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Low temperature cofiring and compatibility with silver electrode of $ZnO–SnO_2–TiO_2–Nb_2O_5$ ceramics with $BaCu(B_2O_5)$ addition

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Abstract

The effect of $BaCu(B_2O_5)$ (BCB) addition on the sintering temperature and microwave dielectric properties of $2.5ZnO–0.2SnO_2–4.8TiO_2–2.5Nb_2O_5$ (ZSTN) has been investigated by the solid-state ceramic route. X-ray diffraction and scanning electron microscopy techniques were used to analysis the structure and microstructure. The microwave dielectric properties were measured by the resonance method. It was found that the addition of BCB can effectively lower the sintering temperature from 1100 °C to 900 °C, and improves the microwave dielectric properties of ZSTN ceramics. The BCB doped ZSTN ceramics can be compatible with Ag electrode, which makes it a promising ceramic for LTCC technology application.

Keywords: C. Dielectric properties; Electronic materials; X-ray diffraction; Microstructure

1. Introduction

The development of communication systems such as mobile systems requires the miniaturization of devices. Low temperature co-fired ceramic (LTCC) multilayer devices have been extensively investigated for the miniaturization of microwave dielectric components [1]. LTCC multilayer devices consist of alternating microwave dielectric ceramics and internal metallic electrode layers. Ag has been widely used as the metallic electrode because of its high conductivity and low cost. However, the melting temperature of Ag is low, about 961 °C, whereas most of the commercial microwave dielectric ceramics usually need high sintering temperature (normally above 1300 °C) [2–4]. Therefore, for the fabrication of multilayer devices, it is necessary to develop microwave dielectric ceramics with a low sintering temperature, which can be co-fired with Ag.

$2.5ZnO–0.2SnO_2–4.8TiO_2–2.5Nb_2O_5$ (ZSTN) ceramics have suitable relative permittivity and quality factors for application of dielectric resonators and filters [5]. It exhibits relative permittivity of 52.5, $Q \times f$ of 18,000 GHz and τ_f of 10.5 ppm/°C. The sintering temperature of ZSTN was above 1100 °C, which is too high to be applicable to LTCC. Zhang et al. reported that 1.5 wt.% $CuO–V_2O_5$ was added to $ZnO–Nb_2O_5–1.92TiO_2–0.08SnO_2$ (ZNST) ceramics can lower sintering temperature from 1100 to 860 °C but the microwave dielectric properties are not satisfied [6].

It is well known that $BaCu(B_2O_5)$ addition often makes it possible to decrease the sintering temperature of many materials [7–12]. For example, using 6 mol.% BCB, the $Ba(Zn_{1/3}Nb_{2/3})O_3$ dielectric can be sintered at 875 °C and good microwave dielectric properties have been obtained with values of $\varepsilon_r = 35$, $Q \times f = 16{,}000$ GHz and $\tau_f = 22.1$ ppm/°C [13]. In this work, $BaCu(B_2O_5)$ additive was made and added to ZSTN ceramics in order to investigate the possibility of using BCB as a low temperature sintering additive. Furthermore, its effect on sintering temperature, microstructure and microwave dielectric properties of the ZSTN ceramics was investigated.

2. Experimental procedure

Specimens of the ZSTN ceramics were prepared by a conventional mixed oxide route from the high-purity oxide

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powders (≥99%) of ZnO, SnO_2, TiO_2 and Nb_2O_5. Stoichiometric proportions of the above raw materials (2.5:0.2:4.8:2.5, by mole) were weighed and mixed in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 850 °C for 4 h. To synthesize the BCB ceramic powder, $Ba(OH)_2{\cdot}8H_2O$ (>99%), CuO (>99%) and H_3BO_3 (>99%) were mixed for 4 h in a nylon jar with zirconia balls, then dried and calcined at 800 °C for 4 h. With subsequent ball-milling with the addition of 0–4.0 wt.% BCB, the powders were uniaxially pressed under the pressure of about 150 MPa into disks measuring 8 mm in diameter and 4 mm in thickness. And the ceramic pellets doped with BCB were sintered at 850–950 °C for 2 h in air.

