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Microwave dielectric properties of $BaO–4.3TiO_2–0.5ZnO$ ceramics with $BaCu(B_2O_5)$

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Abstract

Effect of $BaCu(B_2O_5)$ (BCB) addition on microwave dielectric properties and sintering behaviors of $BaO–4.3TiO_2–0.5ZnO$ system (BTZ) ceramics were investigated to develop middle-k dielectric composition with low sintering temperatures. When a small amount of BCB was added to BTZ system, the sintering temperature can be lowered from 1100 °C to 900 °C due to the formation of BCB liquid phase. The system added with 7 wt% BCB was sintered at 900 °C for 2 h and ε_r of 31, $Q \times f$ of 18,200 GHz and τ_f of 3.8 ppm/°C were obtained. The suitability of BTZ ceramics for tape casting and cofiring with Ag electrodes was investigated, and no evidence of chemical reaction between Ag and ceramics was observed. The dielectric properties of the stacked multilayer plate without any electrodes were also measured. The result shows that the as-prepared BTZ ceramics are suitable for low-temperature co-fired ceramics applications.

Keywords: A. Sintering; C. Dielectric properties; E: Capacitors; LTCC

1. Introduction

Recently, low temperature co-fired ceramic (LTCC) multilayer devices have been widely investigated. LTCC multilayer devices consist of alternating microwave dielectric ceramics and internal metallic electrode layers [1,2]. In LTCC technique, dielectric layers are commonly fabricated by tape casting, followed by screen printing of the electrodes, lamination, and firing [3]. Silver has been widely used as internal electrode in the multilayer devices because of its high conductivity and low cost. Because the melting point of Ag is about 960 °C, it is required to develop microwave dielectric ceramics that have low sintering temperatures and can be co-fired with Ag.

In $BaO–TiO_2$ binary ceramic system, many compounds present higher dielectric constant, high quality factor (Q) value and low temperature coefficient of resonate frequency τ_f. Because of the difficulty of sintering the $BaO–TiO_2$ system ceramics, additives such as ZnO, SnO_2, ZrO_2 and Nb_2O_5 [4–6] were always used to promote sintering and optimize the microwave properties. Among the compounds, $BaO–4.3TiO_2–0.5ZnO$ (BTZ) ceramics have suitable dielectric constant and quality factors for applications of dielectric resonators and filters. It shows good microwave dielectric properties with ε_r of 36, $Q \times f$ of 18,000 GHz and τ_f of 18 ppm/°C. However, the sintering temperature of BTZ was above 1150 °C, which is too high to be applicable to LTCC.

In this work, $BaCu(B_2O_5)$ as a low temperature sintering additive was prepared and added to BZT ceramics. The effects of additive on the sintering temperature, microstructure and microwave dielectric properties of the BTZ ceramics were investigated. Furthermore, the suitability of $BaO–4.3TiO_2–0.5ZnO$ (BTZ) ceramics for tape casting was studied. The dielectric properties of stacked and fired tapes with and without Ag electrodes at low and high frequencies are presented.

2. Experimental procedure

High purity oxide compounds of $BaCO_3$, ZnO and TiO_2 were mixed according to $BaTi_{4.3}Zn_{0.5}O_{10.1}$ and milled for 4 h in anylon jar with zirconia balls, then dried, and calcined at 1000 °C for 4 h. To synthesize the BCB ceramic powder, $BaCO_3$ (>99.9%), CuO (>99%) and H_2BO_3 (>99%) were milled for 4 h in a nylon jar with zirconia balls, then dried and calcined at 700 °C for 3 h with the same heating rate as the former. After remilling with BCB additions, the powder was

