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Effects of the ZBS addition on the sintering behavior and microwave dielectric properties of $0.95Zn_2SiO_4$-$0.05CaTiO_3$ ceramics

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Abstract:

The effects of zinc borosilicate addition (denoted as ZBS) on densification and dielectric properties of a binary composite of Zn_2SiO_4-$CaTiO_3$ (denoted as ZSCT) ceramics have been investigated as a function of ZBS content and sintering temperature. Densities of the specimens were enhanced with an increase of ZBS and then decreased. High-density ZSCT+20.0wt%ZBS sintered at 925°C showed promising microwave dielectric properties: relative dielectric constant (ε_r)=7, quality factor ($Q\times f$)= 19,265GHz at 15.5 GHz, and temperature coefficient of resonant frequency (τ_f)=-21 ppm/°C, which demonstrated a potential candidate for application of low temperature co-fired ceramics field in millimeters and THz range.

1. Introduction

The ongoing development of modern communication technology, such as high density, high RF and fast digital applications requiring hermetical packaging and good thermal management, has pushed the continuing miniaturization of microwave devices. Recently, low temperature cofired ceramics (LTCC) multilayer devices have

been intensively investigated to reduce device size by enabling a significant number of circuit components to be integrated within a module in a multilayer substrate[1][2][3]. In LTCC, a low sintering temperature lower than the melting point of metal electrodes (961°C for Ag) is critical instead of using more expensive electrodes such as Ag-Pd binary or Pt-Pd-Au ternary alloys. Unfortunately, most of well-known microwave ceramics with good dielectric properties in the microwave range need high sintering temperatures, which put it a constraint on LTCC application.

On the other hand, the utilizable frequency region has been expanded to millimeterwaves and even extends to THz band for the shortage of conventional frequency regions. Therefore, in the millimeterwave region or THz band, the permittivity ($\mathcal{E}_r$) value is expected to be small for no need for miniaturization and reducing time delay[4]. However, the lack of advanced materials in the millimeterwaves and THz band is a major constraining factor. Among the low $\mathcal{E}_r$ materials, Zn_2SiO_4 ceramics are particularly promising candidates[5] because of high quality factor ($Q \times f$) value and adjustable temperature coefficient of resonant frequency. But they were produced by the cold isostatic press (CIP) method, which cannot be used for mass production and the high sintering temperature (~1,300°C) is an another limitation for its application in LTCC technology[6][7][8].

In this study, the microwave dielectric ceramics based on Zn_2SiO_4 was chosen as the host material. To compensate the τ_f value (-61 ppm/°C) of ZS ceramics[5], $CaTiO_3$ with positive τ_f value (+859 ppm/°C)[9][10] was added to form a composition of

$0.95Zn_2SiO_4$+$0.05CaTiO_3$ ceramics [11] with near-zero τ_f value and the ε_r values are below 7.4, which are lower than that of other Zn_2SiO_4 systems with near-zero τ_f value[12]. Zinc borosilicate glass used as sintering agent are the most commonly used glass materials in glass/ceramic composites for microelectronic packaging[13]. In this work, the densification and microwave dielectrics of ZSCT with different amount of ZBS addition were investigated. The intention of this study is to systematically investigate the dielectric properties of ZBS doped ZSCT ceramics prepared by solid-state reaction method and consider the possibility of the ceramics in modern electronic systems for LTCC application. Since the results of the study greatly depend on the quality of the ceramics, emphasis has been placed on the relationship between microwave dielectrics properties of ZSCT ceramics with different ZBS and the sintering temperature.