Shrinkage of the specimens during heat treatment was measured using a horizontal loading dilatometer with alumina rams and boats (Model DIL402C, Netzsch Instruments, Germany). The crystal structures of the specimens were analyzed by an X-ray diffractometer (Rigaku D/MAX-2400, Japan) with Cu Ka radiation generated at 40 kV and 100 mA. The bulk densities of the sintered samples were measured by the Archimedes method. The microstructures observation of well-polished and etched surfaces of the samples was performed using scanning electron microscopy (JEOL JSM-6460LV, Japan).

Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method using a Network Analyzer (8720ES, Agilent, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, U.S.A.). The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \tag{1}$$

where f_T, f_0 were the resonant frequencies at the measuring temperature T and T_0 (25 °C), respectively.

In order to investigate the compatibility of 4 wt.% BCB added ZSTN ceramics with Ag electrode, two kinds of samples, one is that the ceramic powders mixing with 20 wt.% Ag powders, another is that the ceramic sheet prepared by tape casting with Ag electrode, were made and cofired at 875 °C, respectively. To prepare the ceramic sheet, the ceramic powder was first mixed with solvents and dispersants in a ball mill for 4 h, and then plasticizers and binders were added and mixed for another 4 h to obtain slurry. After tape casting and drying, the ceramic tapes were obtained and diced into proper sized ceramic sheet. The Ag electrode was then printed on the ceramic sheet by screen printing technology for cofiring. After that the ceramic sheets with silver electrodes were stacked and made to multilayer structure through isostatic pressing. Both kinds of cofired samples were then analyzed by XRD, SEM and EDX to detect if there is any interaction between the dielectric ceramics and electrodes.

3. Results and discussion

Comparing with glasses added to reduce the sintering temperature of the materials, $BaCu(B_2O_5)$ not only has a low sintering temperature (830 °C), low melting point (850 °C), but also exhibits more excellent microwave dielectric properties with permittivity of 7.4, $Q \times f$ values of 23,000 GHz and τ_f values of −35 ppm/°C. So we utilize BCB to reduce the sintering temperature of the ZSTN ceramic. To identify whether the BCB additive would be effective to lower the sintering temperature of ZSTN or not, the linear thermal shrinkages of as-pressed pellets as a function of temperature were firstly measured. The results are represented in Fig. 1. The results demonstrate that the onset temperature of shrinkage is lowered by the small addition of BCB. The shrinkage of ZSTN without BCB does not occur as rapidly as that of doped with the BCB. It is noteworthy that the densification of ZSTN with 4 wt.% of BCB addition begins below 800 °C and the shrinkage reaches a maximum value at approximately 900 °C. All of these imply that the BCB act as a good low temperature sintering aid to lower the sintering temperature of ZSTN ceramics.

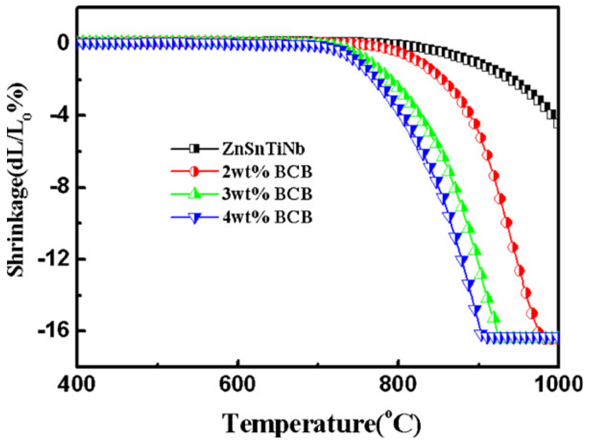

Fig. 1. Shrinkage of the BCB-added ZSTN ceramics as a function of temperature.