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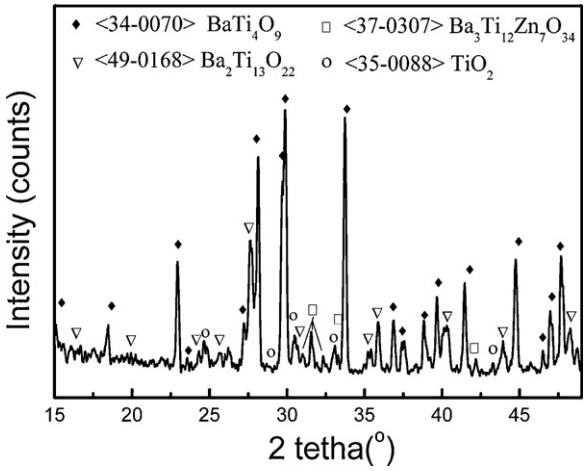

Fig. 1. The X-ray diffraction patterns of BaO–4.3TiO_2–0.5ZnO (BTZ) sample sintered at 1100 °C/2 h.

dried and pressed into discs and sintered at 850–950 °C for 2 h in air. The heating rate of the sintering process is 5 °C/min.

The $BaTi_{4.3}Zn_{0.5}O_{10.1}$ ceramic powder with 7 wt% BCB additions was mixed with solvents and a dispersant in a ball mill for 4 h. After addition of plasticizers and a binder, mixing was continued for another 24 h. The solvents used were ethanol and Toluene (Aldrich Chemical), the dispersant was Triolein, the binder was polyvinyl butyral (B98), and the plasticizers were dibutyl phthalate (S160) and polyethylene glycol (UCON 50HB2000). This slurry composition is denoted as a PVB-based binder system. The tape casting was carried out with a laboratory caster (LY-150-1, Beijing Orient Sun-tec Co., Ltd., Beijing, China) with a single 200-mm wide doctor blade and a casting speed of 0.8 m/min. The lamination pressure, and dwell time were 17 MPa, and 20–30 min for stacking 10–15 layers to produce the multilayered sample.

Shrinkage of the specimens during heat treatment was measured using a horizontal loading dilatometer with alumina rams and boats (Model DIL402C, Netzsch Instruments, Germany). Powder X-ray diffraction analysis was performed by an X-ray diffractometor (Rigaku D/MAX-2400, Japan) on the calcined and sintered specimens to identify the phases. Microstructure observation was conducted by using a scanning electron microscope (JEOL JSM-6460LV, Japan). The bulk densities of the sintered specimens were measured by Archimedes method. Microwave dielectric properties were measured by the TE01δ shielded cavity method using a Network Analyzer (8720ES, Agilent, USA) and a temperature

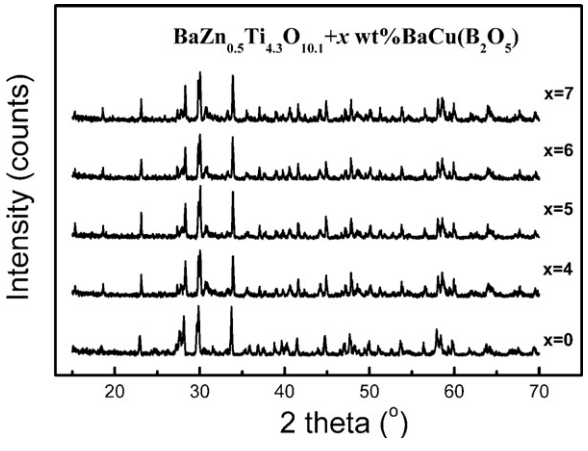

Fig. 2. The X-ray diffraction patterns of BTZ sintered at 1100 °C/2 h and BTZ + x wt% BCB (x = 0, 4, 5, 6, 7) additions samples sintered at 925 °C/2 h.