2. Experimental procedure

The ZBS addition with the composition of 60.0%ZnO, 30.0%B_2O_3, and 10.0%SiO_2 (in mol) was directly mixed with high-purity oxides, ZnO (99%), SiO_2 (99%), B_2O_3(99%) from the West Long Chemical Co., Ltd., Guangdong, China. Zn_2SiO_4 and $CaTiO_3$ compounds were individually synthesized by a conventional solid-state reaction method through using analytical-grade oxide powders(>99.99%) of ZnO, SiO_2, TiO_2,$CaCO_3$ as starting materials. They were mixed according to the nominal composition Zn_2SiO_4 (denoted as ZS), $CaTiO_3$ (denoted as CT), respectively, and ball-milled in a polyethylene bottle with agate balls using distilled water as a medium. The mixture was then dried and calcined at 1150□ and 1100□ for 2h respectively.

The calcined powders were re-milled for 4h according to the desired composition: $0.95Zn_2SiO_4$-$0.05CaTiO_3$ doped with different contents (5wt.%, 10.0wt%, 15wt.% and 20wt.%) of ZBS addition. The powder mixture, with poly vinyl alcohol (PVA) as an organic binder(0.70wt.%) and granulated was subsequently uniaxially pressed into cylindrical compacts 13mm in diameter and 5.2-6.8mm in thickness using a uniaxial press (200 MPa). The green pellets were heated at 1.5°C/min up to 600°C and held for 1h to remove the binder. The samples were sintered at 855-1065°C for 2h with a heating rate of 5°C /min in air after de-binding, and then cooled to room temperature.

The bulk density of the sintered samples was measured by the Archimedes' method using distilled water as the immersion medium. The crystalline phase and microstructure were determined by X-ray powder diffraction(XRPD). Two-theta scans between 10° and 80° were determined by a Bruker-AxsD8 diffractometer using Cu-Kα radiation at a scan rate of 1° min^{-1}, operated at 40 kV and 40 mA. The microstructure observation and an energy dispersive spectra (EDS) were performed from the fractured surface by scanning electron microscopy (SEM; Hitachi SU70, Japan).

The dielectric constants and unloaded Q values were measured in the TE_{011} mode using the Hakki and Coleman method[14], where a cylindrically shaped specimen is positioned between two silver plates. An E8362B network analyzer was used as the measuring system. The temperature coefficient of frequency (τ_f) values were evaluated in the temperature range between 20 and 80°C, and were calculated by the following equations:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times 60} \times 10^6 (\text{ppm}/^\circ\text{C}) \qquad (1);$$

Where *f* represent the resonant frequency. Subscripts of 20 and 80 are referred to the testing temperature, respectively.

3. Results and discussion

Fig.1 shows the XRD patterns of the ZSCT+*x*wt.%ZBS ceramics with 5.0≤*x*≤ 20.0, sintered at various temperatures for 2h. It is clearly observed that the peaks of all the samples annealed at various temperatures are good match with the standard ICSD card for Zn_2SiO_4 (no.37-1485, willemite) and $CaTiO_3$ (no.82-0228, Perovskite) , as anticipated. The peaks indicated the presence of Zn_2SiO_4 as the main crystalline phase, and $CaTiO_3$ as the minor crystalline phase.

