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Sintering behavior and microwave performance of $CaSiO_3$ ceramics doped with $BaCu(B_2O_5)$ for LTCC applications

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ABSTRACT

$CaSiO_3$ (CS) ceramics exhibit excellent microwave performance as a microwave material, however, its sintering temperature is too high and limits its application in the microwave field. In this work, the densification process and microwave performance of the $BaCu(B_2O_5)$ (BCB) doped CS ceramics were researched. The results showed that the sintering temperature of CS ceramics can be lowered from 1340 °C to 930 °C by BCB additive. In order to obtain ceramic samples with excellent microwave properties and high density, adding 4 wt% BCB to CS ceramics was considered to be optimal. Under this formulation, BCB-CS ceramics sintered at low sintering temperatures (950 °C for 3 h), possessed outstanding microwave performance of $\varepsilon_r = 4.7$, $Q \times f = 34807.5\ GHz$, $\tau_f = -21.5\ ppm/°C$. Moreover, CS ceramics doped with BCB had a good chemical compatibility with silver powder, which indicated that BCB-CS ceramic was a prospective candidate for low temperature co-fired ceramic (LTCC) applications.

1. Introduction

Microwave materials have been commonly used in our lives nowadays, for instance, GPS, artificial intelligence, direct broadcast satellites and advanced wireless communication systems [1–3]. Recently, the applicable frequency region has been extended to millimeter waves [4]. To meet the requirement of millimeter-wave frequencies, microwave devices equipped with low dielectric constant (ε_r), high quality factor ($Q \times f$), and temperature coefficient of resonance frequency (τ_f) near zero are needed. These excellent microwave dielectric properties contribute to the miniaturisation of low temperature co-fired ceramic (LTCC) multilayer appliances. LTCC technology [5] has the advantages of high integration capability for passive devices, low cost and compatibility with Au, Ag or Cu. Among these electrodes, Ag is universally chosen in electronic products [6]. However, most microwave ceramic synthesis temperatures are higher than the melting point of silver [7,8], which may restrict its further application. Therefore, the microwave dielectric materials ought to be well sintered below 960 °C so as to be co-fired with the Ag electrode.

As it well known, $CaSiO_3$ (CS) ceramic has upstanding dielectric properties of low dielectric constant and low dielectric loss, which means $CaSiO_3$ ceramic is very likely used as candidate for LTCC applications. The density of $CaSiO_3$ ceramic sintered at 1340 °C could reach the maximum of 2.439 g/cm^3 obtained by Wang et al. [9]. They have found that $CaSiO_3$ ceramics synthesized by sintering nano-powders at 1000 °C, which exhibit excellent microwave performance: $\varepsilon_r = 6.69$, $Q \times f = 25398\ GHz$. However, the sintering conditions of pure CS ceramics are very harsh, the higher temperature and the higher porosity [10]. Wang et al. [4] prepared CS ceramics sintered at 1250 °C by adding Al_2O_3 with excellent microwave performance: $\varepsilon_r = 6.66$, $Q \times f = 24626\ GHz$. Unfortunately, it was far less than the requirements of LTCC technology. Adding low melting point additives to reduce sintering temperature is generally considered to be the simplest and most effective method [11–13]. SnO_2 can expand the calcining temperature range of $CaSiO_3$ ceramics remarkably, while the sintering temperature is still so high for LTCC applications [14]. TiO_2 reduces the sintering temperature associated with the degeneration of microwave properties [15]. Among the various low melting point additives, $BaCu(B_2O_5)$ (BCB) can greatly promote the sintering process of ceramics by virtue of its low melting point (850 °C) and excellent microwave

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performance: $\varepsilon_r = 7.4$, $Q \times f = 50000\ GHz$, $\tau_f = -32\ ppm/°C$[16,17]. Fang et al. prepared $Ca_{0.35}Li_{0.25}Nd_{0.35}Ti_{0.97}Al_{0.03}O_3$ ceramics with eximious microwave properties sintered at 950 °C doped with 5 wt% BCB [18]. MgO–$2B_2O_3$-4 wt% BCB ceramic was obtained by Zhou et al. sintered at 925 °C, which showed well microwave behavior with high of $Q \times f = 30589\ GHz$, low ε_r of 4.8 and $\tau_f = -40\ ppm/°C$[19]. $LaNbO_4$ ceramics with 1 wt% BCB were produced by Xiao et al. [20] at 925 °C and provided with preferable microwave dielectric properties: $\varepsilon_r = 21.2$, $Q \times f = 22600\ GHz$ and $\tau_f = 10.01\ ppm/°C$. These literature mentioned above indicate that BCB is an ideal sintering additive along with excellent microwave performance for LTCC.