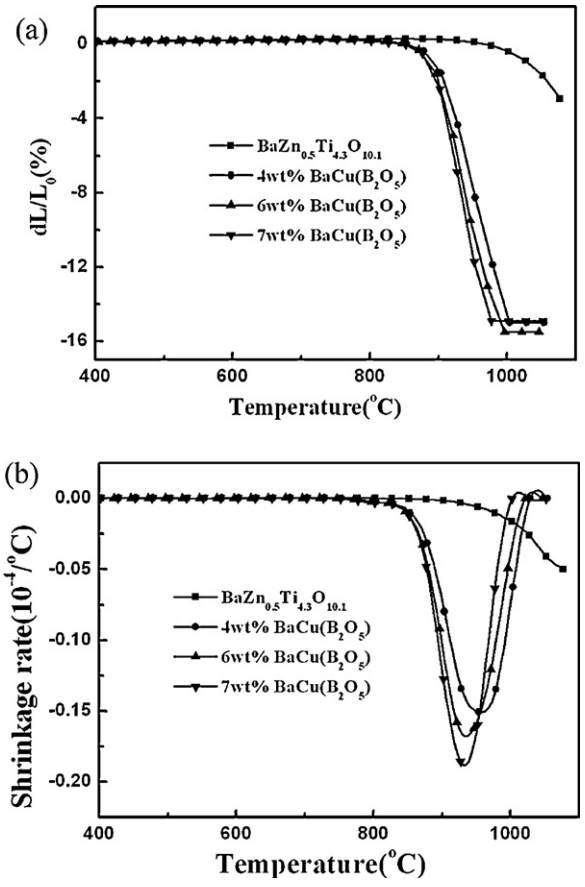

Fig. 3. The shrinkage (a) and shrinking rate (b) as a function of temperature for the pressed BTZ + x wt% BCB additions samples.

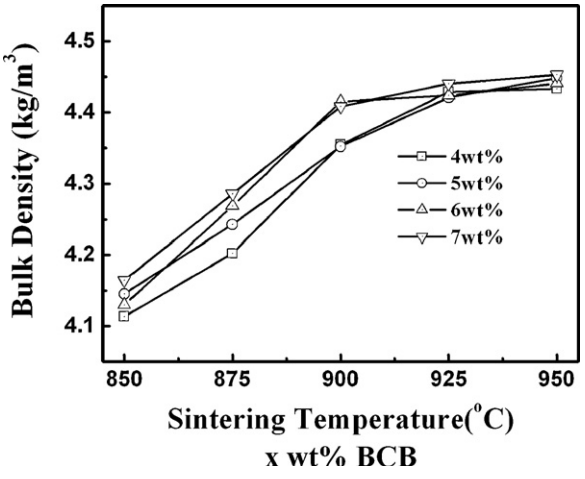

Fig. 4. The bulk density of BTZ + x wt% BCB ceramics as a function of sintering temperature.

chamber (DELTA 9023, Delta Design, USA). The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

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

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

For compatibility tests, silver electrodes were screen printed on the surface of the sintered multilayer plate, followed by post firing in the temperature range of 850–950 °C for 10 min.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of BaO–4.3TiO_2–0.5ZnO system (BTZ) sample sintered at 1100 °C for 2 h,

