



Investigation of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ -based temperature stable dielectric ceramics for LTCC applications

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Abstract

A low temperature co-fired ceramic (LTCC) was fabricated at 910 °C /2 h from the powder mixture of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$, TiO_2 and a B_2O_3 – La_2O_3 – MgO – TiO_2 glass (BLMT), and the influence of TiO_2 on microstructure and dielectric properties of the composite was investigated in the composition range (wt%) of 20BLMT–(80–x) $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ –x TiO_2 (x=0, 2.5, 5, 7.5, 9 and 10). The results showed that all samples consisted of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$, TiO_2 , LaBO_3 and $\text{LaMgB}_5\text{O}_{10}$ phase. And LaBO_3 , $\text{LaMgB}_5\text{O}_{10}$ and a small amounts of TiO_2 were crystallized from BLMT glass during sintering process. As x increases, dielectric constant and temperature coefficient of resonance frequency of the composites demonstrated gradually increase, whereas the quality factor of the sample of x=0 wt% was about 41,500 GHz and the ones maintained stable at a high level of 49,000–51,000 GHz for other samples. The composite with x=9 wt% had an optimal microwave dielectric properties with the dielectric constant of 20.2, quality factor of 50,000 GHz and temperature coefficient of resonant frequency of –0.33 ppm/°C.

1 Introduction

For meeting the requirements of miniaturization, integration and high reliability of electronic devices, low-temperature co-fired ceramics (LTCC) technology has played an increasingly significant role in the development to Internet of Things, the Tactile Internet (5th generation wireless systems), electronic warfare, satellite broadcasting and intelligent transport systems [1, 2]. The ideal LTCC materials owe several features such as low sintering temperature (below 950 °C), an appropriate dielectric constant (ϵ_r), high quality factor ($Q \times f$) and a near-zero temperature coefficient of resonant frequency ($|\tau_f| \leq 10$ ppm/°C) [3]. Unfortunately, most of the dielectric ceramics with good microwave dielectric properties cannot be used for LTCC application due to the sintering temperatures above 1000 °C. Therefore, lowering

the sintering temperature as well as maintaining an excellent dielectric properties simultaneously is the key to promote the LTCC materials.

$\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ is a new member of the Li_2O – ZnO – TiO_2 ternary microwave dielectric ceramics with the middle- ϵ_r (20.6), high $Q \times f$ value (106,700 GHz) and large negative τ_f (–48 ppm/°C), and the sintering temperature of it is around 1075 °C [4]. Obviously, the sintering temperature and τ_f value are a huge barrier for it to be further applied in LTCC technology. In order to realize $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics for LTCC applications, low-melting sintering aids such as $\text{BaCu}(\text{B}_2\text{O}_5)$ and Li_2O – ZnO – B_2O_3 glass for lowering the sintering temperature and a positive τ_f -tailoring material (e.g., $\text{TiO}_2 + 465$ ppm/°C, $\text{Li}_2\text{TiO}_3 + 20.3$ ppm/°C) for modifying to near-zero τ_f value are used simultaneously [4–7]. It can be found from our previous works that B_2O_3 – La_2O_3 – MgO – TiO_2 (BLMT) glass is a promising candidate due to its low transformation temperature (644 °C) [8, 9]. In addition, TiO_2 is chosen as the positive τ_f -tailoring material in this study. In this paper, a series of LTCC composites based on 20BLMT–(80–x) $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ –x TiO_2 (x=0, 2.5, 5, 7.5, 9 and 10, in wt%) are fabricated, meanwhile the effects of the TiO_2 on the crystallization and microwave dielectric properties of the material are investigated.