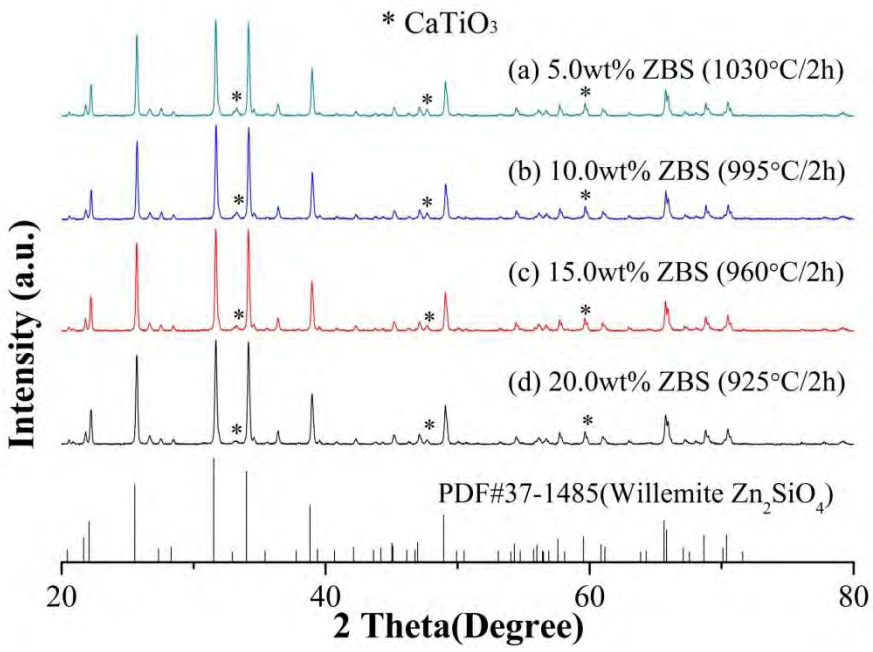


Fig.1 XRD patterns of $0.95Zn_2SiO_4$-$0.05CaTiO_3$ system with different contents of ZBS sintered at various temperatures: (a) 5.0wt%ZBS, sintered at 1030°C, (b) 10.0wt%ZBS, sintered at 995°C, (c) 15.0wt%ZBS, sintered at 960°C, (d) 20.0wt%ZBS, sintered at 925°C for 2h.

The relative density of ZSCT ceramics with various amount of ZBS addition at different sintering temperature for 2 h are shown in Fig.2. It appears that the density of samples with different content of addition ($5.0 \leq x \leq 20.0$) increased firstly, subsequently decreased with further increasing of sintering temperature. The results also demonstrate that the onset of densification mechanism for the specimens moves towards much lower temperatures with the addition of glasses. The densification temperature of ZSCT+*x*wt%ZBS (x=15,20) was around 960°C, while that of ZSCT+10.0wt%ZBS and ZSCT+5.0wt%ZBS were around 995°C and 1030°C respectively. This corresponded with the fact that the lowest pore density and the uniform grain size sintered at the densification temperature shown in Fig.3. Cross-sectional SEM images with backscattering mode in Fig.3 demonstrate that these specimens sintered at the densification temperature have dense microstructures. To further identify the minor crystalline phase ($CaTiO_3$) from the main crystalline phase(Zn_2SiO_4), EDX analysis was performed and the testing results of the ZSCT+5.0wt%ZBS ceramic sintered at 1030 °C for 2h are shown in table 1. According to the semi-quantitative molar ratio of Zn/Si, the large rounded-shape grains (1) were identified as Zn_2SiO_4 due to a Zn/Si ratio of about 2:1. The small square block-shape gains (2) were identified as $CaTiO_3$ due to a Ca/Ti ratio of about 1:1.

The densification mechanism of the composites can be explained as liquid-phase sintering by considering ZBS addition is uniformly dispersed in the glass phase matrix for the well wettability between the glass and ceramic powder[15][16], which could

act as lubrication during sintering process, wetting solid particles, and providing capillary pressure between them, thus resulting in a faster grain growth of ceramics[17]. However, the overquik grain growth would preclude the pore venting process as further increase sintering temperature and eventually decrease the relative density in ceramics.

The theoretical density (TD) of ZSCT was calculated by the following equation:

$$\rho = \frac{\nu 1 M 1 + \nu 2 M 2}{\nu 1 M 1 / \rho 1 + \nu 2 M 2 / \rho 2} \quad (2);$$

Where ρ, M and ν represent the theoretical density, mole mass and mole ratio, respectively, of each part of mixture. Subscripts of 1 and 2 are referred to the ZS and CT, respectively. Here, ν_1=0.95, ν_2=0.05; M_1=222.87g/mol, ρ_1=4.252g/cm^3 (estimated from JCPDS no. 37-1485); M_2=135.98 g/mol, ρ_2=4.030 g/cm^3 (estimated from JCPDS no. 82-0228). The TD value of $0.95Zn_2SiO_4$-$0.05CaTiO_3$ was 4.2447 g/cm^3 calculated by equation (2). For ZSCT+20.0wt%ZBS ceramics, the 94.5%, 96.2%, 96.9%, 97.2%, and 96.8% of TD were obtained with ease at 855, 890, 925, 960 and 995°C, respectively.