Fig. 2 represents the bulk densities of the ceramics with the addition of 1–4 wt.% BCB as a function of sintering temperature from 850 to 950 °C. The density of the undoped

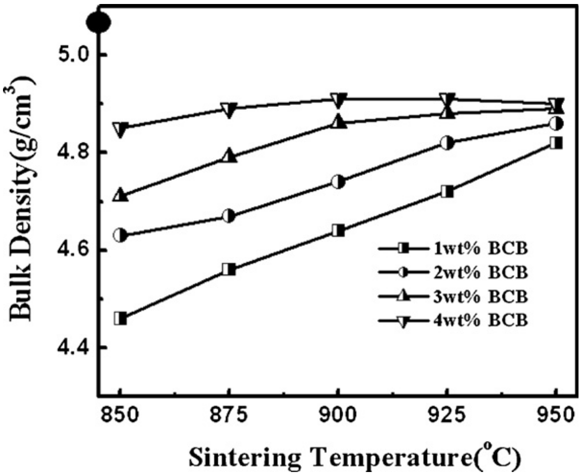

Fig. 2. Bulk densities of the ZSTN ceramics with the addition of 1–4.0 wt.% BCB as a function of sintering temperature from 850 to 950 °C, the dot on the vertical axis shows the density of an undoped ZSTN ceramic sintered at 1100 °C.

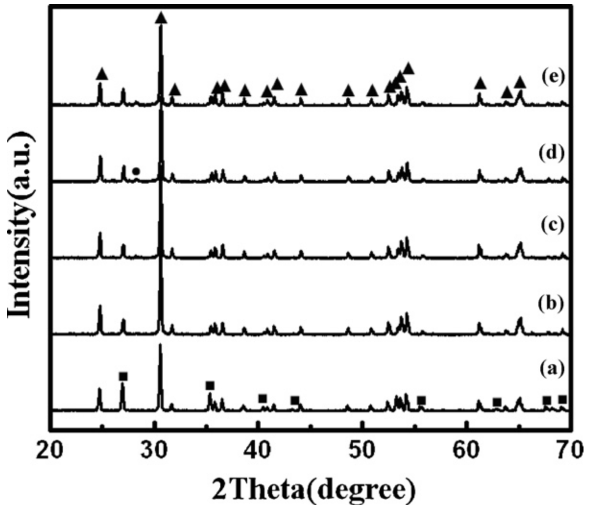

Fig. 3. The X-ray diffraction (XRD) patterns of the ZSTN ceramics with different amounts of BCB additive: (a) 0 wt.% sintering at 1100 °C (b) 1.0 wt.%, (c) 2.0 wt%, (d) 3.0 wt.% and (e) 4.0 wt.% sintering at 900 °C (■-$(Zn_{0.17}Nb_{0.33})_{0.5}Ti_{0.5}O_2$, ▲-$ZnTiNb_2O_6$, •-$Ba_2Cu(BO_3)_2$).

ZSTN ceramic is about 5.08 g/cm^3 when the sintering temperature is 1100 °C. For the BCB-doped ceramics, the bulk densities increase with enhancing of BCB content. As shown in Fig. 1, the densities of the samples doped with ≤2.0 wt.% BCB remain relatively low, which indicates that ≤2.0 wt.% BCB is not enough for densifying the ceramics efficiently at these low sintering temperatures. Then, when the BCB content increased to 3.0 wt.%, the samples could reach the max of densities around 925 °C. But when the BCB content increased to 4.0 wt.%, the samples could reach high densities around 900 °C. These results demonstrate that low-temperature sintering ZSTN is successfully achieved by the addition of BCB.

The X-ray diffraction (XRD) patterns of the ZSTN samples with different amounts of BCB additive are shown in Fig. 3, where the undoped ceramic was sintered at 1100 °C, and the BCB-doped ceramics were sintered at 900 °C. From Fig. 3, it can be observed that all of the samples contain two phases: $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (PDF: 39-0291) and $ZnTiNb_2O_8$ (PDF: 48-0323). Compared with the pure ZSTN ceramic, one special phenomenon was observed that the diffraction peaks of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase decreased with increasing the adding amount of BCB. However, the intensities of the diffraction peaks of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ merely change slightly with increasing the content of BCB. When the addition of the BCB is above 3 wt.%, a third phase of $Ba_2Cu(BO_3)_2$ is observed because of the decomposition of BCB.