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2 Experimental

Glass of 42.9B₂O₃–17.1La₂O₃–25.7MgO–14.3TiO₂ in mol% was prepared by traditional glass melting method [8, 9]. The BLMT glass powder was obtained after the quenched glass was planetary-milled in aluminum jar with ethyl alcohol and ZrO₂ balls for 2 h, and then dried and screened through a 200-mesh sieve. Li₂CO₃, ZnO and TiO₂ were weighted according to the stoichiometry of Li₂Zn₃Ti₄O₁₂ and mixed in a Nylon tank using ethyl alcohol and ZrO₂ balls by planetary ball mill for 2 h. The mixture was dried and calcined at 900 °C for 8 h to form Li₂Zn₃Ti₄O₁₂ phase. Then the BLMT glass powder, calcined Li₂Zn₃Ti₄O₁₂ powder and TiO₂ powder were weighed with the ratio of 20BLMT–(80–x)Li₂Zn₃Ti₄O₁₂–xTiO₂ (x = 0, 2.5, 5, 7.5, 9 and 10) and planetary-milled with ZrO₂ balls and ethyl alcohol for 2 h. After drying, the mixture was granulated by adding 8 wt% poly(vinyl butyral) solution for getting the uniformity particle size and good fluidity power. Preformed pellets of 15 mm in diameter and 7–8 mm in height were obtained from the powder using a cylindrical steel mold, and then were pressed at 2 MPa by hydraulic pressing, followed by sintering between 790 and 920 °C for 2 h in air at a heating rate of 5 °C/min.

X-ray diffraction analysis (XRD, D8 ADVANCE, Bruker, Germany) was using to identify the crystalline phases of samples. The backscattered electron (BSE) micrograph and element-distribution mapping (EDM) of sample was examined by field emission scanning electron microscope (FESEM, Magellan 400, FEI, USA). The bulk density was measured applying the Archimedes method. The dielectric properties of the samples with the diameter of 12 mm and the height of 6 mm were collected by the Hakki–Coleman dielectric resonator method in the TE011 mode using an Agilent E8363A PNA series network analyzer in frequency range of 1–20 GHz. The τ_f value was gauged by using the temperature test cabinet (VTL7003, Vötsch, Germany) according to the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \times 10^6 (\text{ppm}/^\circ\text{C})$$

where f_{85} and f_{25} represent the resonant frequencies at 85 and 25 °C, respectively.

3 Results and discussion

Figure 1 shows XRD patterns of the composites sintered at 910 °C for 2 h. The sample with x = 0 wt% consists of Li₂Zn₃Ti₄O₁₂ (JCPDS no. 44-1038), LaBO₃ (JCPDS file no. 12-0762), LaMgB₅O₁₀ (JCPDS no. 35-0120) and very small

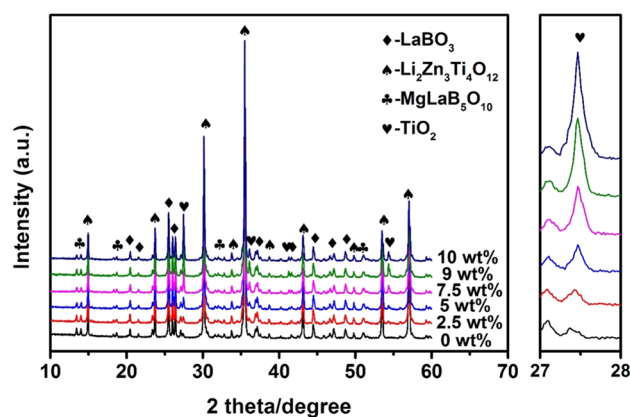


Fig. 1 XRD patterns of the composites sintered at 910 °C for 2 h

amounts of TiO₂ (JCPDS file no. 21-1276). According to our previous work [8, 9], LaBO₃, LaMgB₅O₁₀ and TiO₂ phase are crystallized from the BLMT glass. However, it can be easily seen that the peak intensity of TiO₂ enhances as x increases from 2.5 to 10 wt% compared to that of composite with x = 0 wt%. It means the positive τ_f -tailoring material TiO₂ does not chemically react with the BLMT glass or Li₂Zn₃Ti₄O₁₂ ceramic, which is a great advantage to modify the τ_f value of the composite to near-zero.