In our work, we prepared BCB to modulate the sintering temperature of CS ceramics. The relationship between calcination performance and microwave behavior of BCB and CS ceramics was systematically studied. In addition, the chemical compatibility between CS ceramics and Ag electrodes was examined in detail.

2. Materials and methods

Raw materials included pure grade (>99%) powders of $CaCO_3$, SiO_2, H_3BO_3, $BaCO_3$, CuO, and all of them were purchased from the West Long Chemical Co. Ltd. Solid-state reaction method was selected to prepare CS and BCB. For the synthesis of BCB ceramic powder, H_3BO_3, $BaCO_3$ and CuO were mixed for 6 h by ball milling in a PTFE bottle with ethanol, the mixture was dried and subsequently calcined at 800 °C for 4 h. To synthesize the CS ceramic powder, the $CaCO_3$ and SiO_2 were mixed by ball milling with distilled water for 6 h, the mixture was dried and subsequently calcined at 1200 °C for 2 h. Thereafter, the CS powders were ball-milled again with different amount of BCB additive (1, 2, 4, 6, 8 wt%). After drying, powders were mixed with some 6 wt% PVA solution, and subsequently pressed at 130 MPa into pellets of 13 mm diameter and a height of 6.0–6.5 mm. These compacts were heated at 600 °C for 1 h to eliminate the PVA at a heating speed of 1.5 °C/min. Afterwards, pellets were calcined at 880–990 °C for 3 h at a heating speed of 5 °C/min in air and obtained x wt% BCB + CS ceramics (x = 1, 2, 4, 6, 8).

The bulk densities (ρ) of the ceramics were calculated by the Archimedes method, where meanwhile chose distilled water as medium and precision density balance(BS201S)was used with a precision of ± 0.0001 g/cm^3. X-ray diffractometer (XRD; Bruker-AxsD8, Germany, $CuK_{\alpha 1}$, 40 kV and 40 mA) was employed to determine the crystal structures of the pellets. The field-emission scanning electron microscopy (SEM, Hitachi SU70, Japan) was carried out to observe the surfaces microstructure of sintered specimens without polishing.

The Hakki-Coleman method [21], modified by Courtney [22], was applied to measure the microwave dielectric properties in the TE_{011} mode using the E8362B(Agilent, USA) network analyzer. The τ_f values between 20 and 80 °C were given by the following formula:

$$\tau_f = \frac{f_{80} - f_{20}}{60 \times f_{20}} \times 10^6 (ppm/°C) \quad (1)$$

where, f_{20} and f_{80} are the resonant frequencies at 20 °C and 80 °C, respectively.

The chemical compatibility of the BCB doped CS ceramics and Ag electrode was investigated by co-firing the 20 wt% Ag, 20 wt% BCB and CS powders at 880–950 °C for 3 h. The phase compositions and microstructure analysis were performed by XRD and SEM equipped with energy dispersive spectra analysis (EDX, Hitachi SU70, Japan).

3. Results and discussion

Fig. 1 demonstrates the XRD patterns of 4 wt% BCB + CS ceramics sintered at 880–990 °C. It can be readily seen from the figure that samples obtained at various temperatures exhibit a single calcium silicate phase without BCB phase occurred. That means the BCB liquid phase didn't crystallize at the sintering process and formed ultimately an amorphous phase. Similar phenomena can be traced in a number of related researches [23,24].