Fig. 4 is the SEM micrographs of the ZSTN ceramics doped with (a) 0 wt.% sintering at 1100 °C, (b) 1.0 wt.% (c) 3.0 wt.% and (d) 4.0 wt.% BCB sintered at 900 °C. For the undoped sample [Fig. 3(a)], the ceramic has a relatively dense microstructure, and the average grain size is about 4 μm. Probably because of the fast growth of the grains, some pores were been trapped in large grains. For the samples doped with BCB, a reduced grain growth rate was observed since the sintering aid promoted the densification of ceramics while inhibited the grain growth due to a higher surface energy. The grain sizes of the BCB-doped samples are much smaller than those of pure ZSTN ceramic. Besides, because the liquid phase melts and distribute along the grain boundaries during sintering where it solidifies into a second phase hence minimize the voids, the grains of the BCB doped samples become more non-spherical (with shape edges) rather than spherical shape of undoped ZSTN.

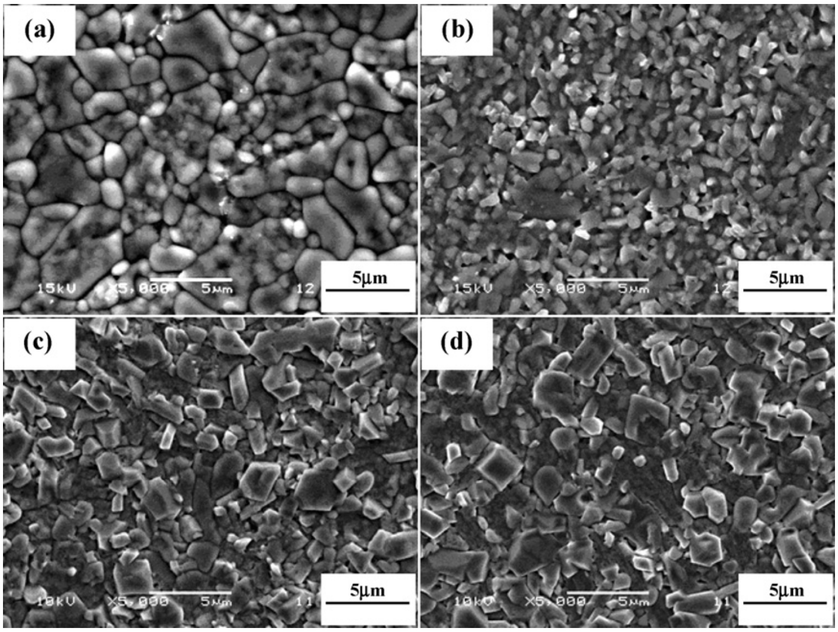

Fig. 4. Scanning electron micrographs of the ZSTN samples doped with different BCB: (a) 0 wt.% sintering at 1100 °C (b) 1.0 wt.%, (c) 3.0 wt.% and (d) 4.0 wt.% sintering at 900 °C.

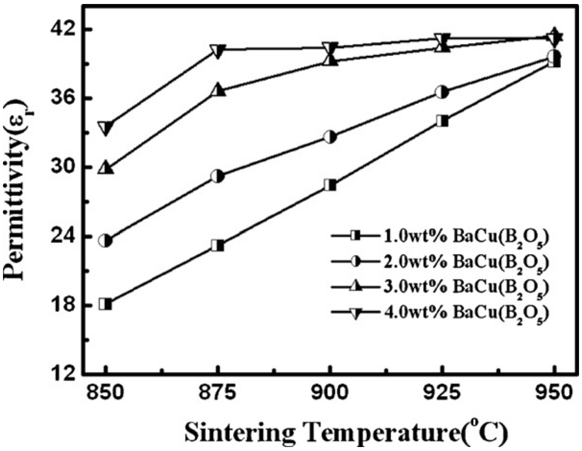

Fig. 5. The relative permittivity of ZSTN ceramics with BCB additions as a function of sintering temperature.

