = −10.8 ppm/˚C). The V_2O_5-doped $Li_2ZnTi_3O_8$ ceramics were well cofired with Ag inner paste without cracks and diffusion, indicating its significant potential for LTCC applications.

Keywords

$Li_2ZnTi_3O_8$, Low Temperature Co-Fired Ceramics, Microwave Dielectric Properties

1. Introduction

Low temperature co-fired ceramics (LTCC) technology has drawn worldwide attention for more than thirty years, since its advantages in miniaturizing and integrating electronic components and modules. Silver is usually used as inner electrode for LTCC technologies, due to its relatively low cost and high conductivity. However, the low melting point of silver (961˚C) prevents it from co-firing with most of ceramic materials. To match with silver inner paste, lowering down the sintering temperature of the used ceramics to around 900˚C is very necessary. What's more, for the fabrication of electronic components, the ceramic materials should have suitable permittivity (ε_r), near zero temperature coefficient of resonant frequency (τ_f), and low dielectric loss (usually replaced by Q*f value for microwave dielectric ceramics) [1].

Much attention has been paid to the LTCC applications of Li-containing compounds, such as Li_2TiO_3, Li_2MgSiO_4, $Li_3Mg_2NbO_6$, Li_3NbO_4, and Li_2O-Nb_2O_5-TiO_2 [2] [3] [4] [5] [6]. In 2010, George and Sebastian [7] firstly reported $Li_2ZnTi_3O_8$ ceramics with good microwave dielectric properties (Qf = 72,000 GHz, $\varepsilon_r = 25.6$, and $\tau_f = -11.2$ ppm/˚C). However, its relatively high sintering temperature (1075˚C) limits its application for LTCC components. Several sintering aids, such as H_3BO_3, Bi_2O_3, B_2O_3, and glass, have been successfully used to lower down the sintering temperature of $Li_2ZnTi_3O_8$ ceramic because of the low melting point or softening point of these sintering aids [8]-[16]. V_2O_5 has also been used as sintering aid for some Li-containing compounds [16] [17] [18], but its effectiveness on $Li_2ZnTi_3O_8$ ceramics has not been reported. Other than that, the co-firing ability of those materials with silver inner paste was seldom discussed by using multilayer component technologies. In this work, the sintering and microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics after V_2O_5 doping, as well as its co-firing behavior with Ag inner electrodes were investigated.

2. Experimental

Reagent grade Li_2CO_3 (99 wt%, Aladdin, China), V_2O_5 (99 wt%, Aladdin, China), TiO_2 (99.9 wt%, Yaxing, China), and ZnO (99.7 wt%, Maixin, China) powder were used. According to the stoichiometries of $Li_2ZnTi_3O_8$, those oxides were weighed and then ball milled in planetary ball mill machine for 3 h with alcohol and zirconia balls as the medium. After the milling, the mixtures were dried at 75˚C and then calcination process was performed at 850˚C for 3 h. Following the calcination process, V_2O_5 with different amounts were added to the $Li_2ZnTi_3O_8$ powder. The mixture were re-milled for 3 h. Polyvinyl alcohol (PVA) binders were added into dried powder and then sieved. The sieved powders were pressed into disks under a pressure of 150 MPa. Finally, the samples were sintered at temperature range from 850˚C to 925˚C for 3 h in the air.

The densities of the ceramic disks were measured based on the Archimedes' method. Crystal structures of the ceramics were analyzed using X-Ray diffraction (XRD) (XRD-7000 diffractometer). Scanning electron microscope (SEM) (JEOL JSM-64) and energy dispersive spectrometer (EDS) (Oxford X-max N50) were used to observe the morphologies and material compositions of the as-sintered disk surfaces. Microwave dielectric properties of the ceramics were measured according to Hakki and Coleman's methods [19] [20], and the same method was also used to measure τ_f values of the samples at temperature from 25˚C to 75˚C.

The calcined $Li_2ZnTi_3O_8$ powder was mixed with V_2O_5, solvent, binder, plasticizer, and dispersant, and then ball milled for approximately 36 h as the slurry.

