Influence of CaO–B_2O_3–SiO_2 crystallizable glass on microstructure and microwave dielectric of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramics for LTCC substrate applications

Yang Lv, Wanfeng Zhou, Zhaowen Dong, Siqi Yuan, Xiaocong Ding, Tao Ma, Song Cui

PII: S0925-8388(20)32576-7

DOI: https://doi.org/10.1016/j.jallcom.2020.156212

Reference: JALCOM 156212

To appear in: *Journal of Alloys and Compounds*

Received Date: 4 February 2020

Revised Date: 13 June 2020

Accepted Date: 24 June 2020

Please cite this article as: Y. Lv, W. Zhou, Z. Dong, S. Yuan, X. Ding, T. Ma, S. Cui, Influence of CaO–B_2O_3–SiO_2 crystallizable glass on microstructure and microwave dielectric of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramics for LTCC substrate applications, *Journal of Alloys and Compounds* (2020), doi: https://doi.org/10.1016/j.jallcom.2020.156212.

Credit author statement

Yang Lv: Conceptualization, Data curation, Writing- Original draft preparation Software.

Wanfeng Zhou: Methodology, Data Curation, Formal analysis.

Zhaowen Dong: Conceptualization.

Siqi Yuan: Writing - Review & Editing.

Xiaocong Ding: Investigation, Resources.

Tao Ma: Supervision.

Song Cui: Software, Validation.

Influence of CaO-B_2O_3-SiO_2 crystallizable glass on microstructure and microwave dielectric of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramics for LTCC substrate applications

Yang Lv[1], Wanfeng Zhou[1], Zhaowen Dong[1], Siqi Yuan[1], Xiaocong Ding[1], Tao Ma[1], Song Cui[1]
[1]*The 43rd Research Institute of China Electronics Technology Group Corporation*
Hefei, 235000, People's Republic of China

Abstract

The low temperature co-fired ceramic (LTCC) material was developed with the $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic added CaO-B_2O_3-SiO_2 crystallizable glass via the traditional solid-state reaction process. The addition of CBS glass can reduce the sintering temperature of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic from 950 ^{o}C to 850 ^{o}C without an obvious degradation of the microwave dielectric properties as the low-loss phases $CaSiO_3$ and CaB_2O_4 phases were crystallized during sintering. The $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 glass composite sintered at 850 ^{o}C for 15 min exhibited the dielectric constant value (ε_r) was 6.7, the quality factor (Q×f) was 40,100 GHz at 15 GHz, and the τ_f value was -44 ppm/^{o}C. The LTCC green tape based on the optimized $LiMg_{0.9}Zn_{0.1}PO_4$-CBS2 glass composite composition was obtained by the standard tape-casting process. Tapes with Ag conductor paste printed were laminated and co-fired at 850 ^{o}C which revealed the good compatibility between the ceramic and silver. The sintered ceramic demonstrated the CTE value of 8.5 ppm/^{o}C (25 ^{o}C-300 ^{o}C), the maximum thermal conductivity of 5.6 W/M·K at 25 ^{o}C and the flexural strength of 180 MPa, indicating it was a promising LTCC substrate material.

Key words: LTCC, $LiMg_{(1-x)}Zn_xPO_4$, co-fire, microcrystalline glass

1 Introduction

The rapid development of wireless telecommunication and RF transmitter/receiver technology puts forward the requirement of electronic modules with high-integrated and high performance in microwave frequencies. The low temperature co-fired ceramics (LTCC), which are characterized by a three-dimensional package structure with embedded resistor-capacitor components, can significantly reduce the size and weight of microwave modules [1-2]. The insert loss of LTCC microwave substrate circuits plays a crucial role to determine LTCC materials, which should be featured with a low dielectric loss and co-fired with low resistivity metallic electrodes such as Ag or Au. It should be noted that the conductor pastes added with Pd or Pt are always used by LTCC devices material system to enhance the sinterability at 950 ^{o}C. However, adding Pd or Pt into the conductor paste can also deteriorate the loss in microwave substrate circuits. In the LTCC substrate application, the internal and external conductor paste always used pure low loss pastes such as Ag or Au, and co-fired with the dielectric material at 850 ^{o}C for less than 30 min[3]. Due to the limited sintering capability of these electrodes, the LTCC substrate materials sintered at 850 ^{o}C are in great demand, and the interfacial reaction between the LTCC and metal electrode is of equal importance[4].

The commercial LTCC material systems are glass-ceramic (crystallizable glass) or glass+ceramic. Ferro's A6M LTCC green tape was considered as the typical glass-ceramics material based on the CaO-B_2O_3-SiO_2 crystallizable glass[5]. The low-loss phases such as $CaSiO_3$ and CaB_2O_4 can mainly crystallize during sintering at 850 ^oC for 15 min, which accompanied the glass ceramic with excellent microwave dielectric properties of ε_r =5.9, and the dielectric loss was below 0.002 at 1GHz-100 GHz. However, the complicated and unstable crystallized behavior of glass made this material extremely difficult to control, and the flexural strength was about 170 MPa, which was not suitable enough to be applied in the highly integrated packaging process. For glass+ceramic system, the ceramics such as Al_2O_3, mullite, cordierite always display good microwave dielectric properties and can be easily regulated. The low soften point glass such as B_2O_3-SiO_2 based glass was added to regulate the densification behavior of the ceramic[6]. 9k7 LTCC material with Al_2O_3 + CaO-La_2O_3-B_2O_3 glass sintered at 850 ^oC exhibited the relatively lower dielectric loss (<0.0009 at 10 GHz), making it was a very outstanding highly integrated LTCC packaging substrate material.

