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Effects of $BaCu(B_2O_5)$ addition on microwave dielectric properties of Li_2TiO_3 ceramics for LTCC applications

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ABSTRACT

$BaCu(B_2O_5)$ (BCB) was used in this study to reduce the sintering temperature of Li_2TiO_3. BCB effectively regulated the τ_f value of low-temperature co-fired ceramic (LTCC) materials. X-ray diffraction patterns indicated that only the Li_2TiO_3 phase occurred within the doping range of 1 wt%–3.5 wt%. Scanning electron microscopy images showed compact and uniform grains in the samples with 2.0 wt% BCB. The samples also obtained the highest density and excellent microwave dielectric properties when sintered at 900 and 950 °C (i.e., ε_r = 15.19 and Qf = 58,084 GHz at 900 °C; ε_r = 15.21 and Qf = 58,143 GHz at 950 °C, respectively). BCB also effectively reduced the τ_f values of Li_2TiO_3 (e.g., τ_f = 15.23 ppm/°C with 2.0 wt% BCB and τ_f = 9.95 ppm/°C with 4.0 wt% BCB). The materials prepared with BCB were chemically compatible with silver and showed potential in LTCC applications.

1. Introduction

With the rapid development of wireless communication, an increasing number of studies have focused on low-temperature co-fired ceramic (LTCC) technology because of its many advantages, including facilitating the fabrication of miniature multilayer materials. A high quality factor (Qf), an appropriate dielectric constant (ε_r) and a near-zero temperature coefficient of resonant frequency (τ_f) are essential in microwave dielectric material research. As a metallic electrode, Ag has been widely used because of its high conductivity and low cost. However, due to the melting temperature of Ag being around 961 °C, the typical sintering temperature of LTCC materials must be decreased to around 900 °C or lower [1–5].

Li_2TiO_3 is extensively studied due to its good microwave dielectric properties (Qf=63,000) [6]. However, pure Li_2TiO_3 ceramics are not easily applied in practice because of their high sintering temperature (~ 1300 °C) and positive τ_f (~ +22.3 ppm/°C) [7–10]. Li_2TiO_3 usually requires sintering aids, such as H_3BO_3, LZB, LBSCA and $ZnO–B_2O_3$ etc, to lower sintering temperature. However, the glassy phase of these sintering aids with higher dielectric loss could be detrimental to the microwave dielectric properties. The $BaCu(B_2O_5)$ (BCB) sintering aid could reduce this damage because of its good microwave dielectric properties [10–12].

$BaCu(B_2O_5)$ (BCB) is also known for its good microwave dielectric properties (ε_r = 7.4 and Qf = 50,000 GHz). Nevertheless, BCB has a negative τ_f (~ −32 ppm/°C) and low melting point (~ 850 °C) [13–15]. BCB is often used as a sintering aid and as a material to adjust the τ_f value.

In the present study, BCB was used to lower the sintering temperature of Li_2TiO_3 ceramics and decrease their τ_f values. The chemical compatibility of these ceramics with Ag was also investigated.

2. Experimental procedure

High-purity powders of Li_2CO_3 (99%) and TiO_2 (99%) were used as starting materials. Li_2CO_3 and TiO_2 were milled according to the mole scale of 1:1 in nylon pots with zirconia balls; they were dried and calcined at 850 °C for 3 h to obtain the presintering powders. In the synthesis of BCB powder, high-purity powders of $BaCO_3$ (99%), CuO (99%) and H_3BO_3 (99.5%) were weighed and mixed in a nylon jar with zirconia balls and then dried and calcined at 800 °C. Thereafter, 1.0 wt % to 4.0 wt% of BCB was doped to Li_2TiO_3 and the presintering powders. The mixtures were milled in the nylon pots with zirconia balls for 12 h. After drying and mixing with PVA binder, the powders were pressed into cylinders via uniaxial pressing. These specimens were heated to 550 °C, maintained at this temperature for 3 h to remove the organic binder and sintered at 850, 900 and 950 °C. Then, 2.0 wt% BCB-doped Li_2TiO_3 powders with 30% Ag sintered at 900 °C. The chemical compatibility of the Li_2TiO_3 ceramic with Ag was investigated by co-firing the mixed powders with 30 wt% Ag powders in ambient

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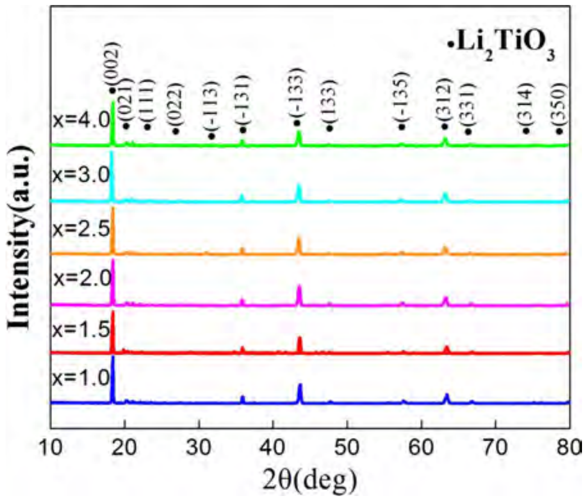

Fig. 1. XRD patterns of Li_2TiO_3 ceramics added with x wt% BCB and sintered at 900 °C for 3 h.

atmosphere at 900 °C for 3 h. Some Li_2TiO_3 ceramic specimens doped with 2.0 wt% BCB and coated with Ag electrode (EL 43-038) were co-fired at 900 °C for 3 h in air.