The BSE micrograph and ESM of the composite with x = 9 wt% sintered at 910 °C for 2 h are showed in Fig. 2. It can be found from Fig. 2a that the composite exhibits compact microstructure with grain sizes in the range 3–10 μm and seems to be composed of two kinds of phases which are present in gray and white. However, EDM reveals that there are more than two phases, in which the Li element belongs to the ultralight elements so that it cannot be detected by EDM [10]. It also can be easily seen from Fig. 2b, c that the most area of gray grains has a composition rich in Zn and Ti element corresponding to Li₂Zn₃Ti₄O₁₂ phase, yet some small gray grains (white arrows) are richer in Ti element than other gray grains and no other element is detected in these grains beside Ti element, suggesting that these grains belong to the TiO₂ phase. It is notable that some gray grains enrichment in Mg maybe correspond to MgLaB₅O₁₀ phase as shown in Fig. 2e. The area of white grains has a composition rich La and B element as shown in Fig. 2d, f, which is consistent with the composition of LaBO₃ phase. The results indicate that four phases co-exist in the sample, which is agree with the discussion in previous XRD analysis shown in Fig. 1.

Figure 3a–c demonstrates the bulk density, dielectric constant, and $Q \times f$ value of BLMT–Li₂Zn₃Ti₄O₁₂–TiO₂ composite as functions of sintering temperature. The bulk density of sintered samples increases, and then slightly declines after reaching a maximum with increasing the sintering temperatures as shown in Fig. 3a. The maximum density is obtained at 900 °C for composite with x = 0 wt%, and the

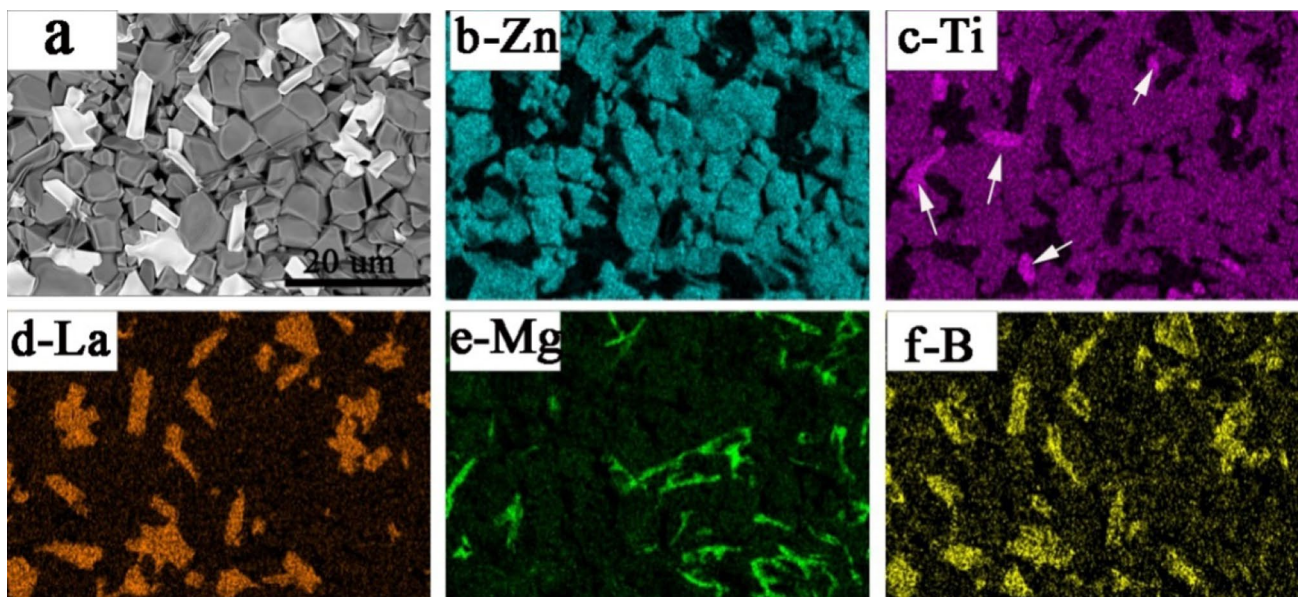


Fig. 2 BSE micrograph and ESM of the composite with $x=9$ wt% sintered at $910\text{ }^{\circ}\text{C}$ for 2 h