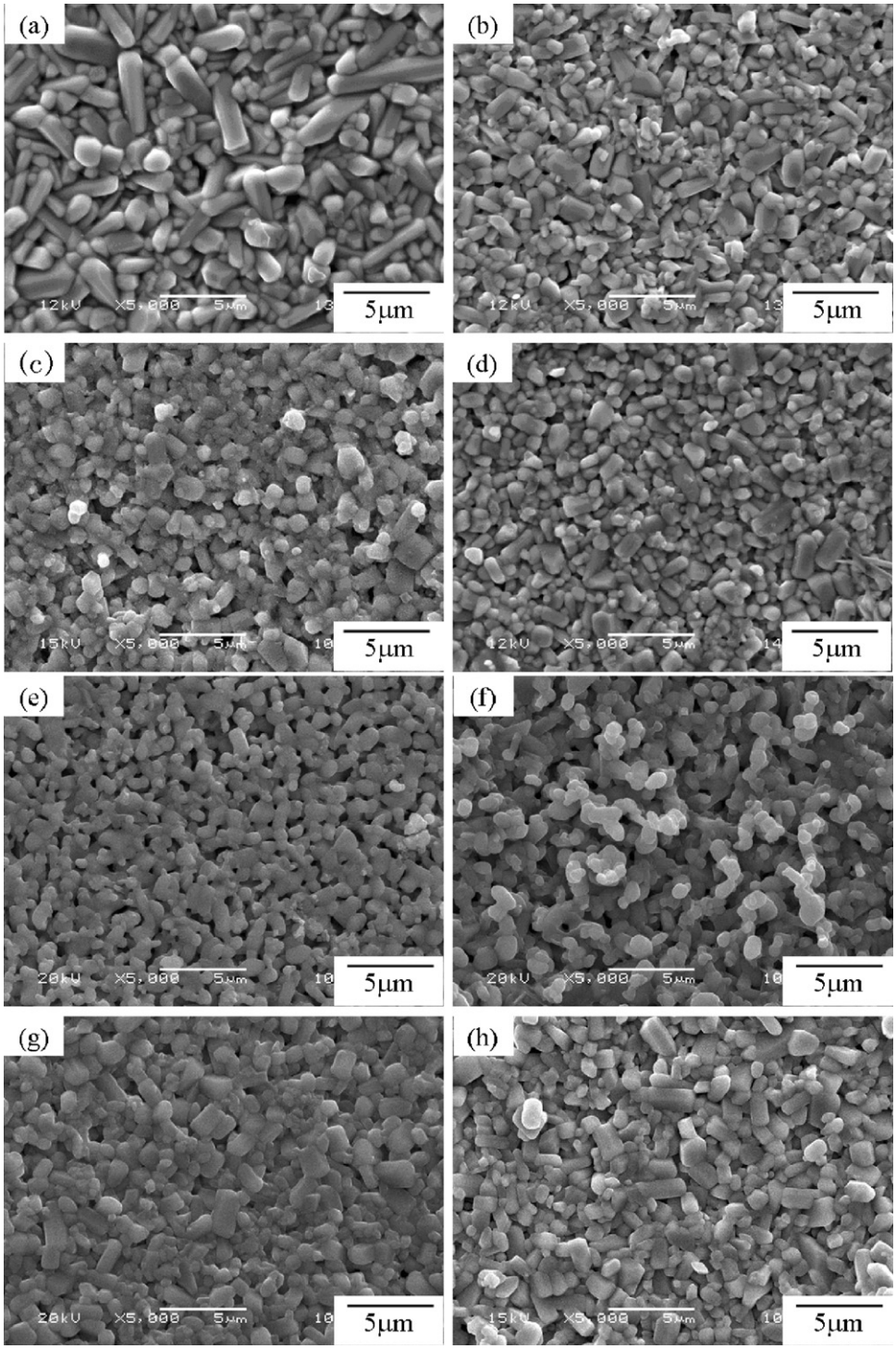

Fig. 5. The SEM micrographs of BTZ + x wt% BCB ceramics. (a) x = 0, 1100 °C/2 h; (b) x = 4, 900 °C/2 h; (c) x = 5, 900 °C/2 h; (d) x = 7, 900 °C/2 h; (e) x = 5, 850 °C/2 h; (f) x = 5, 875 °C/2 h; (g) x = 5, 925 °C/2 h; (h) x = 5, 950 °C/2 h.

which indicates that is a typical multi-phase systems. The main crystal phases of the BTZ ceramics were $BaTi_4O_9$, $Ba_2Ti_{13}O_{22}$, accompanied by minor phases of $Ba_3Ti_{12}Zn_7O_{34}$ and TiO_2. Among the phases, $BaTi_4O_9$ and $Ba_2Ti_{13}O_{22}$ have shown the superior dielectric properties in the microwave frequency and were most widely discussed previously [7–9]. As shown in Fig. 2, with the addition of $BaCu(B_2O_5)$ (BCB) additive sintered at low temperature, BTZ ceramics maintain the same phase composition, while $BaTi_4O_9$ was still the major phase, but $Ba_3Ti_{12}Zn_7O_{34}$ and TiO_2 increased and $Ba_2Ti_{13}O_{22}$ decreased slightly.