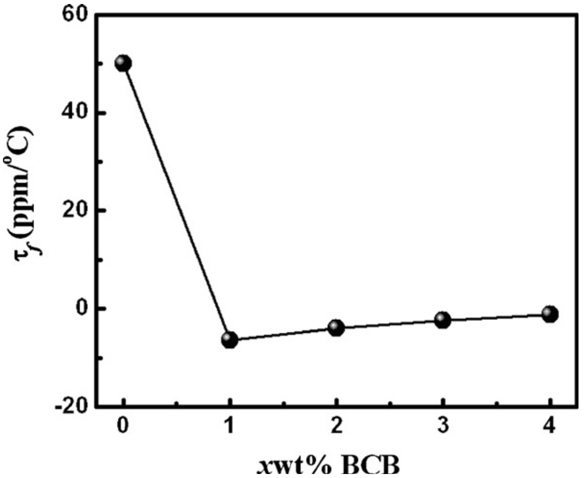

Fig. 7. Temperature coefficient of resonant frequency (τ_f) of ZSTN samples as a function of BCB content.

Fig. 5 shows the relative permittivity (ε_r) curves of ZSTN doped with BCB as a function of sintering temperature. The relationship between ε_r values of BCB-doped ceramics and sintering temperatures presents a trend similar to that between densities and sintering temperatures. The relative permittivity increased slightly with enhancing sintering temperature and the amount of BCB. The relative permittivity of BCB-doped samples is lower than those of pure ZSTN ceramic due to the decrease of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase with high ε_r value about 94[14] and the increase of BCB liquid phase with lower ε_r value. Many factors are believed to affect the microwave dielectric loss and these factors can be divided into two areas: the intrinsic loss and the extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity. The quality factor values ($Q \times f$) of ZSTN ceramics with various amounts of BCB at different sintering temperatures are shown in Fig. 6. For the ceramics doped with BCB, porous specimens were obtained after sintering at low temperature, the presence of the pores might cause the $Q \times f$ value decreasing, so the $Q \times f$ values were relatively low. The $Q \times f$ values increase with increasing the sintering temperature. Because the phase of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ with a lower $Q \times f$ value (about 15,000 GHz) [14] decrease, the $Q \times f$ values of BCB doped ZSTN samples are higher than that of pure ZSTN samples. Increasing BCB addition induced the decreasing in $Q \times f$ values because of more liquid phase and emerged third phase in the samples.

Fig. 7 illustrates the temperature coefficients of the resonant frequency (τ_f) of ZSTN samples as a function of BCB content. The τ_f values decrease obviously as the BCB was added. Combining with Fig. 3, the similar consistency of the variation of τ_f values and the change of XRD peak can also be observed. With the addition of BCB, the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase with very high τ_f value (237 ppm/°C) [14] decreases, so the τ_f values of ZSTN samples doped with BCB decrease. The τ_f values increase slightly with increasing the addition of BCB content because of increasing of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase. In general, with 4.0 wt.% BCB addition, the ZSTN ceramics sintered at 900 °C

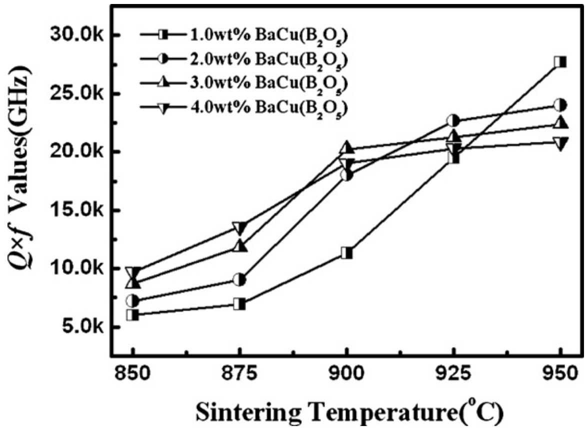

Fig. 6. The $Q \times f$ values of ZSTN ceramics with BCB additions as a function of sintering temperature.