Thomas and Sebastian reported that $LiMgPO_4$ ceramic can be sintered at a relatively low temperature about 950 ^oC with a dense microstructure and low permittivity ε_r =6.6, Q×f =79,100 GHz and τ_f = -55 ppm/^oC. Its good chemical compatibility between Ag electrode made it as a very promising glass free LTCC substrate material[7]. Limited Zn^{2+} substitution of $LiMgPO_4$ improved the Q×f value from 79,100 GHz to 99,700 GHz, and TiO_2 was added as a temperature coefficient compensatory material to tailor the relatively negative large τ_f value to near zero[8]. A $LiMgPO_4$ based LTCC green tape was reported in their further study that a four-layer green tape sintered at 950 ^oC for 2 h exhibited the microwave dielectric properties: ε_r ~ 6.8 and tan δ=0.0002[9]. However, its sintering temperature and holding time were still higher than the low loss LTCC substrate application. CaO-B_2O_3-SiO_2 glass ceramic was investigated as a remarkable LTCC packaging substrate material due to its low sintering temperature and good microwave dielectric performance in the high frequency. Its wide liquid phase region was beneficial to the densification of the ceramic, and the crystallized low loss phase enhanced the microwave dielectric properties simultaneously. These characteristics of CaO-B_2O_3-SiO_2 glass were considered as a good addition for the glass+ceramic LTCC material system.

This study, on the one hand, intends to develop a novel LTCC material system of the CaO-B_2O_3-SiO_2 as an alternative glass, and $LiMg_{0.9}Zn_{0.1}PO_4$ solid solution as a ceramic material and, one the other hand, systematically to investigate the sintering behavior, microstructure and microwave dielectric properties of the composite. Furthermore, to further verify the practical application of glass composite material in manufacturing the LTCC substrate, the $LiMg_{0.9}Zn_{0.1}PO_4$-CBS based green tape aims to be fabricated by casting process and the mechanical properties of the sintered ceramic will be investigated.

2 Experimental procedure

2.1 Preparation of $LiMg_{0.9}Zn_{0.1}PO_4$-CBS glass composite

$LiMg_{0.9}Zn_{0.1}PO_4$ ceramic powder was synthesized by calcining the powder mixtures of Li_2CO_3 (>99 %), $NH_4H_2PO_4$ (>99 %), $(MgCO_3)_4\cdot Mg(OH)_2\cdot 5H_2O$ (>99 %) and

ZnO (>99.9 %) at 800 ^{o}C for 4 h, respectively, by means of a conventional solid-state route. The calcined powder was then milled with zirconia balls in the de-ionized water and then dried. The glass corresponding to 40 mol% CaO-15 mol% B_2O_3-45 mol% SiO_2 (CBS1) and 45 mol% CaO-25 mol% B_2O_3-30 mol% SiO_2 (CBS2) was prepared from high purity $CaCO_3$ (>99 %), H_3BO_3 (>99 %) and SiO_2 (>99 %). The well-mixed powder melted in a platinum crucible at 1400 ^{o}C for 2 h. The melt glass was quenched directly into water and ball-milled for 4 h in the de-ionized water and then dried. Glass-ceramic samples with $LiMg_{0.9}Zn_{0.1}PO_4$+x wt% CBS (x=5,10.15,20) were well-weighed and milled. The powder was uniaxially pressed into pellets (10 mm in diameter and 7 mm in height). The pellets were sintered at 850 ^{o}C for 15 min with the heating rate of 5 ^{o}C/min.

The crystal structures of the calcined powders and sintered ceramics were examined by an X-Ray Diffractometer (XRD, D/Max2500V, Rigaku, Japan) using CuKα radiation. Differential scanning calorimeter (DSC) analysis of samples was performed by the Netzsch STA 449F3 up to 900 °C at the heating rate of 10 °C/ min. The grain morphologies and compositions were analyzed by a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). The Agilent N5230C Network Analyzer (Agilent, Santa Clara, CA, USA) was used for the measurement of microwave dielectric properties in Hakki-Coleman Method [10, 11]. The temperature coefficient of resonant frequency (τ_f) is defined as follows:

$$\tau_{\mathrm{f}} = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

where f_2 and f_1 represent the resonant frequencies at T_2 and T_1, respectively.

2.2 Preparation of $LiMg_{0.9}Zn_{0.1}PO_4$-CBS green tape

The mutually good miscibility between the solvent and binder was a key premise as the colloidal can encase the powder to form the desirable slurry. The tape casting slurry was prepared by mixing the solvent (50 wt% ethanol+50 wt% isopropanol) and binder (PVB) with ball milling for 5 h, followed by adding $LiMg_{0.9}Zn_{0.1}PO_4$-CBS mixtures and mixing for 12 h. After adding the plasticizers (triethanolamine) and milling for another 12 h, the slurry was cast onto a 50 μm-thick silicone-coated Mylar carrier tape by a tape casting machine at the speed of 0.2 m/min. Tapes with thickness of 127 μm were cut and printed with 33-398 (Ferro Corp.) Ag electrode paste, then thermolaminated (10 layers) at the temperature of 70 ^{o}C under the pressure of 3000 psi for 20 min. The hot-pressed pellets were sintered at 850 ^{o}C for 15 min.

The green tape pellets sintering shrinkage in X/Y and Z directions were calculated by the following equation:

$$\text{Shrinkage rate} = \frac{D_1 - D_0}{D_0} \tag{2}$$

where the D_0 and D_1 denote the dimension of the pellets before and after sintering, respectively. To confirm the co-fired compatibility between the LTCC green tape and silver, the microstructures of sintered samples were analyzed by the field emission scanning electron microscopy, and SEM (SSX-550, Shimadzu, Japan) with EDS analysis. The thermal conductivity of the sintered samples was measured by the laser heat conduction instrument (LFA457, Netzsch, Deutschland). The flexural strength of the sintered samples was measured in the three-point blending method with the Precision Universal Tester (AGS-X, Shimadzu, Japan).