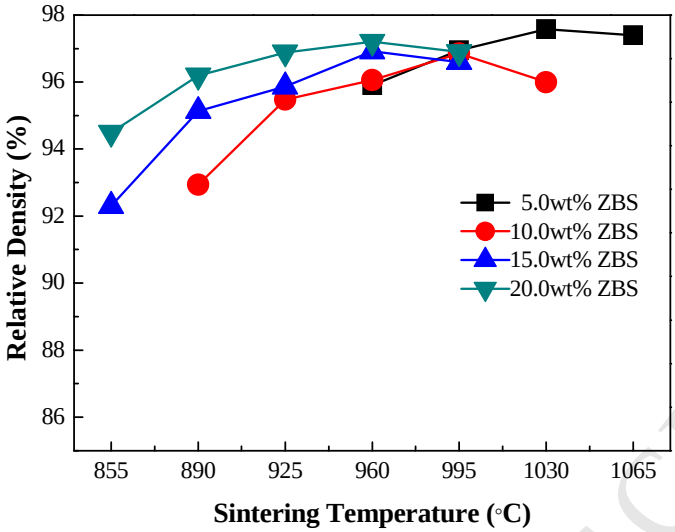


Fig.2 Relative density of the ZSCT+*x*wt.%ZBS ceramics as a function of sintering temperature and amount of ZBS addition