Traditional LTCC procedures, including tape casting, printing, lamination, isostatic pressing, cutting, and sintering, were performed for cofiring ability test. Elements distribution was carried out by energy dispersive spectrometer using line scan analysis.

3. Results and Discussions

The sintered densities of $Li_2ZnTi_3O_8$ ceramics with various V_2O_5 proportions and sintered at various temperatures are shown in **Figure 1**. The addition of V_2O_5 effectively increased the densities of $Li_2ZnTi_3O_8$ ceramics, even with a small V_2O_5 amount of 0.25 wt%. The sintered densities of $Li_2ZnTi_3O_8$ ceramics increased with the sintering temperatures when the addition amounts of V_2O_5 are less than 0.25 wt%, while there are no obvious changes when the addition amounts of V_2O_5 are over 0.5 wt%, which means that the 0.5 wt% addition amount of V_2O_5 is sufficient for the low temperature sintering of $Li_2ZnTi_3O_8$. The density of $Li_2ZnTi_3O_8$ ceramics with 0.5 wt% V_2O_5 addition and sintered at 900˚C can reach 3.75 g/cm^3, which was approximately 94.4% of the theoretical value of $Li_2ZnTi_3O_8$ ceramic (3.974 g/cm^3) [7]. The densification effect was due to the low melting point of V_2O_5 (about 650˚C) and the consequent appearance of liquid phase. The appearance of liquid phase promoted the rearrangement and growth of grains and therefore increased the densities of $Li_2ZnTi_3O_8$ ceramic, while further increasing of sintering temperature caused the abnormal grain growth and therefore decreased the densities of the samples.

Figure 2 shows the XRD spectrum of sintered $Li_2ZnTi_3O_8$ ceramics with various V_2O_5 doping amounts at sintering temperature of 900˚C. All the spectrum matched well with $Li_2ZnTi_3O_8$ phase (JCPDS#86-1512), consistent with the reports of George [7] and Fang [21]. This suggested that the phase composition of $Li_2ZnTi_3O_8$ were insensitive to V_2O_5 doping. The morphologies of V_2O_5-doped $Li_2ZnTi_3O_8$ ceramics with various addition amounts and sintered at 900˚C are shown in **Figure 3**. Those sintered samples exhibited relatively dense microstructure, and both small- and large-sized grains existed. As shown in **Figure 4**,

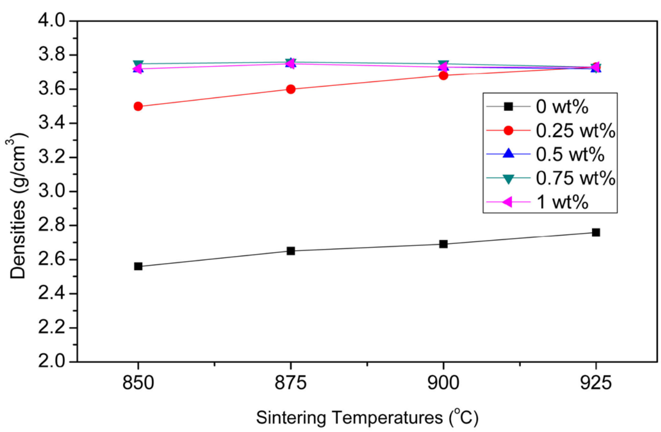

Figure 1. Densities of $Li_2ZnTi_3O_8$ ceramics as a function of sintering temperatures and the V_2O_5 addition contents.

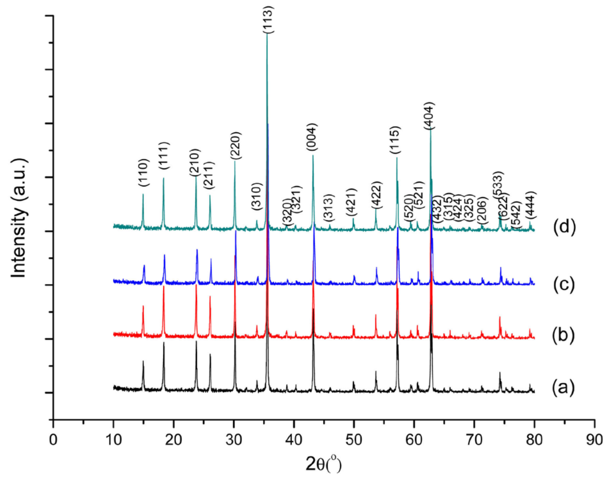

Figure 2. XRD patterns of $Li_2ZnTi_3O_8$ ceramics doped with different amounts of V_2O_5 and sintered at 900˚C; (a) 0.25 wt%; (b) 0.5 wt%; (c) 0.75 wt%; and (d) 1 wt%.