3 Result and discussion

3.1 Crystallization behavior and microstructure

Figure 1 illustrated the XRD patterns of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic added with 15 wt% CBS glass (CBS1 and CBS2) sintered at 850 °C for 15 min. In CBS1 glass added samples, all the main peaks can be indexed in terms of $LiMgPO_4$, whereas some minor peaks at 26°, 27° and 29° were recognized as $CaSiO_3$ (JCPDS# 42-0547) phases. Mg^{2+} was substituted by Zn^{2+} into the crystal structure of $LiMgPO_4$ to a certain degree because the similar ionic radius between Mg^{2+} (0.72 Å, CN=6) and Zn^{2+} (0.74 Å, CN=6) was consistent with the research result of Thomas. The reported CaO-B_2O_3-SiO_2 ternary system contained two species of tetrahedron structure: $[BO_4]$ and $[SiO_4]$, where the higher bond strength of $[SiO_4]$ than that of $[BO_4]$ made it combine with the free Ca^{2+} initially and generated as $CaSiO_3$ phase, and then the residual Ca^{2+} and $[BO_4]$ to form CaB_2O_4 phase. It was observed the $CaSiO_3$ phase and CaB_2O_4 (JCPDS#30-0155) phase can both exist in CBS2 glass added sample which affirmed that more content of boron in CBS glass tended to be crystallized as CaB_2O_4 phase. This crystallization behavior can explain the reason why CBS2 glass added samples have more CaB_2O_4 than that of CBS1 glass.

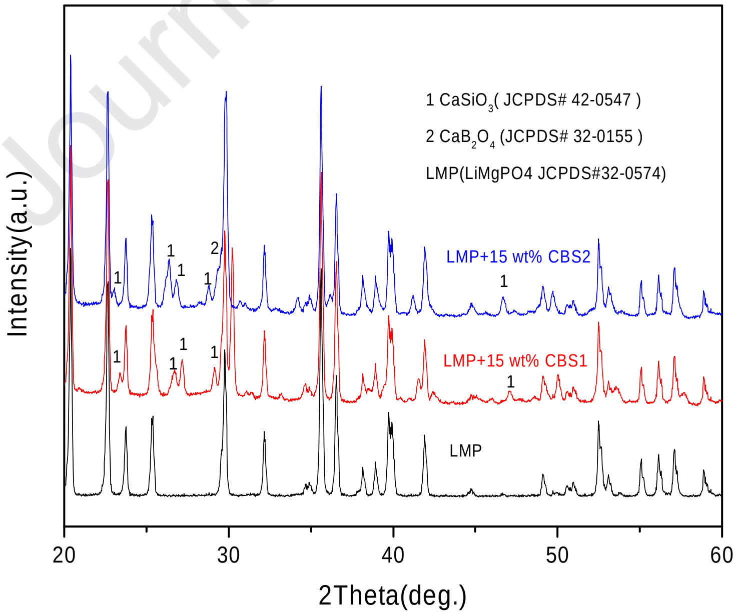


Figure 1 XRD patterns of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic added with 15 wt% CBS glass(CBS1 or CBS2) sintered at 850 °C for 15 min.

Figure 2 depicts the XRD patterns of $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt%CBS2 composite sintered at 700 °C-850 °C for 15 min. It can be observed that all the diffraction peaks are $LiMg_{0.9}Zn_{0.1}PO_4$ without any secondary phase when the composite is fired at 700

°C-750 °C. The $CaSiO_3$ and CaB_2O_4 phases appear in succession when the firing temperature is up to 800 °C and 850 °C, indicating the crystallization temperature of $CaSiO_3$ and CaB_2O_4 are in the range of 750 °C-800 °C, and 800 °C-850 °C, respectively. The DSC curves in Fig. 3 illustrate the T_g and T_c point of $LiMg_{0.9}Zn_{0.1}PO_4$-CBS glass composite. It can be observed both CBS glass added samples have two exothermic peaks which corresponded to the crystallization peaks of $CaSiO_3$ and CaB_2O_4. The second exothermic peak of CBS1 added samples was gentler and narrower than that of CBS2, which can be affiliated to the less crystallization tendency of CaB_2O_4 phase in boron insufficient glass. However, this difference in crystallization behavior may influence the sinterability and microwave dielectric property of the ceramic.

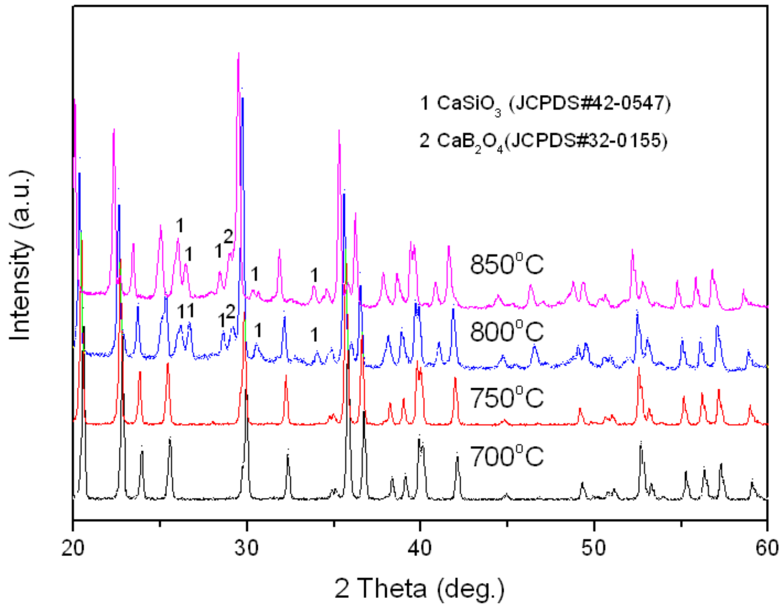


Figure 2 XRD patterns of $LiMg_{0.9}Zn_{0.1}PO_4$ -15 wt% CBS2 composite sintered at 700 °C-850 °C for 15 min.