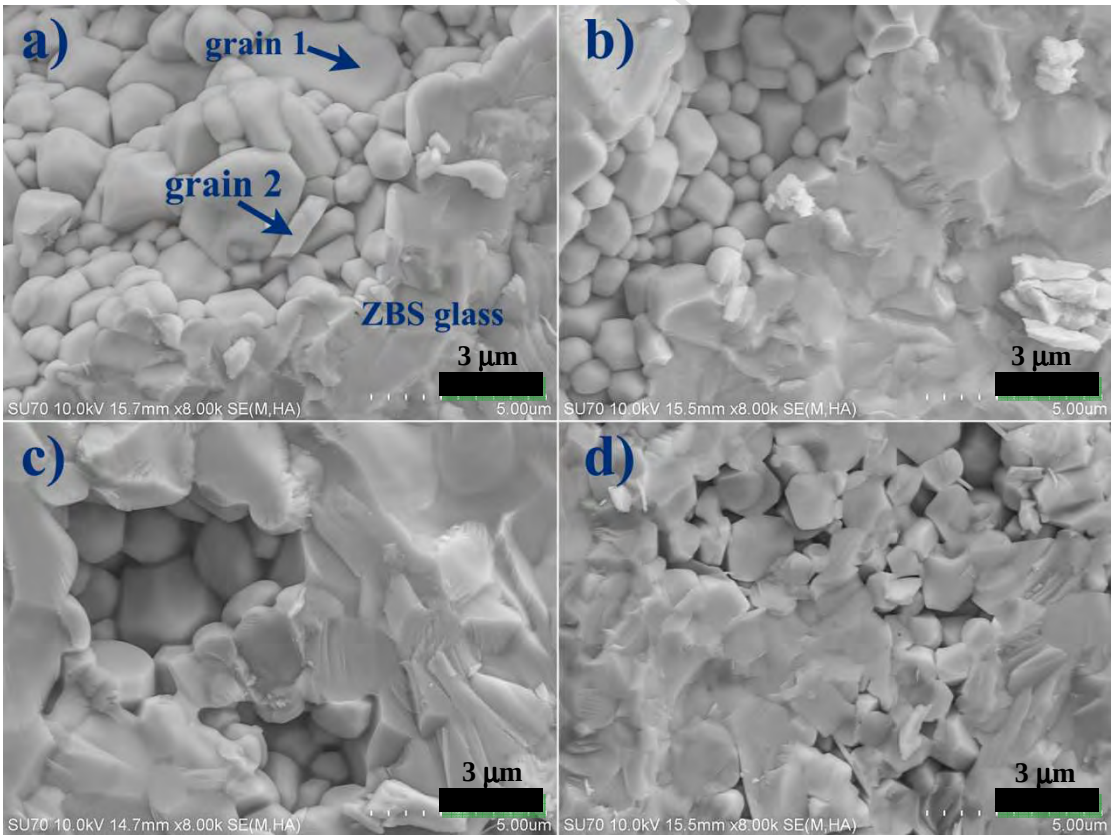


Fig.3 Cross-sectional scanning electron microscopy images of ZSCT+*x*wt.%ZBS ceramics with backscattering mode as a function of sintering temperature and amount of ZBS addition: (a)x=5, 1030°C /2h, (b)x=10, 995°C /2h, (c) x=15, 960°C /2h, (d)x=20, 925°C /2h.

Table 1

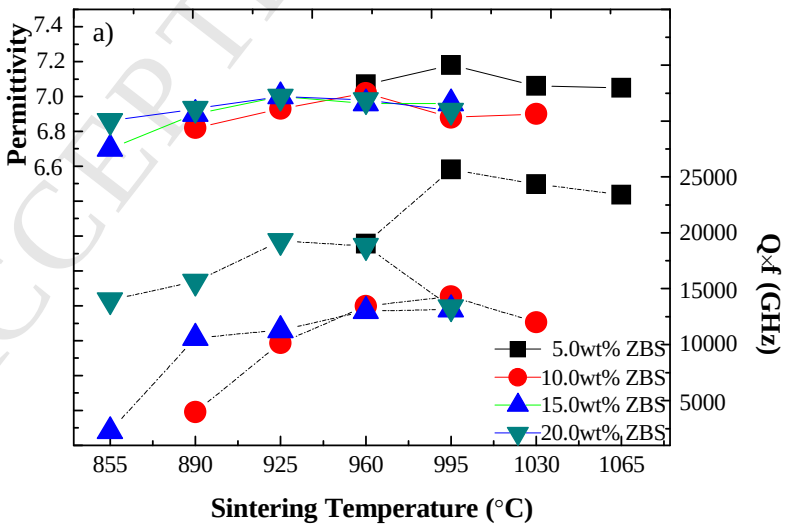
EDX analysis of ZSCT+5.0wt%ZBS ceramic sintered at 1030 °C for 2h.

	Grain 1	Grain 2
The two main elements A/B	Zn/Si	Ca/Ti
Molar ratio of A/B	1.96	0.94
Composition	Zn_2SiO_4	$CaTiO_3$

Fig.4 shows the ε_r, $Q\times f$, and τ_f values of the ZBS-doped ZSCT ceramics sintered at various temperatures for 2h. The ε_r and $Q\times f$ values of all specimens with different ZBS contents increased firstly, subsequently decreased with the increasing of sintering temperature, which displayed the same trend of relative density with the sintering temperature. However, the peak values of ε_r and $Q\times f$ appeared at a lower sintering temperature than that of relative density appeared which probably account for the formation of a large amount of liquid phase as sintering temperature above 900°C. Moreover, the maximum ε_r value of the ZBS-doped ZSCT ceramics decreased as the amount of ZBS increased for the higher ratio of glass with the relative low ε_r to ZSCT ceramics. According to Fig.4(a), the $Q\times f$ values of the sample doped with 20.wt%ZBS reached the maximum (19,265GHz at 15.5 GHz) when the sintering temperature was 925 °C and decreased monotonically with the increasing of sintering temperature. Similar trend was obtained for the specimens with 15.wt%ZBS and the maximum $Q\times f$ value (13,013GHz at 15.0 GHz) was obtained as the sintering temperature was 960 °C. Additionally, the $Q\times f$ value (25,674GHz at 14.8 GHz) of the ZSCT+5.0wt%ZBS ceramics were much larger than that of other samples, although the relatively high sintering temperature is beyond the range of LTCC. Generally, many factors are commonly believed to decide the microwave dielectric properties