In order to evaluate the sintering behavior of the BCB doped BTZ ceramics, the linear thermal shrinkages of as-pressed pellets as a function of temperature were measured. The results are presented in Fig. 3. It is shown that the shrinkage of BCB doped BTZ specimens occurs at the temperature around 850 °C and gets the highest shrinkage around 925 °C, while for the pure BTZ specimen much higher temperature (roughly above 1100 °C) is required for obtaining a significant shrinkage.

Fig. 4 shows the bulk density of BTZ ceramics with various amounts of BCB additions as a function of sintering temperature. The bulk density of pure BTZ ceramics sintered at 1150 °C is 4.49 g/cm^3. For BTZ samples with BCB additions, it is found that the density of samples slightly increases with the increasing of BCB amount. As shown in Fig. 4, the bulk density of the samples doped with ≤5.0 wt% BCB sample increases sharply with increasing temperature and reached the maximum values above 925 °C, which indicates that ≤5.0 wt% BCB addition is not enough to densify the ceramics efficiently at low sintering temperatures. Then, when the BCB content increased to 7.0 wt%, the bulk density of BTZ samples with BCB additions increases sharply with temperature increasing and has a constant value above 900 °C. The bulk density of BTZ sample with 7 wt% BCB addition sintered at 900 °C for 2 h reached almost 4.42 g/cm^3. All these results reveal that BCB additive can effectively reduced the sintering temperature of BTZ ceramics while maintaining high density.

Fig. 5 shows the SEM micrographs of BTZ ceramics doped with different amount of BCB and sintered at different temperature. For the pure samples [Fig. 5(a)], the ceramic has a relatively dense microstructure, the colume-like grains with the sizes in a range of 3–10 μm can be observed. For the ceramics added with BCB [Fig. 5(b)–(d)], the grain sizes are much smaller than those of pure BTZ ceramics due to its lower sintering temperature. But with the amount of BCB increasing, the grain grows slowly and the porosity decreases due to the liquid phase effect (the melting point of BCB is around 850 °C). Meanwhile the density and grain size increased with the increase of sintering temperature, as shown in Fig. 5(e)–(h).

Fig. 6 shows the dielectric constant (ε_r) values of BTZ ceramic with various amounts of BCB addition as a function of sintering temperature. As reported, the $BaCu(B_2O_5)$ ceramic sintered at 800 °C has a dielectric constant (ε_r) of 7.4, a quality factor ($Q \times f$) of 50,000 GHz and a temperature coefficient of resonance frequency (τ_f) of −32 ppm/°C[10]. From Fig. 5, it can be observed that the dielectric constant shows the same tendency as the bulk density. With the sintering temperature increases, the dielectric constant increases first, and then saturated. As a result, the observed change in dielectric constant is attributed to the improved densification process with BCB additions.

Fig. 7 presents the $Q \times f$ values of the BTZ ceramics with various BCB additions as a function of sintering temperature.

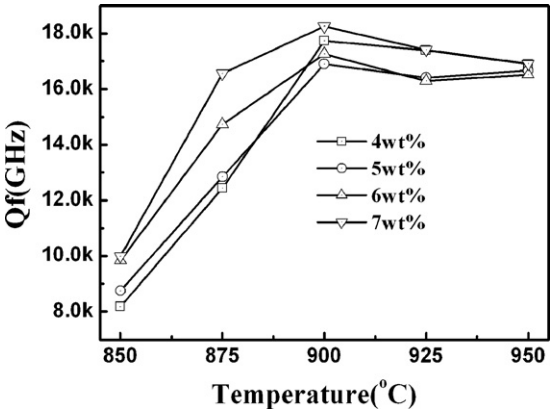

Fig. 7. The $Q \times f$ values of the BTZ + x wt% BCB ceramic as a function of sintering temperature.