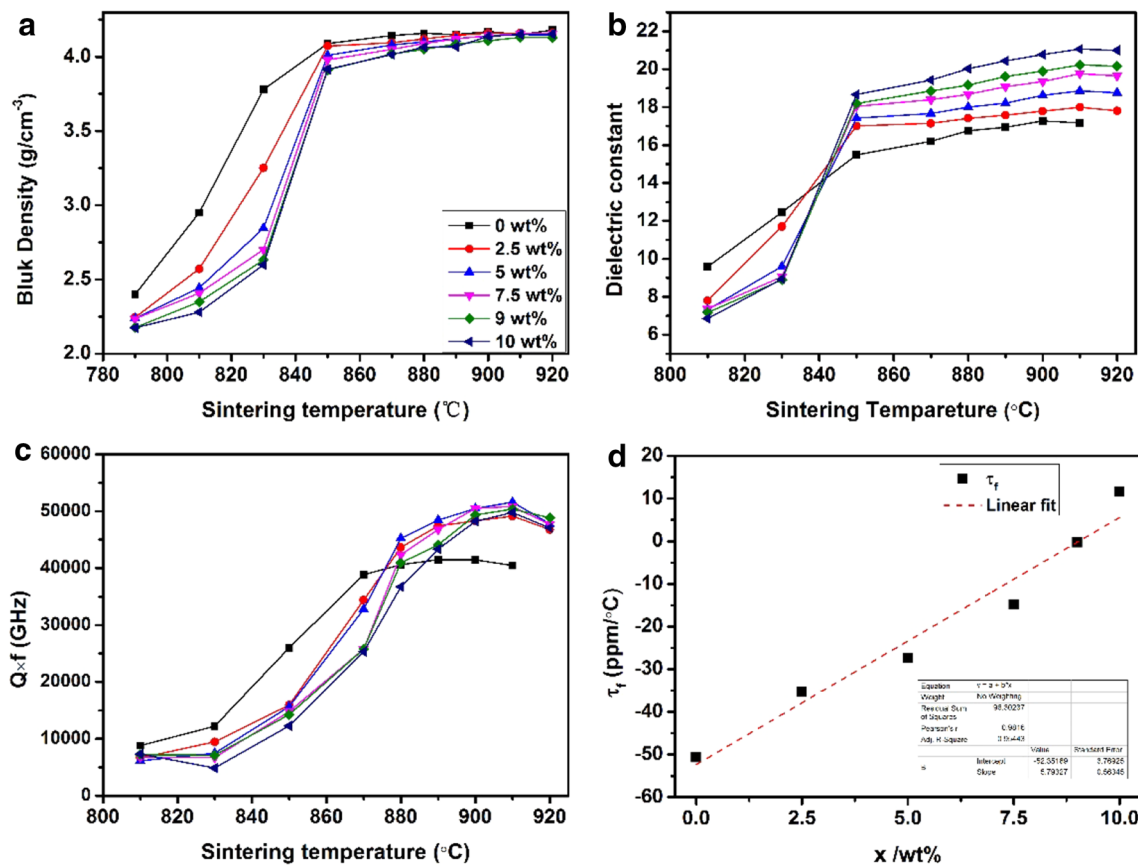


Fig. 3 The bulk density (a), dielectric constant (b), $Q \times f$ (c) and τ_f values (d) of BLMT– $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ – TiO_2 composites

Table 1 Comparison of sintering temperature and dielectric properties of recently reported $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ LTCC materials with this study

Composition	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	T_s (°C)	Ref
1.5 wt% $\text{BaCu}(\text{B}_2\text{O}_5) + \text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$	19.4	57,600	−39.5	900/2 h	[4]
2.5 wt% (2 Li_2O –3 ZnO –5 B_2O_3 glass) + LiTiO_3 + 20 vol% $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$	22	28,407	−5.2	900/2 h	[5]
2.0 wt% (0.4 B_2O_3 –0.6 CuO) + (0.8 $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ + 0.2 LiTiO_3)	17.5	71,000	−44.4	925/5 h	[7]
3.0 wt% (0.4 B_2O_3 –0.6 CuO) + (0.2 $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ + 0.8 LiTiO_3)	18.5	42,000	−37.6	925/5 h	[7]
1.5 wt% (2 Li_2O –3 ZnO –5 B_2O_3 glass) + $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$	19.1	63,751	−48.9	900/2 h	[5]
0.4 $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ + 0.6 $\text{Ba}_3(\text{VO}_4)_2$	16.9	51,322	+3.3	950/4 h	[16]
20BLMT–71 $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ –9 TiO_2 (in wt%)	20.2	50,000	−0.33	910/2 h	This paper