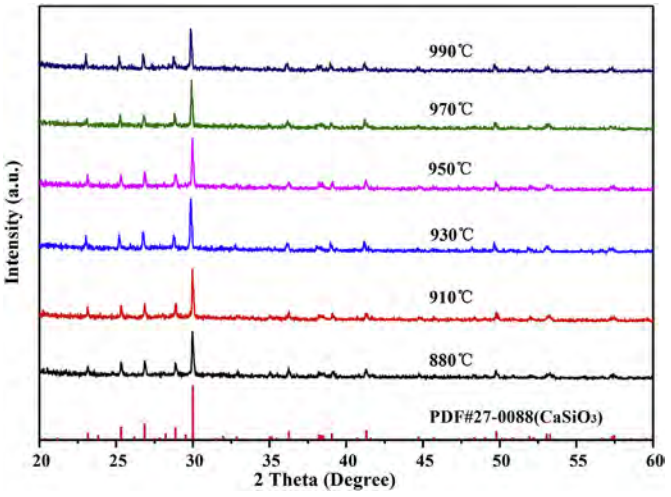

Fig. 1. XRD patterns of the 4 wt% BCB + CS ceramics sintered at 880 °C, 910 °C, 930 °C, 950 °C, 970 °C and 990 °C for 3 h.

Fig. 2 reveals the ρ, ε_r, $Q \times f$ and τ_f of CS ceramics with different contents of BCB calcined at diverse temperatures for 3 h. For all BCB-CS samples, the ceramic densities increased originally and decreased as the sintering temperature increases. Besides, the content of BCB had a significant impact on the density of CS, that is to say, the x ranged from 1 to 8 corresponding to the density of CS varied from 2.6071 g/cm^3 to 2.7735 g/cm^3 sintered at 880 °C. It should be noted that the theoretical density of BCB is 4.3 g/cm^3, while the theoretical density of CS is merely 2.9 g/cm^3. As the BCB content gradually increased, the onset of densification temperature of CS samples gradually decreased from 990 °C to 970 °C, 950 °C, 930 °C and 910 °C. This indicated that the capillary force formed by BCB liquid phase can promote the sintering progress. As shown in Fig. 2(a), the ρ of the ceramics(x ≥ 4) reached the peak value under 960 °C, that means 4 wt% BCB or more additive was sufficient to obtain high densification samples at a lower temperature. The compact density of CS ceramics sintered at 950 °C was 2.7992 g/cm^3 on condition that x = 4. Compared to traditional pure phase sintered CS ceramics [9], the right amount of BCB was conducive to reducing the sintering temperature.

Fig. 2(b) and (c) reveal the relationship between sintering temperature and the values of ε_r and $Q \times f$, respectively. The observed trends of ε_r and $Q \times f$ values are consistent with that of density of CS ceramics. The $Q \times f$ values of the samples are proportional to the sintering temperature at a specific composition, and the optimal values are obtained at the densification temperature. Moreover, samples of all formulations exhibit ε_r below 5 over a wide temperature range from 880 °C to 990 °C. In the case of x = 4, the ε_r reaches the maximum of 4.71 and the $Q \times f$ gets the saturated value of 30589 GHz at 950 °C. It is worthwhile noting that the ε_r values of samples are founded to be less than 5, while the ε_r value of pure CS and the BCB are 6.69, 7.40, respectively. The unconformity can be illustrated by the dielectric constant linear mixing rule (eq. (2)) and Maxwell mixing rule (eq. (3)) [25]:

$$\log k = \sum_i v_i \log k_i \quad (2)$$

$$k^{\blacksquare} = \frac{v_m k_m^{\blacksquare}\left(\frac{2}{3} + \frac{k_d^{\blacksquare}}{3k_m^{\blacksquare}}\right) + v_d k_d^{\blacksquare}}{v_m\left(\frac{2}{3} + \frac{k_d^{\blacksquare}}{3k_m^{\blacksquare}}\right) + v_d} \quad (3)$$