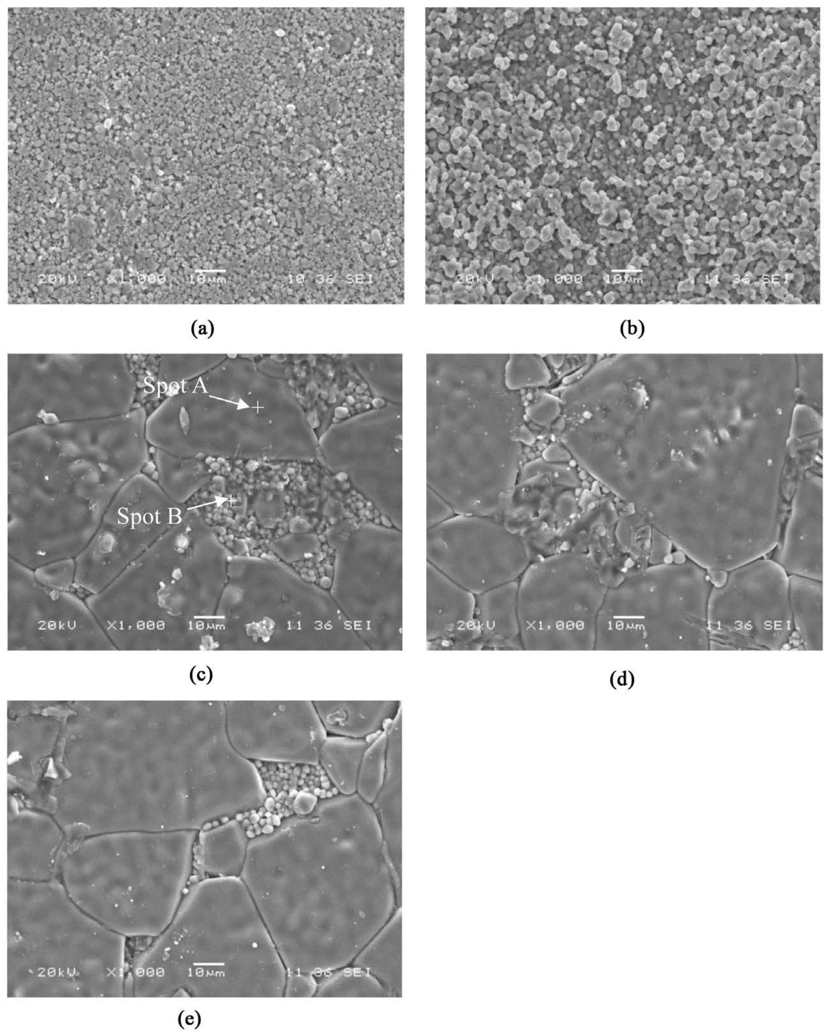

Figure 3. SEM micrographs of $Li_2ZnTi_3O_8$ ceramics doped with different amounts of V_2O_5 sintered at different temperatures; (a) 0 wt%, 900˚C; (b) 0.25 wt%, 900˚C; (c) 0.5 wt%, 900˚C; (d) 0.75 wt%, 900˚C; (e) 1 wt%, 900˚C.