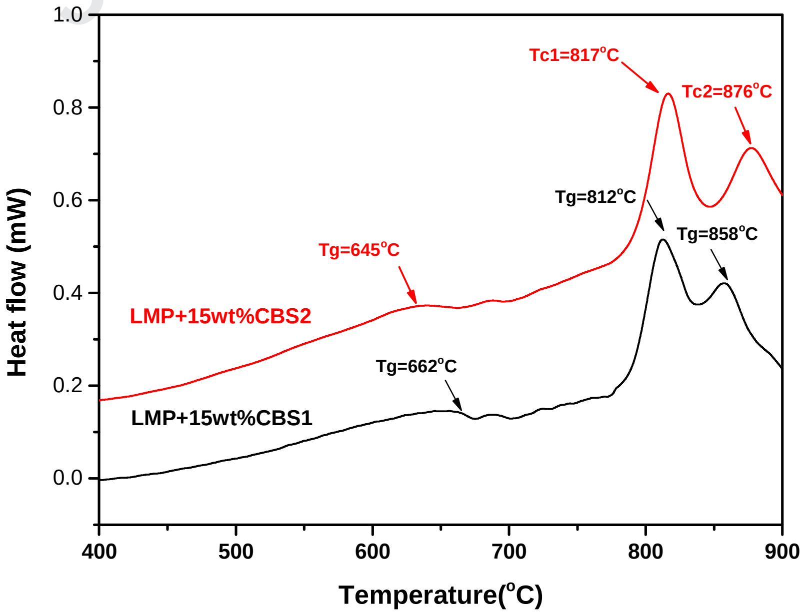
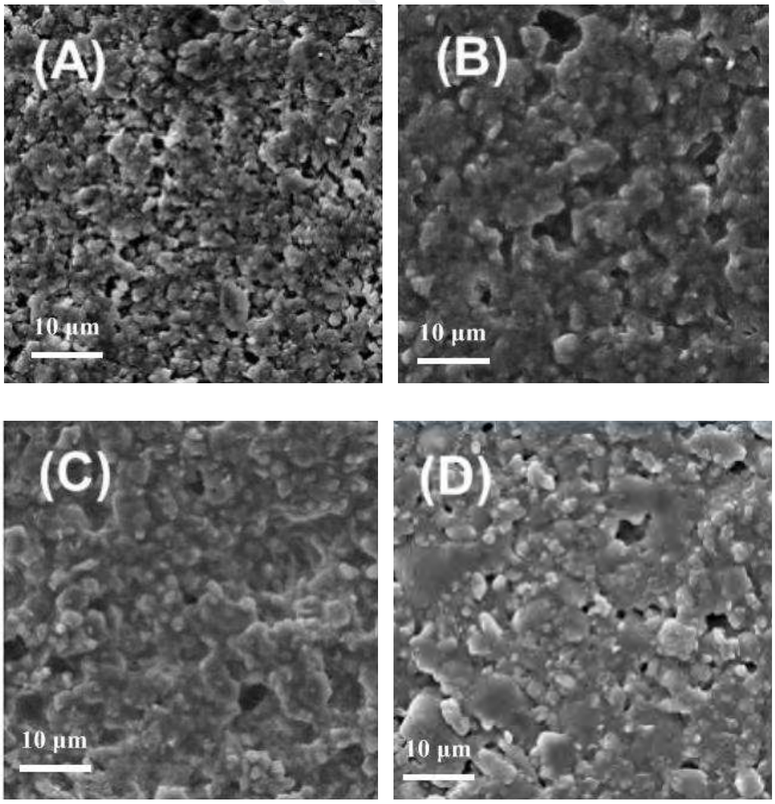


Figure 3 DSC curves of $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS glass composite.

Figure 4 illustrates the microstructure of $LiMg_{0.9}Zn_{0.1}PO_4$-x wt% CBS ceramics sintered at 850 ^oC for 15 min. Fig.4 (A-D) indicate the grain morphology of the $LiMg_{0.9}Zn_{0.1}PO_4$ specimens added with different CBS1 content and sintered at 850 ^oC. It could be observed many pores remained in the specimen (Fig. 4 (A)) with 5 wt% CBS1 glass owing to an insufficient densification. The specimens were found to be denser when increasing the glass content to 10 wt% and 15 wt%, and the porosity of the samples decreased at the same time. It is indicated that the liquid phase can not only improve the densification behavior by speeding up the particle rearrangement at the early period of sintering and mass transportation at the middle period of sintering, but also can slightly promote the grain growth[12,13]. Fig. 4(E-F) show the microstructure of $LiMg_{0.9}Zn_{0.1}PO_4$ added with 15 wt % and 20 wt % CBS2 glass. All the samples showed a relatively compact structure and pores can be rarely observed. With the same content of added glass , the sample with CBS2 (Fig. 4(E)) glass had a denser microstructure than that of CBS1 (Fig. 4(C)), which meant the different glass had different effects on the densification of the ceramic. Furthermore, it was calculated based on Fig. 3 that the $\Delta T(T_c\text{-}T_g)$ of CBS1 glass added sample was 50 ^oC as well as the ΔT of CBS2 glass added sample was 72 ^oC. More content of boron in CBS2 glass may have a relatively larger region of the liquid phase, which may give the higher driving force in the densification progress of the ceramic.



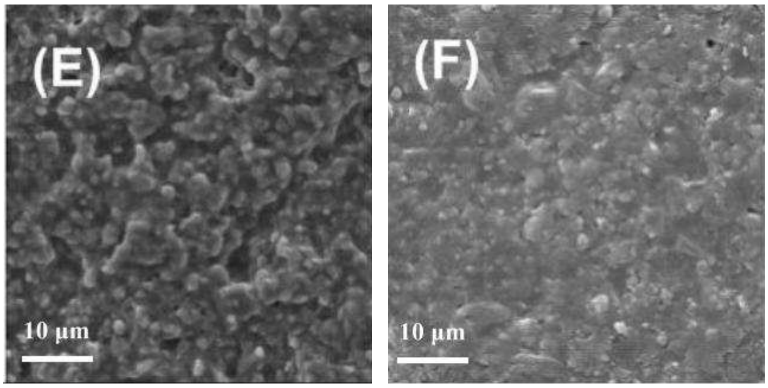


Figure 4 SEM micrographs of $LiMg_{0.9}Zn_{0.1}PO_4$ -x wt% CBS ceramic: (A)x=5, CBS1; (B)x=10, CBS1; (C)x=15, CBS1; (D)x=20, CBS1; (E)x=15, CBS2; (F)x=20, CBS2 sintered at 850 °C for 15 min.