where v_i, k_i are the volume fraction and the dielectric constant of each

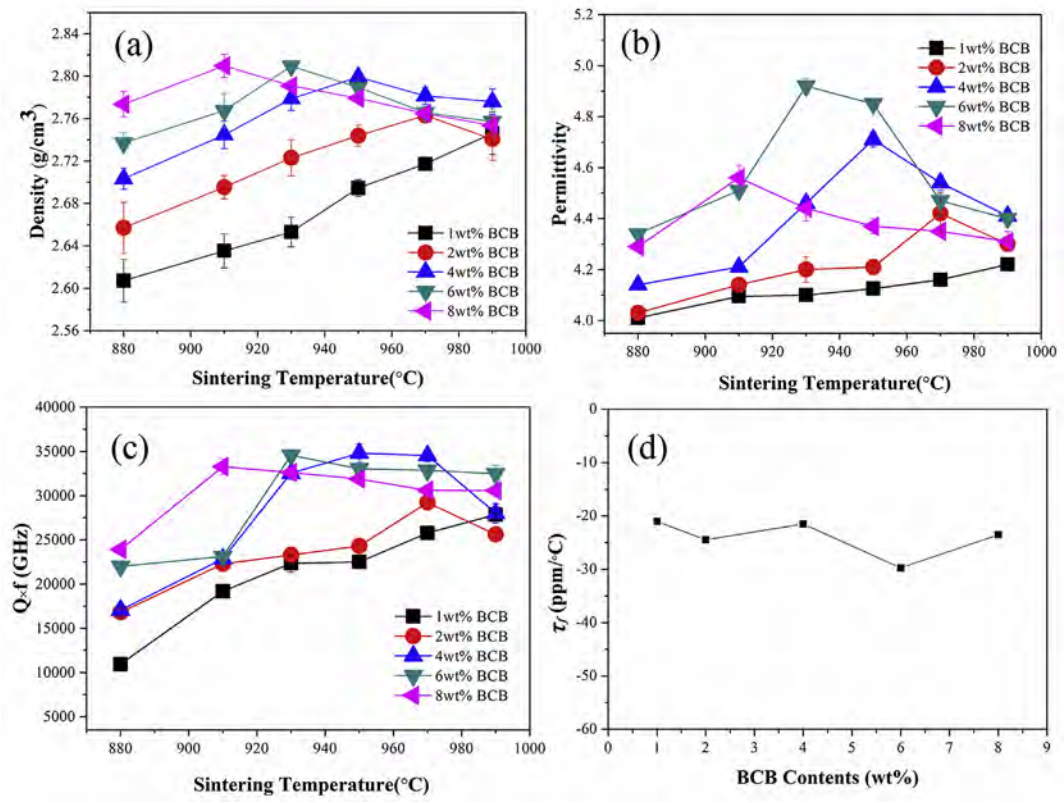

Fig. 2. The ρ(a), ε_r(b), $Q \times f$(c) values of x wt% BCB + CS ceramics sintered at various temperatures, and its τ_f values(d) as a function of x for samples with maximum density.

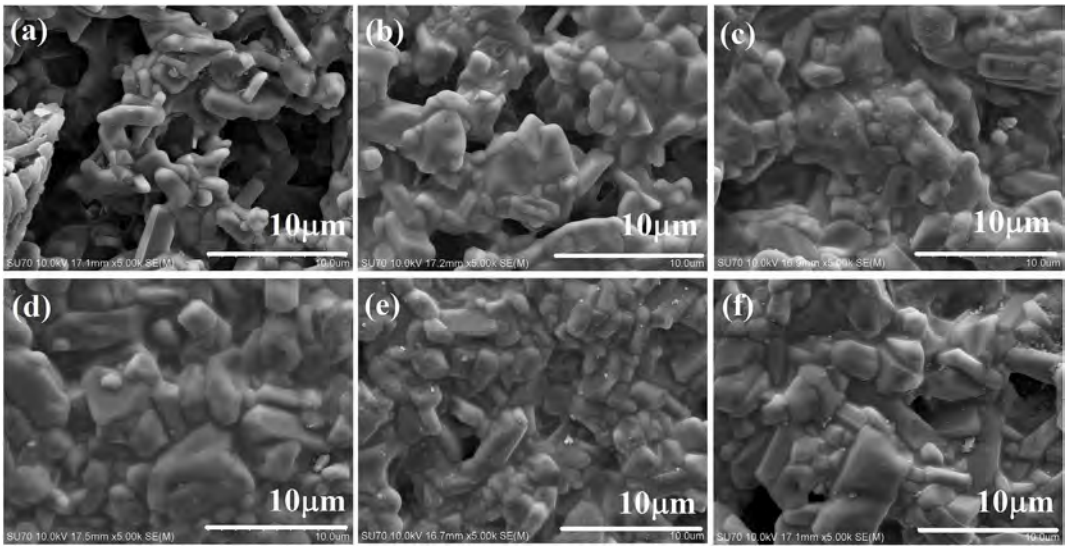

Fig. 3. SEM images of the 4 wt% BCB + CS ceramics sintered at: (a)880 °C, (b)910 °C, (c)930 °C, (d)950 °C, (e)970 °C and (f)990 °C.