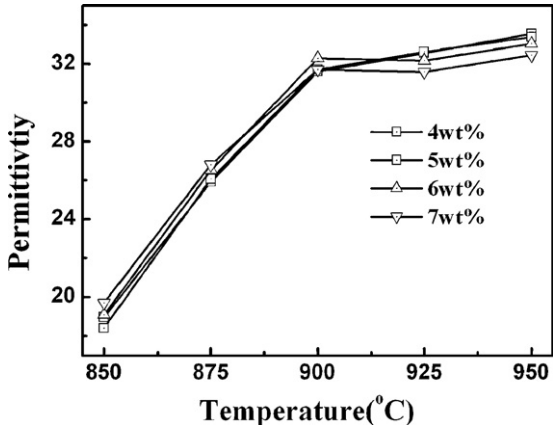

Fig. 6. The dielectric constant (ε_r) values of BTZ + x wt% BCB ceramic as a function of sintering temperature.

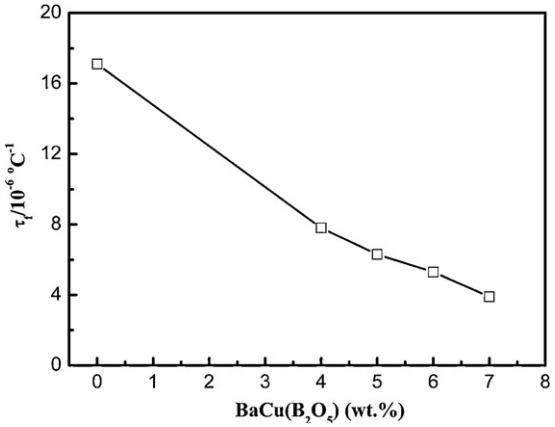

Fig. 8. The τ_f values of the BTZ + x wt% BCB ceramic as a function of sintering temperature.

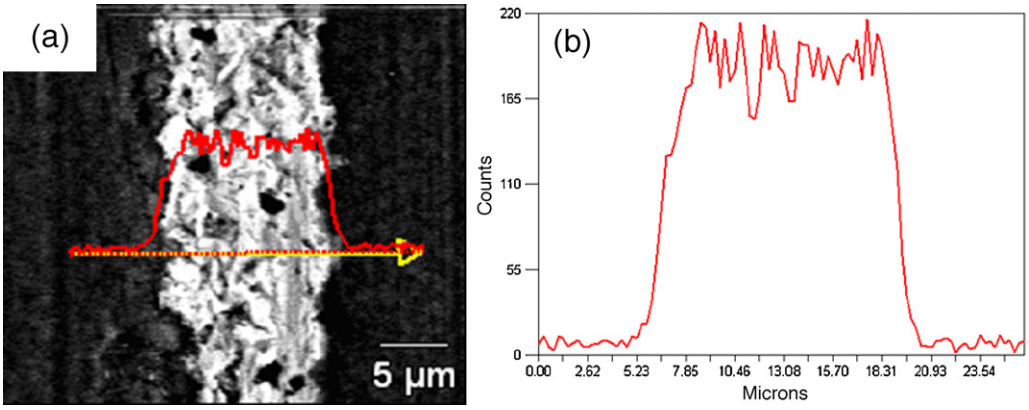

Fig. 9. EDS line scan of the interface between a silver electrode and BTZ ceramic body.

The $Q \times f$ values of the BCB-doped BTZ ceramics are strongly dependent on the sintering temperature and amount of BCB additions. For almost all the samples, with increasing sintering temperature, the $Q \times f$ values increased and reached a maximum value at 900 °C and then decreased slightly. As we know, the microwave dielectric loss includes not only intrinsic losses which were mainly contributed by the lattice vibrational modes but also extrinsic losses caused by densification/porosity, the secondary phases, grain sizes and oxygen vacancies. The relative density plays an important role in controlling dielectric loss, as has been shown in other microwave dielectric materials. As a liquid-phase sintering aid, BCB additions could form liquid phases in the sintering process, which accelerated the sintering process. As a result, the ceramics could be well densified at a lower sintering temperature, which also increased the quality factor.