3.2 Sinterability and dielectric properties

The shrinkage rate of the $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic with different amounts CBS1 glass additions is given in Figure 5. It can be seen that the shrinkage rate was linearly changed by increasing the sintering temperature from 700 °C to 850 °C, and then decreased when the firing temperature was 900 °C. This tendency towards variation may be explained by the increasing amount of the low-melting-point liquid phases caused by elevating the firing temperature. The liquid phase can speed up the densification of the ceramic, which can decrease the sintering temperature of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic from 950 °C to 850 °C. However, the crystallization of the glass increased the viscosity of the liquid phase, which may obstruct the densification process of the ceramic. The shrinkage rate was increased by raising the glass content, and the compact sintered samples can be achieved when x value was 15 wt% -20 wt%, which echoed with the microstructure of the sintered samples.

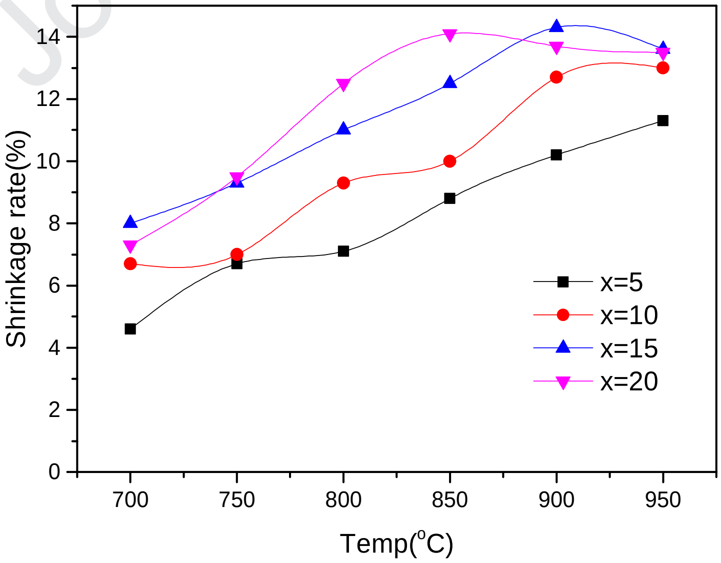


Figure 5 Shrinkage rates of the $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic with different amounts of CBS1 glass added.

Figure 6 shows the ε_r and Q×f values of $LiMg_{0.9}Zn_{0.1}PO_4$-x wt% CBS (CBS1 and CBS2, x=5-20) sintered at 800 ^oC -850 ^oC as a function of the x value. The dielectric constant ε_r of the ceramics initially increased with the content of glass and then began to decrease, which was similar to the trend of the shrinkage rate of the ceramic(Fig. 5). The dielectric permittivity also increased by increasing the sintering temperature from 800 ^oC to 850 ^oC. This permittivity behavior can be ascribed to the reduced porosity of the samples. The pores filled with air can effectively reduce the relative permittivity ε_r of the ceramic[14, 15]. It can be observed that the permittivity values of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic added by CBS2 are higher than the one added of CBS1 when the samples were sintered at 850 ^oC. However, permittivity values of samples sintered at 800 ^oC exhibited the opposite results. This is basically ascribed to the mixing rule of dielectrics as expressed by the Maxwell-Wagner's equation, while the ε_r values of $LiMg_{0.9}Zn_{0.1}PO_4$, $CaSiO_3$ and CaB_2O_4 ceramic were approximately 6.8, 5.0 and 7.2, respectively[16].

The τ_f value of $LiMg_{0.9}Zn_{0.1}PO_4$-x wt% CBS2 sintered at 850 ^oC was measured in the range from -55 ppm/^oC to -45 ppm/^oC. The variation of the τ_f value was not obvious probably due to the similar τ_f value of $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic and the CBS glass. However, compared with commercial LTCC substrate materials such as A6M (~ -54 ppm/^oC) and 9K7 (~ -67 ppm/^oC), τ_f value of $LiMg_{0.9}Zn_{0.1}PO_4$-CBS2 glass composite can satisfy the requirements of LTCC substrate materials. The Q×f value of $LiMg_{0.9}Zn_{0.1}PO_4$-x wt% CBS is shown in Fig 5(B). It can be observed that the Q×f value was highly depending on the sintering temperature of the ceramic, the maximum Q×f value was ~ 21,500 GHz when the sintering temperature was 800 ^oC, and then it went to ~ 40,000 GHz when the sintering temperature was 850 ^oC. It may be explained that the relatively high density and compact microstructure of the sintered body made contributions to the relatively low loss. Furthermore, the crystallization of silicate and borate in the ceramic also enhanced the Q×f value. However, Q×f value of the optimized composition was still less than that of $LiMg_{0.9}Zn_{0.1}PO_4$ reported by Thomas, among which the increased dielectric loss possibly resulted from the residual glass phase. Additionally, the ceramic of $LiMg_{0.9}Zn_{0.1}PO_4$ with 15 wt% CBS2 glass added sintered at 850 ^oC for 15 min demonstrated the best microwave dielectric properties of: ε_r value ~6.7, Q×f value ~ 40,100 GHz and τ_f value of -44 ppm/^oC.