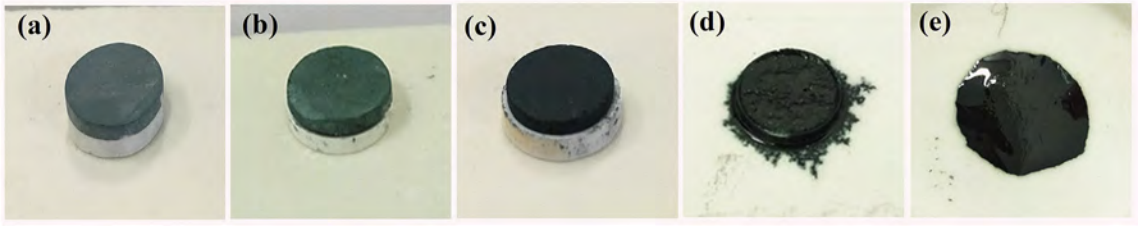

Fig. 4. Photographs of tests to evaluate sintering characteristics between BCB (top one) and CS (bottom one): (a)before sintering, after sintering at (b) 780 °C, (c) 830 °C, (d) 850 °C and (e) 870 °C for 1 h.

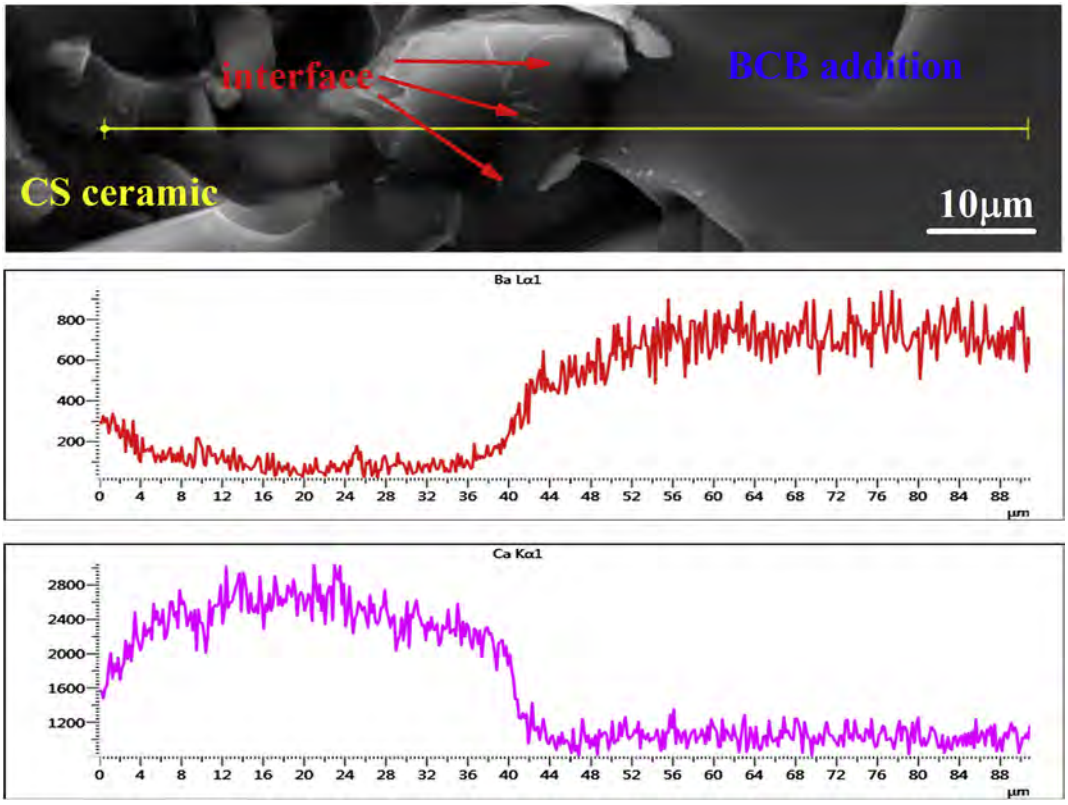

Fig. 5. Images of SEM and EDX line scan of CS and BCB heated together at 850 °C for 1 h.