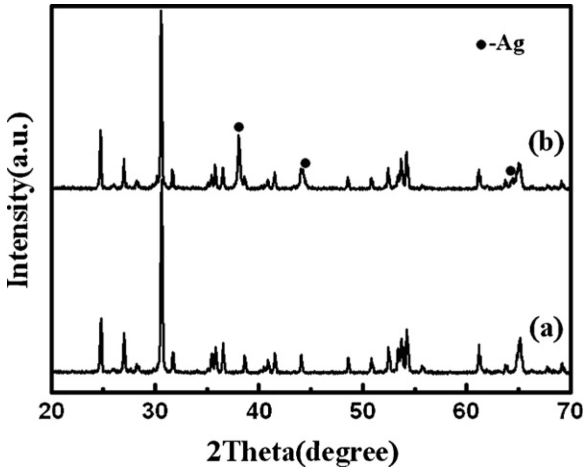

Fig. 8. The X-ray diffraction (XRD) patterns of the ZSTN samples with 4 wt.% BCB additive cofired with Ag powders at 875 °C: (a) 4 wt.% BCB doped ZSTN sample and (b) 4 wt.% BCB doped ZSTN sample cofired with Ag powders.

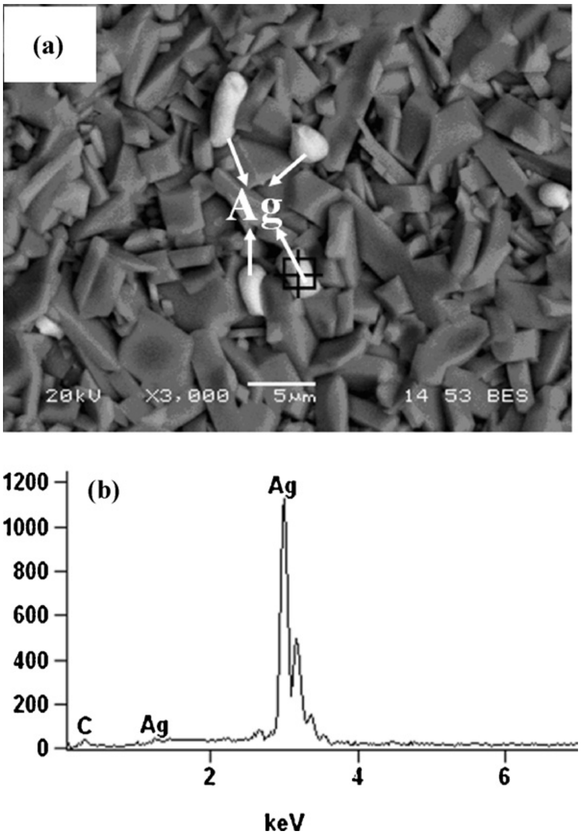

Fig. 9. The SEM profiles and EDS analysis of ZSTN samples with 4 wt.% BCB additive cofired with Ag powders at 875 °C: (a) SEM and (b) EDS, the white particle is Ag.

have excellent microwave dielectric properties of $\varepsilon_r = 40.4$, $Q \times f = 19{,}000$ GHz, $\tau_f = -1.2$ ppm/°C.