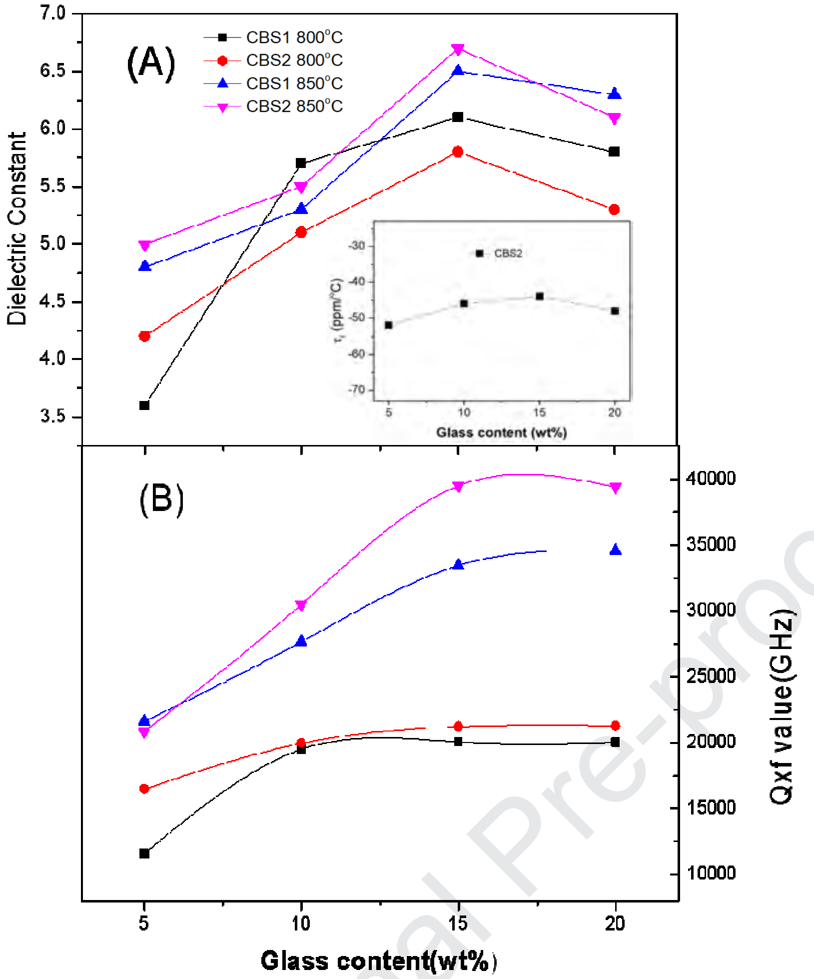


Figure 6 ε_r , Q×f and τ_f values of $LiMg_{0.9}Zn_{0.1}PO_4$-x wt%CBS (CBS1 and CBS2, x=5-20) ceramics sintered at 800 °C-850 °C as a function of the x value.

To further investigate the dielectric properties of $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 LTCC material in different frequencies, samples of different dimensions were prepared for the measurement and the results are shown in Table 1. It can be seen the present $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 LTCC material exhibited an excellent microwave dielectric properties in a wide range of frequency. Moreover, the dielectric properties of some commercial LTCC substrate material are given in Table 2. Compared to those commercial materials, the relatively low dielectric constant value and low dielectric loss of $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 ceramic are regarded as a promising LTCC substrate material.

Table 1 Relative dielectric constant and loss tangent for $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 ceramic sample measured at different frequencies.

Frequency	1MHz	1GHz	10 GHz	15GHz
ε_r	7.1	7.0	6.8	6.7
tan $\delta(\times 10^{-4})$	1.3	2.2	3.4	3.9

Table 2 Comparison of microwave dielectric properties of the present work with

commercial LTCC substrate materials.

Suppliers	Compositions	ε_r	tan δ	Sintering temperature
Ferro	A6M (CaO-B_2O_3-SiO_2)	5.9	≤0.002 (1-100 GHz)	850 ^oC
DuPont	951(Al_2O_3+Glass)	7.8	≤0.014(10 GHz)	850 ^oC
	9k7(Al_2O_3+Glass)	7.1	≤0.0009(10 GHz)	850 ^oC
Heraeus	HL2000	7.3	≤0.0026 (2.5 GHz)	850 ^oC
Kyocera	GL330	7.7	≤0.0004 (2 GHz)	880 ^oC
Murata	LFC(CaO-Al_2O_3-SiO_2-B_2O_3+Al_2O_3)	7.7	≤0.004 (6 GHz)	880 ^oC
This work	$LiMg_{0.9}Zn_{0.1}PO_4$-15wt% CBS2	6.7	≤0.00039 (15 GHz)	850 ^oC

3.3 Green tapes and substrate properties

The composition of $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 was selected for the tape casting, and the amount of additive was calculated according to the composite density and particle size shown in Table 3.The optimal fine slurry was carried out during the casting trials to obtain high quality tapes[17, 18]. The green tape appeared to be dense and exhibited the good processing abilities during punching, printing and laminating processes. Ten-layer green tapes printed with testing patterns of Ag pastes were laminated and co-fired at optimized sintering curves shown in Fig. 7. It can be seen from Fig. 7(d) that the border between the ceramic and the Ag conductor line was quite clear and no inter-diffusion was observed. A more detailed microstructure of the sintered and co-fired substrates with Ag electrode was presented in Fig. 8. The sintered ceramic appeared to be dense and homogeneous with the removal of all organic additives. The Ag line and the ceramic can be distinguished obviously in the cross-section microstructure of the substrate. The thickness of the Ag line was about 7 μm and the dielectric layer was about 110 μm. The Energy-Dispersive X-Ray Spectrum (EDS) line map shown in Fig. 8(b) further confirmed that there was no diffusion of the electrode into the ceramic. These results indicated the good chemical compatibility between the electrode and the ceramic in the multilayer ceramic substrate.

Table 3 Optimized slurry compositions for the ceramic-glass mixtures.