and can be divided into two parts: the intrinsic loss and the extrinsic loss. Intrinsic loss is mainly caused by lattice vibration modes while extrinsic loss is dominated by lattice defect, crystallizability, cation ordering second phases, impurities, oxygen vacancies, inner stress, and densification or porosity. In ZSCT-ZBS system, it is difficult to determine the key influential factor, however, it's not doubt that the melting mechanism and the last exist micro-morphology of ZBS play crucial role in this system, especially for the ZSCT ceramic with large amount of ZBS addition.

The τ_f values of ZSCT ceramics with different ZBS contents sintered at various temperatures are depicted in Fig.4(b). It's obvious demonstrated that the τ_f value decreased apparently with the amount of ZBS addition increased. The variation of the τ_f values with different ZBS contents range between -2 and -21 ppm/°C and the τ_f value of specimen with 20.0wt% ZBS content sintered at 925°C is -21 ppm/°C.



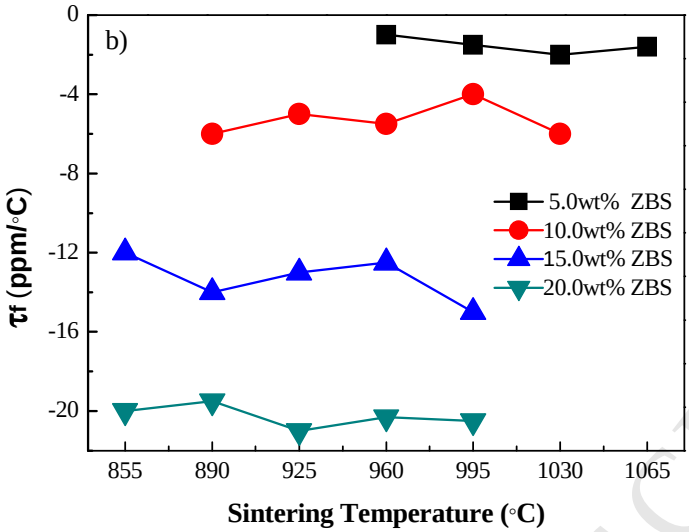


Fig.4 Variation of microwave dielectric properties of the ZSCT+*x*wt.%ZBS ceramics as a function of sintering temperature: (a) relative dielectric constant (ε_r) and Quality factor ($Q\times f$), (b) temperature coefficient of the resonant frequency (τ_f).

In order to investigate the reactivity between ZSCT and ZBS, green compacts of ZBS was placed on the top of porous ZSCT green pellets and cofired at 925°C for 2h in air. Fig.5 shows the samples before and after firing. ZBS showed nearly nonreactivity with ZSCT and a negligible reaction product could be found by interface SEM images in Fig.6. The phenomena confirm that the ZBS addition could be an excellent candidate for ZSCT LTCC. Furthermore, it is clearly observed that sintered ZBS possessed porous structure, which put constraints on the further improving microwave properties of ZSCT with a large amount of addition.

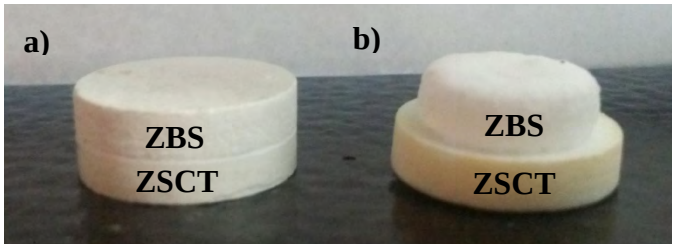


Fig.5 Compact of ZBS and ZSCT (a) before firing, (b) after firing at 925°C for 2h.