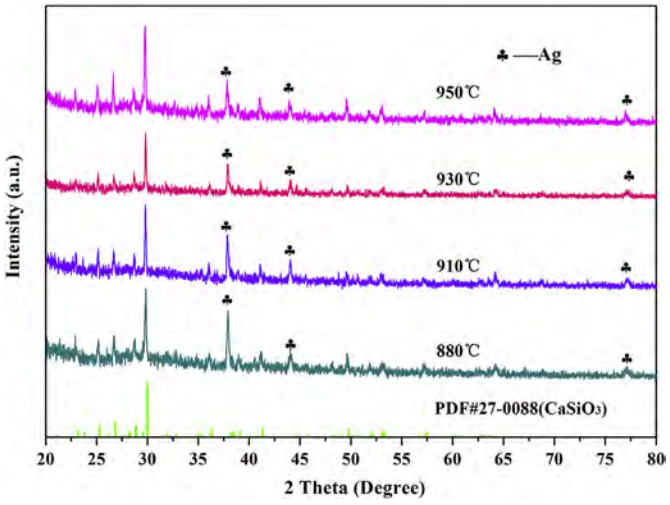

Fig. 6. XRD patterns of CS ceramics doped with 20 wt% BCB and 20 wt% Ag powders sintered at 880 °C, 910 °C, 930 °C and 950 °C for 3 h.

crystalline phase respectively; v_m, k_m represent the volume fraction and dielectric constant of the matrix material, and v_d, k_d are the volume fraction and dielectric constant of the second phase, respectively.

For 4 wt% BCB + CS samples, the calculated values were 6.7173, 6.6916 respectively, whereas, the actual value was less than 5. The deviation was mainly due to the pores in the samples, grain size, the thickness and resistivity of the grain boundary [25,26]. Hence, these factors resulted in the ε_r of all samples in the final experimental tests lower than the theoretical values.

The $Q \times f$ peak value was proportional to BCB content on the premise that x≤4, while the $Q \times f$ peak value changed slightly and remained at about 34000 GHz when x > 4. Generally, the $Q \times f$ value is affected by not only internal elements such as lattice vibration mode, but external factors including porosity, lattice defects, crystallinity and internal stress [27]. This phenomenon was attributed to the fact that the liquid phase formed by BCB reduced the porosity of the ceramics, promoted the release of stress and then reduced the dielectric loss.

Fig. 2(d) reveals the relationship between τ_f values and x for sintered samples with maximum density. Compared with the CS system ($\tau_f = -60\ ppm/°C$), the τ_f value of BCB-CS ceramics remained between −20 ppm/°C and −30 ppm/°C when BCB was added to CS ceramics. Obviously, composition and crystal structure played important roles in affecting the τ_f value [28–30]. In particularly, the linear thermal expansion was strongly affected by the BCB additive. Furthermore, the fact that τ_f value is also related to the coefficient of linear expansion can be expressed as the following equation:

$$\tau_f = -(\alpha_L + 0.5\tau_\varepsilon) \quad (4)$$

where α_L represents the linear thermal expansion coefficient of approximately 10 $ppm/°C$, τ_ε is the temperature coefficient of relative permittivity. Accordingly, the τ_f value of BCB phase and the amount of BCB additive will both exert an influence on the τ_f value of CS ceramics.

Fig. 3 presents SEM images of the 4 wt% BCB-CS ceramics at different sintering temperatures for 3 h. It was evident that the grains were evenly distributed in the samples, and all the ceramics displayed the presence of nonuniform grain size. Meanwhile, increasing the sintering temperature also contributed to the growth of grain and most of the grain size varied from 1-2 μm to 3–6 μm. It was confirmed that the densification process had been completed when sintering temperature reached 950 °C, which could be explained by the assistance of liquid phase of BCB. In addition, the change of porosity was consistent with the density curve shown in Fig. 2(a) and the density of the sample decreased slightly when the temperature exceeded 950 °C.