Fig. 8 shows the temperature coefficient of the resonant frequency of pure BTZ and BTZ with BCB addition sintered at 900 °C for 2 h. From Fig. 7, it can be found that the τ_f value decreases with increasing the amount of BCB. For one reason, the BCB ceramic has a negative τ_f of −32 ppm/°C, and the τ_f value decreases with BCB amount increasing. For another, the slight increase of the amount of the $Ba_3Ti_{12}Zn_7O_{34}$ ($\tau_f \approx -25$ ppm/°C), TiO_2 ($\tau_f \approx 465$ ppm/°C) and the decrease of $Ba_2Ti_{13}O_{22}$ with the increasing of BCB also affected the τ_f value of the BTZ ceramics with BCB addition. When the system added with 7 wt% BCB sintered at 900 °C for 2 h, excellent microwave dielectric properties with ε_r of 31, $Q \times f$ of 18,200 GHz and τ_f of 3.8 ppm/°C have been obtained.

For compatibility test, the silver electrode was screen-printed onto BCB doped BTZ ceramic green bodies using a screen printer. Fig. 9 shows the SEM image and the EDS analysis of the sample. It can be seen that the silver electrode has good chemical compatibility and coheres closely with BTZ ceramics. Fig. 10 shows the XRD patterns of BTZ ceramic and mixture of BTZ and Ag powder. It can be observed that there are only $BaTi_{4.3}Zn_{0.5}O_{10.1}$ and Ag phases, which implies that no chemical reaction have taken place between the BTZ ceramic and the Ag electrode material. This result is in accordance with the SEM and EDS results as shown in Fig. 9. All these results reveal that BCB doped BTZ ceramic could be selected as suitable candidates for LTCC materials due to its low sintering temperature, good microwave dielectric properties, and compatibility with Ag electrodes.

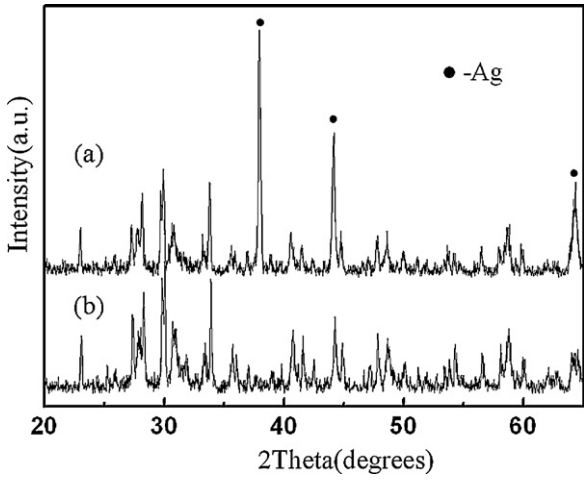

Fig. 10. XRD patterns of mixture of BTZ and Ag ceramic (a) and BTZ ceramic (b).

4. Conclusions

The effects of BCB addition on microwave dielectric properties and microstructure of the BTZ ceramic were investigated. The sintering temperature of BTZ ceramics can be lowed to around 900 °C with small amount of BCB addition. The 7.0 wt% BCB-doped ceramic sintered at 900 °C exhibits very excellent microwave dielectric properties of $\varepsilon_r = 31$, $Q \times f = 18{,}200$ GHz, $\tau_f = 3.8$ ppm/°C. The compatibility of BCB doped BTZ ceramic and Ag electrode was investigated, and no chemical reaction has taken place between the BTZ ceramic and Ag electrode. All the results show that the as-prepared BCB doped BTZ ceramics are suitable for low-temperature co-fired ceramics applications.

Acknowledgments

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