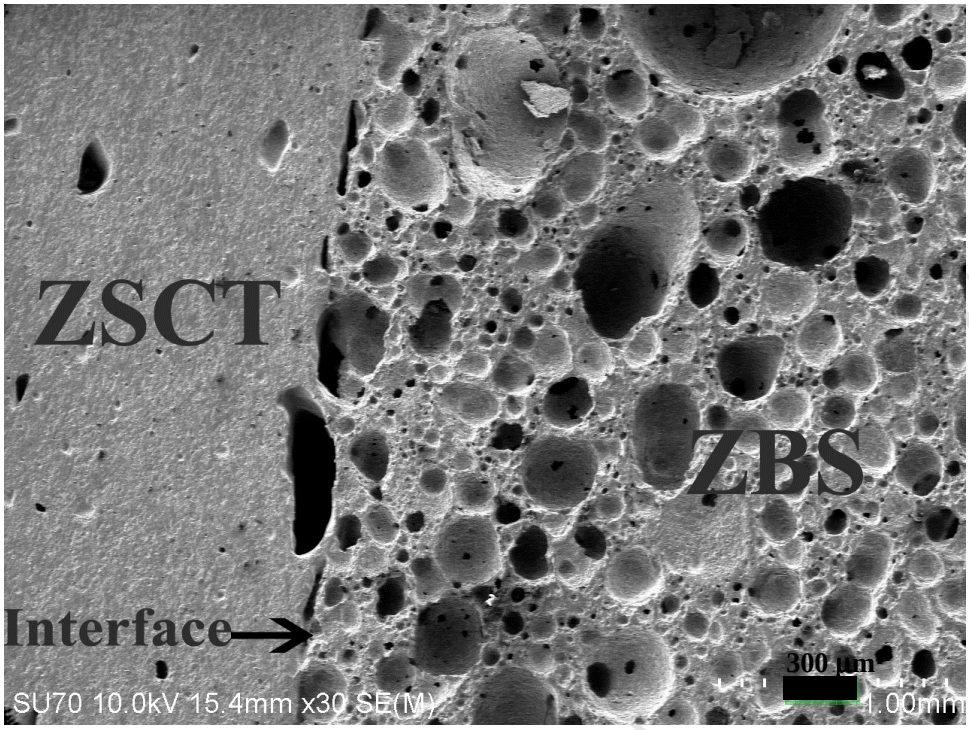


Fig.6 SEM micrographs of interface between ZSCT and ZBS after firing at 940°C for 2h.

4. Summary

The effects of zinc borosilicate addition (ZBS) on densification and dielectric properties of a binary composite of Zn_2SiO_4-$CaTiO_3$ (ZSCT) ceramics have been investigated as a function of ZBS content and sintering temperature. The results indicated that the onset of densification mechanism for the specimens moves towards much lower temperatures with the addition of glasses and the densities of the specimens were enhanced with an increase of ZBS and subsequently decreased. In addition, ZBS showed nearly nonreactivity with ZSCT and a negligible reaction product could be found. Moreover, high-density ZSCT+20.0wt%ZBS sintered at 925°C showed promising microwave dielectric properties: relative dielectric constant ($\mathcal{E}_r$)=7, quality factor ($Q\times f$)= 19,265GHz at 15.5 GHz, and temperature coefficient of resonant frequency (τ_f)=-21 ppm/°C, which demonstrated a potential candidate for

application of low temperature co-fired ceramics field in millimeters and THz range.

Acknowledgements

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1. High-density ZSCT ceramic was obtained with the sintering temperature below 950°C.

2. ZSCT ceramics with addition of ZBS show the well microwave properties in LTCC.

3. ZBS shows nearly nonreactivity with ZSCT and a negligible reaction product could be found.