Figs. 8 and 9 show the crystalline phase and microstructure of the ZSTN samples with 4 wt.% BCB additive cofired with 20 wt.% Ag powders at 875 °C. From the XRD patterns [Fig. 8], cofiring with Ag powders does not produce new phase in the samples. This observation is also confirmed by the SEM and EDS profiles [Fig. 9]. The SEM analysis reflects no interaction of forming new phases after firing, and it is obvious that the reaction of ceramics and Ag powders did not occur from the EDS. Fig. 10 exhibits SEM micrographs and EDS analysis of the interface of 4 wt.% BCB added ZSTN ceramic sheet with Ag electrode in a LTCC component and the corresponding Ag distribution. It is obvious that the ceramic layer and the electrode layer are compatible and almost no crack exists at the interface between them. The element distribution of Ag is also shown in Fig. 10. It shows that Ag is distributed in the central conductor region, and does not diffuse into the ceramic region. Overall, it is concluded that the BCB added ZSTN ceramic is able to match with Ag electrode well.

4. Conclusions

The effects of BCB addition on the microwave dielectric properties and the microstructure of the ZSTN ceramic were investigated. The ceramics with small amounts of BCB addition can be well sintered around 900 °C. The low-firing ZSTN ceramics exhibit excellent microwave dielectric properties. Especially, the temperature coefficient of resonant frequency (τ_f) could be effectively lowered by adding small amounts of BCB. The 4.0 wt.% BCB-doped ceramics sintered at 900 °C have better microwave dielectric properties of $\varepsilon_r = 40.4$, $Q \times f = 19{,}000$ GHz, $\tau_f = -1.2$ ppm/°C. The most important advantage of BCB added ZSTN ceramic is its compatibility with Ag electrode fully. Obviously, the BCB added ZSTN ceramics are very promising candidates as low temperature co-firing ceramic dielectrics for LTCC applications.

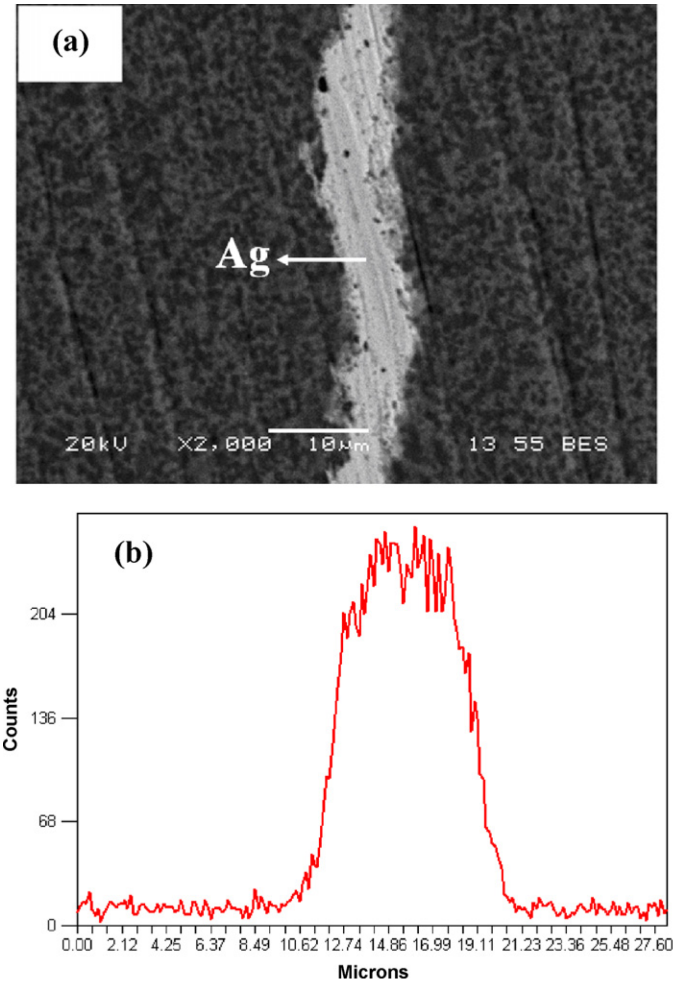

Fig. 10. The SEM and EDS analysis of the interfacial microstructure of (BCB doped ZSTN)/Ag cofired at 875 °C in a LTCC component: (a) SEM and (b) EDS, the white area is Ag.

Acknowledgement

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