T_s sintering temperature, *Ref* references

maximum density are achieved at 910 °C for composites with $x = 2.5$ –10 wt%, which indicates that all composite can be densified sintering below 950 °C. It can be easily seen from Fig. 3b, c that the change in the ϵ_r and $Q \times f$ value is attributed to the variation in sintering temperature and x value during sintering. Obviously, the ϵ_r of the composites have the tendency of increasing with the increasing sintering temperature owing to the densification of composites. The ϵ_r of composites sintered at the optimum sintering temperature could be adjusted to the range of 17–21 with the increasing of x from 0 to 10 wt% due to the increase of higher- ϵ_r TiO_2 (108) phases. The $Q \times f$ value of the composites is not only related to the phase composition but also closely associated with imperfections such as porosity and grains size [10–13]. In this case, the increasing $Q \times f$ value of the composites with the increasing sintering temperature is still influenced by the densification of composites. The $Q \times f$ value of composites sintered at the optimum sintering temperature first increases from 41,500 to 49,000 GHz with the x increasing from 0 to 2.5 wt%, and then maintain stable at a high level of 49,000–51,000 GHz as the x further increases to 10 wt%.

The τ_f value of the composites sintered at their optimum temperatures are shown in Fig. 3d. It is clear that the τ_f value increases from −50 to +11 ppm/°C with x increasing from 0 to 10 wt%. The τ_f for composites is well known to be influenced by the composition and their relative contents [14, 15]. As discussed about the XRD results in Fig. 1, it is easily found that the τ_f increases owing to the increasing of TiO_2 (+456 ppm/°C). Besides, it also can be found that the τ_f value of composites seems to be linear with the x value. Based on the experimental data in Fig. 3d, the linear regression equation of τ_f on the x value with Adj. $R^2 = 0.95443$ are obtained by the Origin software:

$$y = -52.35189 + 5.79327x.$$

It means that the τ_f can be precisely adjusted by adding the suitable content of TiO_2 , and when τ_f of composite is zero, the x is 9.037 wt%, which indicates that the τ_f value of composites is mainly influenced by the phase composition and their relative contents in composites. On the whole,

the promising microwave dielectric properties of $\epsilon_r = 20.2$, $Q \times f = 50,000$ GHz, and $\tau_f = -0.33$ ppm/°C can be obtained when the x is equal to 9 wt%. Table 1 shows that the dielectric properties of composite in our paper compare with recently reported $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ LTCC materials, which indicates that the 20BLMT–71 $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ –9 TiO_2 (in wt%) material displays excellent microwave dielectric properties.

4 Conclusions

In this study, the 20BLMT–(80– x) $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ – x TiO_2 ($x = 0, 2.5, 5, 7.5, 9$ and 10, in wt%) composites system has been fabricated and investigated. The results indicate that all composites are made up of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$, TiO_2 , LaBO_3 and $\text{LaMgB}_5\text{O}_{10}$ phases. And BLMT glass crystallizes forming LaBO_3 , $\text{LaMgB}_5\text{O}_{10}$ and very small amounts of TiO_2 phase during sintering process. All composites can be sintered at 910 °C. Corresponding to the increase of x in system, the ϵ_r and τ_f value of composites augment as well, whereas the $Q \times f$ value of the composite with $x = 0$ wt% is about 41,500 GHz and that of the composites with $x = 2.5$ –10 wt% maintain stable at a high level of 49,000–51,000 GHz. Optimized microwave dielectric properties of composites with $x = 9$ wt% are obtained by sintering at 910 °C/2 h with: $\epsilon_r = 20.2$, $Q \times f = 50,000$ GHz, and $\tau_f = -0.33$ ppm/°C.

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