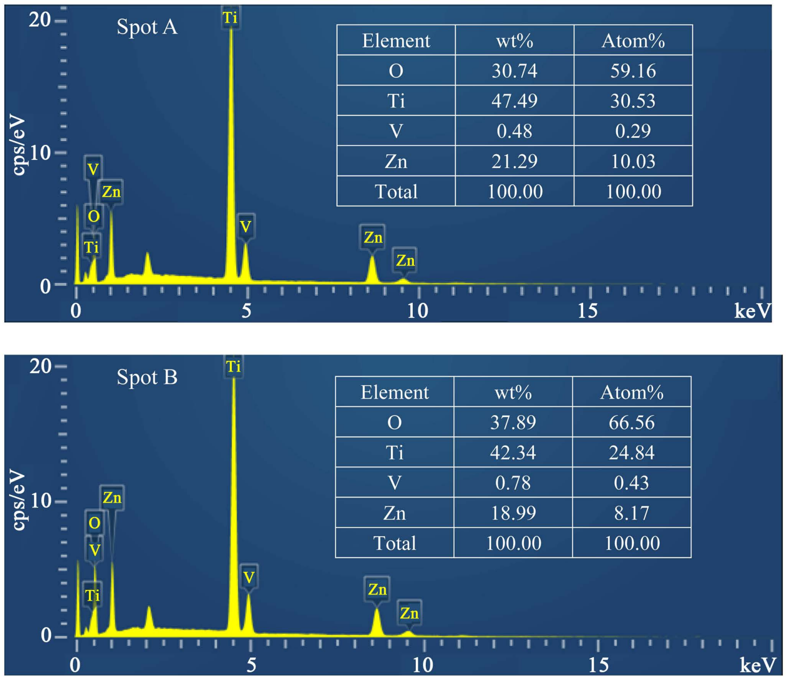

Figure 4. EDS analysis of $Li_2ZnTi_3O_8$ ceramics added with 0.5 wt% V_2O_5 and sintered at 900˚C for 3 h.

for large- (spot A) and small-sized grains (spot B), the atomic ratio of Ti and Zn elements were detected to be approximately the same value of 3. These results agreed well with the molecular formula of $Li_2ZnTi_3O_8$, indicating that the $Li_2ZnTi_3O_8$ phase was the matrix phase and no secondary phase existed, which was also consistent with the XRD spectrum in **Figure 2**.

The microwave dielectric properties of $Li_2ZnTi_3O_8$ with different V_2O_5 doping amounts (sintered at 900˚C) were then detected as shown in **Figure 5**. With the increase of V_2O_5 addition, the ε_r of the $Li_2ZnTi_3O_8$ ceramics raised up to a maximum value of 25.5 at a V_2O_5 content of 0.5 wt% and then decreased afterwards. The change of ε_r had similar trend to that of density, as shown in **Figure 1**. High density usually results in the presence of considerable number of dipoles per unit volume, and consequently large ε_r. The Qf value of $Li_2ZnTi_3O_8$ ceramics was enhanced significantly with increased V_2O_5 doping amount at the range below 0.5 wt%, due to the increased density and the decreased defects and grain boundaries. Further addition of V_2O_5 led to excess liquid phase and consequently decreased Qf value. The τ_f value of the V_2O_5-doped $Li_2ZnTi_3O_8$ ceramics slightly changed from −12 ppm/˚C to around −10 ppm/˚C when 1 wt% amount was added, manifesting that V_2O_5 had little influence on the τ_f of the $Li_2ZnTi_3O_8$ ceramic.

Figure 6 shows the optical image of $Li_2ZnTi_3O_8$ ceramics with the addition of 0.5 wt% V_2O_5 and cofired with Ag at 900˚C for 3 h. No obvious cracks and distortion were observed between $Li_2ZnTi_3O_8$ ceramics and Ag inner electrode interfaces. EDS line scanning was performed to further investigate the cofiring properties of the ceramic and Ag inner electrode. **Figure 7** shows the element