Materials			Compositions (wt %)
Filler ceramic-glass mixture	Density(g/cm^3)	D_{50} (μm)	
$LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2	2.81	2.35	67
Solvent (50 wt% ethanol+50 wt% isopropanol)			17
Binder(PVB B60H)			11
Plasticizer-1(triethanolamine)			2
Plasticizer-2(polyethylene glycol)			3

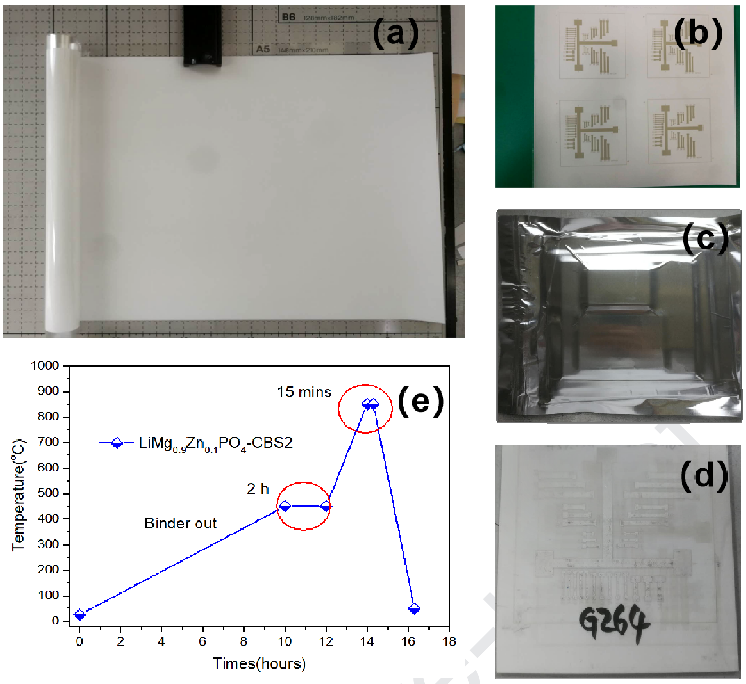


Figure 7 Photographs of (a) the cast green tape, (b) screen printed, (c) isostatically laminated and pressed multilayer in a vacuum package, (e) the final sintered multilayer substrate sample, and (f) the sintering curves.

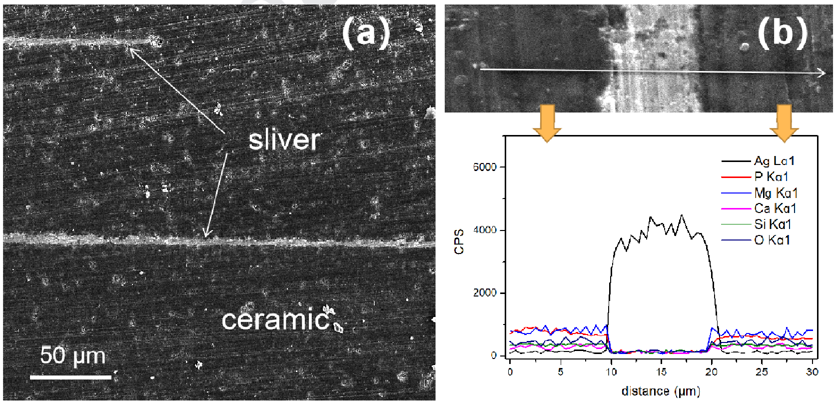


Figure 8 SEM images of (a) the cross-section microstructure of the ceramic and the silver (b) EDS line mapping of the ceramic-metal interface.

The sintered substrate was calculated with the shrinkage rate of 15.5% in the X/Y direction and 17.5% in the Z direction. The shrinkage rate of the green tape sintered sample was bigger than that of powder uniaxially pressed one (14.4% in the X/Y direction) meaning the green tape sintered body has a much denser microstructure. The substrate exhibited the coefficient of thermal expansion (CTE value) of 8.5 ppm/^{o}C (25 ^{o}C-300 ^{o}C) and the maximum thermal conductivity of 5.6 W/M·K at 25 ^{o}C. It should be pointed out that most of the high frequency LTCC substrate materials are designed with their CTE values close to that of GaAs and silicon between 3 ppm/^{o}C -7 ppm/^{o}C, in order to accommodate the surface mounted chips[19]. However, in hybrid integrated circuits, most of the metals like Au, and Ag have CTE >10 ppm/^{o}C. $LiMg_{0.9}Zn_{0.1}PO_4$-15 wt% CBS2 based material has a suitable CTE value which can be accommodated with the use of the package substrate. Additionally, the flexural strength of the ceramic was tested at 180 MPa and the superior flatness showed this material was suitable for the application of hybrid integrated circuits substrate.

4 Conclusion

The glass-ceramic based on $CaO-B_2O_3-SiO_2$ (CBS) glass composition was studied as an alternative LTCC material after mixing with $LiMg_{0.9}$Zn0.1PO_4 ceramic. The CBS glass addition can effectively improve the densification of the $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic in the initial stage of the sintering, and then crystallized as low loss $CaSiO_3$ and CaB_2O_4 phases with the excellent microwave dielectric properties. The $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic with 15 wt% CBS2 glass additions can be co-fired with the silver paste at 850 ^{o}C, exhibiting the ε_r value ~6.7, tan δ ~0.00039 at 15 GHz and τ_f value of -44 ppm/^{o}C. The LTCC green tape based on the optimized $LiMg_{0.9}Zn_{0.1}PO_4$-CBS2 glass composite composition was obtained by the standard tape-casting process. The sintered ceramic exhibited the mechanical properties of CTE value ~ 8.5 ppm/^{o}C (25 ^{o}C-300 ^{o}C), the maximum thermal conductivity 5.6 W/M·K at 25 ^{o}C and the flexural strength 180 MPa. Moreover, the substrate could be co-fired with the embedded Ag electrode, revealing it was a promising LTCC substrate material.