The loss tangent of ceramics is very sensitive to many factors, such as lattice vibration, grain size, porosity and lattice defects [31,32]. To be more specific, the final phase and compactness of BCB undoubtedly have a significant effect on materials. Investigating the sintering

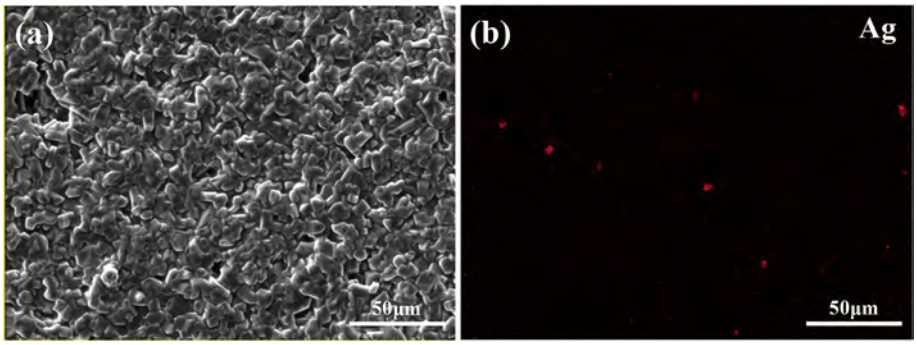

Fig. 7. SEM image EDX elemental maps of 20 wt% BCB added CS ceramic with 20 wt% Ag powders sintered at 930 °C for 3 h.

properties of BCB during the sintering of BCB-CS ceramics will help us analyze its dielectric loss and other properties. In this study, we put a piece of pure BCB on the pure CS pellet and then heated at a range of 780 °C–870 °C for 1 h in air. It appeared that the pellet hardly melted at 780 °C (Fig. 4(b)) and begun to shrink at 830 °C (Fig. 4(c)). With the temperature increased, the BCB gradually penetrated into the CS substrate (Fig. 4(d)). In Fig. 4(e), the BCB had been completely melted, indicating that the low temperature phase of BCB can form a liquid phase at around 870 °C. At the same time, the SEM and line scanning analysis determined by EDX were employed to analyze the interfacial reactions of BCB/CS. Fig. 5 shows SEM image and EDX results of the sintering characteristics between CS pellet and BCB body prepared at 850 °C for 1 h. Here is a visible boundary in the SEM image, which indicates the favorable wettability of the substrate and additive. The EDX analysis reveals that Ba and Ca varied suddenly at the boundary. Besides, it is not sufficient to check boron by EDX. In summary, we can confirm that the BCB scarcely reacts with CS ceramic.

The above results demonstrated that the liquid phase formed by BCB additive at high temperature had a harmonious wetting effect with the CS matrix, which accelerated the evaporation-condensation, surface diffusion and viscous flow of the sintering process, thus effectively promoting the sintering of CS ceramics. However, it is worth noting that the excessive BCB will increase the microwave dielectric loss, so it is necessary to balance the microwave characteristics, BCB amounts and the sintering temperature. Herein, high content (x ≥ 4) of BCB additive can promote the densification of the CS ceramic.

For chemical compatibility test, the powders of CS doped with 20 wt % BCB and 20 wt% Ag were ball-milled and sintered at 880 °C, 910 °C, 930 °C, 950 °C for 3 h. Fig. 6 presents the XRD results of co-fired powders at various temperatures for 3 h. The silver phase in the specimen was detected in XRD result, and certified that there are no chemical reactions between additive and Ag powders. Furthermore, Fig. 7 shows the elements distribution by EDX, it was obvious that silver can be well distributed in ceramic matrix and had good compatibility with CS. Hence, BCB-CS ceramics are expected to be one of the available products for LTCC devices because of the prominent microwave performance. Meanwhile, there was an excellent chemical compatibility between BCB-CS ceramics and silver powders below the preparation temperature of 950 °C.

4. Conclusions

The fabrication of $CaSiO_3$ (CS) ceramics was realized by solid-state reaction method with the additive of $BaCu(B_2O_5)$ (BCB). The sintering temperature of CS ceramics was lowered from approximately 1340 °C–910 °C owing to the assistance of BCB additive. The trends of ε_r and $Q \times f$ values were consistent with the variation of density of CS ceramics. 4 wt% BCB-CS ceramics not only had lower sintering temperature (~950 °C), but also exhibited prominent dielectric properties of $\varepsilon_r = 4.71$, $Q \times f = 34807.5\ GHz$, $\tau_f = -21.5\ ppm/°C$. These results indicated that BCB was an excellent sintering additive and improved the microwave performance of CS ceramics availably. In addition, the fact that BCB-CS ceramics had a prominent chemical compatibility with Ag electrodes indicates that BCB-CS ceramics is expected to be applied to LTCC devices.

Acknowledgements

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