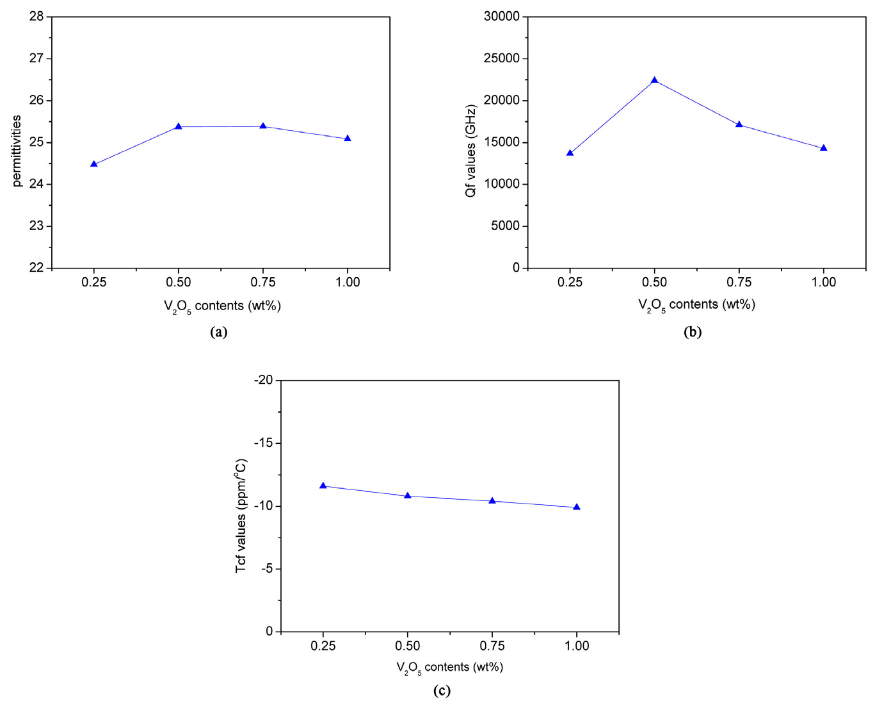

Figure 5. Microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics as a function of V_2O_5 addition content; (a) Relative permittivity; (b) Qf values; and (c) τ_f values.

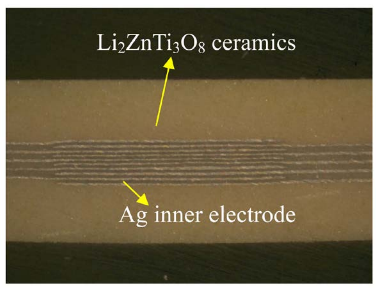

Figure 6. Optical microscopy of $Li_2ZnTi_3O_8$ ceramics cofired with Ag.

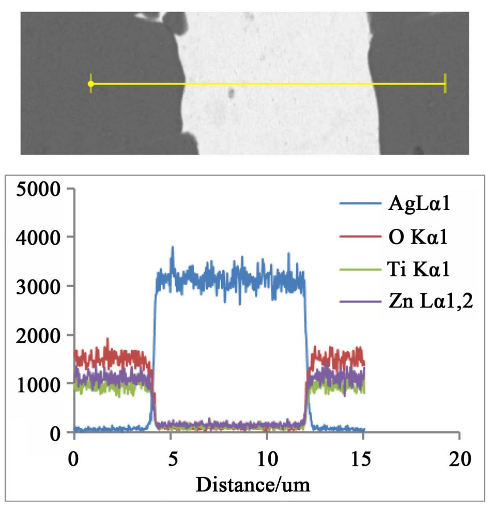

Figure 7. EDS line scanning of the $Li_2ZnTi_3O_8$ ceramics cofired with Ag.

analysis and the corresponding morphology of the line region which cross the ceramic and the Ag electrode. The Ag profile shows a platform in the middle, and both the Zn and Ti profiles show two platforms in the side regions. All the sharp transitions to near-zero level happened at the two interfaces, indicating that reaction and diffusion did not occur between the low temperature sintered $Li_2ZnTi_3O_8$ ceramics and the Ag inner electrodes.

4. Conclusion

$Li_2ZnTi_3O_8$ ceramic was densified at about 900˚C with the addition of V_2O_5. $Li_2ZnTi_3O_8$ ceramic with small amounts (less than 1 wt%) of V_2O_5 had single phase with a spinel crystal structure. When 0.5 wt% V_2O_5 was doped, microwave dielectric properties of $\varepsilon_r = 25.5$, Qf = 22,400 GHz, and $\tau_f = -10.8$ ppm/˚C was obtained. EDS line scanning results showed that $Li_2ZnTi_3O_8$ ceramics could be cofired with Ag inner paste without cracks and diffusion, making it very potential for LTCC applications.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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