References

[1] M. T. Sbeastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review. Int. Mater. Rev. **53(2)**, 57–90 (2008).

[2] O. Dernovsek, M. Eberstein, W.A. Schiller, LTCC glass-ceramic composites for microwave application, J. Eur. Ceram. Soc. **21**(10), 1693–1697 (2001).

[3] J. H. Jean, C. R. Chang, Interfacial reaction kinetics between silver and ceramic-filled glass substrate, J. Am. Ceram. Soc. **87**, 1287–1293 (2004).

[4] M. Ma, Z. Liu, F. Zhang, F. Liu, Y. Li, R. Bordia, Suppression of silver diffusion in borosilicate glass-based low-temperature cofired ceramics by copper oxide addition, J. Am. Ceram. Soc. **99**, 2402–2407(2016) .

[5] S. F. Wang, Y. R. Wang, Y. F. Hsu, C. C. Chiang, Densification and microwave dielectric behaviors of $CaO–B_2O_3–SiO_2$ glass–ceramics prepared from a binary glass composite, J. Alloy. Compd. **498**, 211–216 (2010).

[6] S. H. Kweon , M. R. Joung, J. S. Kim, Low temperature sintering and microwave dielectric properties of B_2O_3-added $LiAlSiO_4$ ceramic, J. Am. Ceram. Soc. **94**, 1995-1998(2011).

[7] D. Thomas, M. T. Sebastian, Temperature-compensated $LiMgPO_4$: a new glass-free low-temperature cofired ceramic, J. Am. Ceram. Soc. **93**,

3828-3831(2010).

[8] D. Thomas, M. T. Sebastian, Effect of Zn^{2+} substitution on the microwave dielectric properties of LiMgPO4 and the development of a new temperature stable Glass Free LTCC, J. Eur. Ceram. Soc. **32**, 2359-64(2012).

[9] D. Thomas, P. Abhilash, M. T. Sebastian, Casting and characterization of $LiMgPO_4$ glass free LTCC tape for microwave applications, J. Eur. Ceram. Soc. **33**, 87-93(2013).

[10] B. W. Hakki, P. D. Coleman, A dielectric resonant method of measuring inductive capacitance in the millimeter range, IEEE Trans. Microwave Theory Technol. **8**,402-410(1960).

[11] W. E. Courtney, Analysis and evaluation of a method of measuring the complexpermittivity and permeability of microwave insulators, IEEE Trans. Microwave Theory Technol. **18**,476-485(1970).

[10] C. Chiang, S. F. Wang, Y. R. Wang, Characterizations of $CaO–B_2O_3–SiO_2$ glass–ceramics: thermal and electrical properties, J. Alloy. Compd. **461(1–2)**, 612–616 (2008).

[12] H. F. Zhou, X. L. Chen, L. Fang, et al, Microwave dielectric properties of $LiBiW_2O_8$ ceramics with low sintering temperature, J. Am. Ceram. Soc. **93**, 3976-3979(2010).

[13] B. J. Jeong, M. R. Joung , S. H. Kweon, Effect of Bi_2O_3 doping on the sintering temperature and microwave dielectric properties of $LiAlSiO_4$ ceramics, J. Am. Ceram. Soc. **95**, 1811-1813(2012).

[14] A. Bittner, U. Schmid, The porosifification of fifired LTCC substrates by applying a wet chemical etching procedure, J. Eur. Ceram. Soc. **29**, 99–104(2009).

[15]] F. Steinhäußer, K. Hradil, S. Schwarz, W. Artner, M. Stöger-Pollach, A. Steiger-Thirsfeld, A. Bittner, U. Schmid, Wet chemical porosifification of LTCC in phosphoric acid: anorthite forming tapes, J. Eur. Ceram. Soc. **35** 4181–4188(2015).

[16] X. Zhou, E. Li, S. Yang, Effects of $La_2O_3–B_2O_3$ on the flexural strength and microwave dielectric properties of low temperature co-fired $CaO–B_2O_3–SiO_2$ glass-ceramic, Ceram. Int. **38(7)**, 5551–5555 (2012).

[17] N. Joseph, J. Varghese, M. Teirikangas, T. Vahera, and H. Jantunen, Ultra-Low-Temperature Cofifired Ceramic Substrates with Low Residual Carbon for Next-Generation Microwave Applications, ACS Appl. Mater. Interfaces. **11**, 23798−23807 (2019).

[18] J. Varghese, P. Ramachandran, M. Sobocinski, T. Vahera, and H. Jantunen, ULTCC Glass Composites Based on Rutile and Anatase with Cofifiring at 400 °C for High Frequency Applications, ACS Sustainable Chem. Eng. **7**, 4274−4283 (2019).

[19] S. Arun, M. T. Sebastian, K. P. Surendran, $Li_2ZnTi_3O_8$ based high k LTCC tapes for improved thermal management in hybrid circuit applications, Ceram. Int. **43**, 5551–5555 (2017).

Highlights

1. This paper gives the method of fabricating the LTCC substrate material which the crystallizable glass which can remarkably enhance the sinterability and dielectric property of ceramic host.

2. The ideal content of the liquid phase and crystallized low-loss phase generated in $CaO-B_2O_3-SiO_2$ glass by regulating the B_2O_3 content may co-work in the glass ceramic system.

3. The glass ceramic can be co-fired with inner or exterior Ag electrode in a grimly conditions with 850 ^{o}C for 15 min showed a dense microstructure.

4. The green tape was cast with the homogeneous slurry and then printed, laminated and sintered by the standard LTCC substrate manufacturing process. The sintered ceramic show the coefficient of thermal expansion (CTE value) of 8.5 ppm/^{o}C (25 ^{o}C-300 ^{o}C), the maximum thermal conductivity of 5.6 W/M·K at 25 ^{o}C and the flexural strength of 180 MPa.

Declaration of interest statement

We declared that there have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Yours sincerely

Yang Lv.