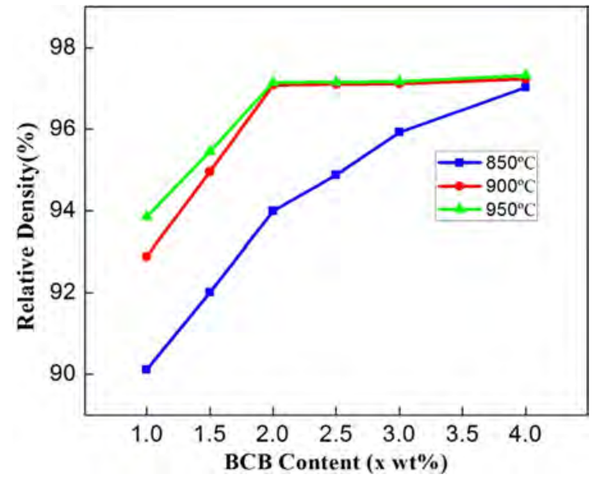

Fig. 3. Relative density values of Li_2TiO_3 with x wt% BCB.

The phase structure was analysed using X-ray diffraction (XRD: DX-2700) using Cu Kα radiation. The micrographs of the samples were examined via scanning electron microscopy (SEM: JOEL JSM6490LV). The Archimedes method was used to measure the bulk densities of the samples. The relative densities were obtained on the basis of the ratios

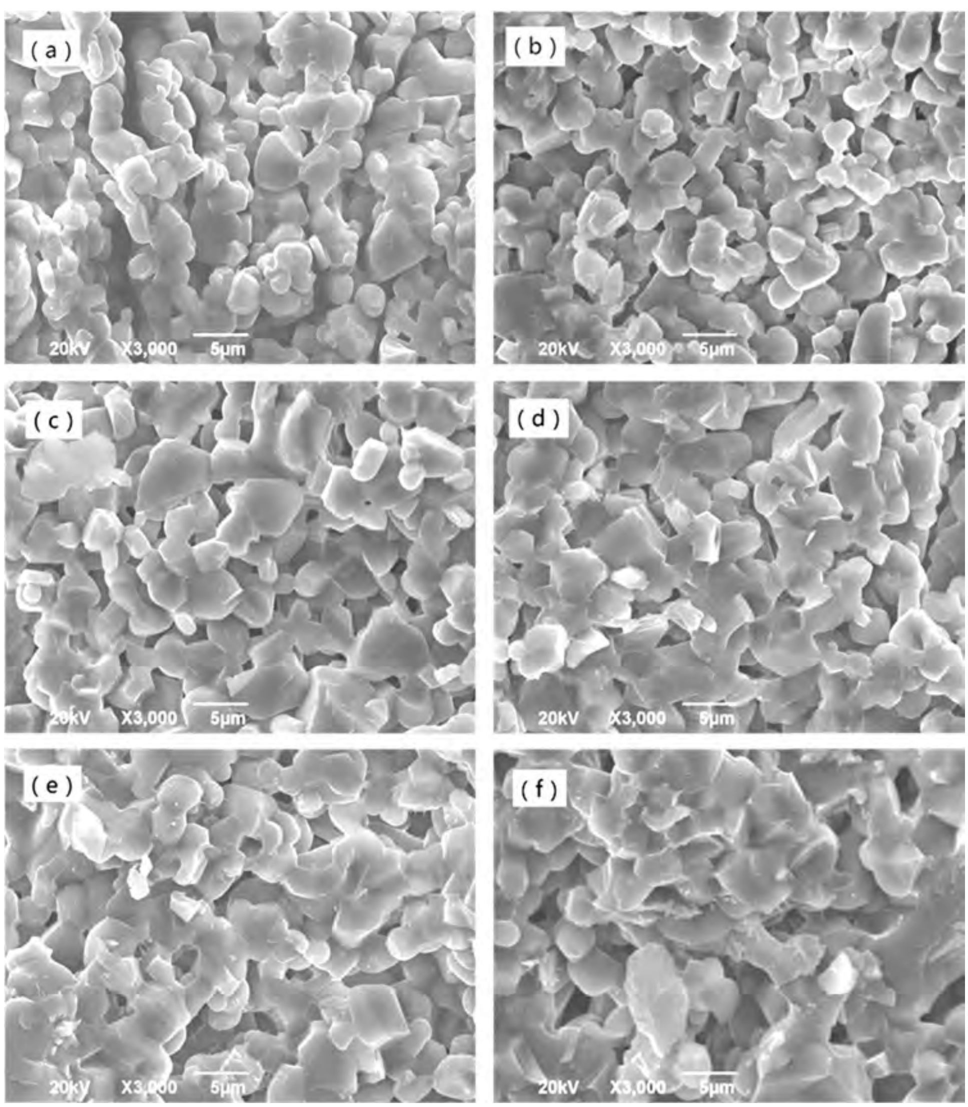

Fig. 2. SEM micrographs of Li_2TiO_3 with x wt% BCB. (a) x = 1.0, (b) x = 1.5, (c) x = 2.0, (d) x = 2.5, (e)x = 3.0 and (f) x = 4.0.

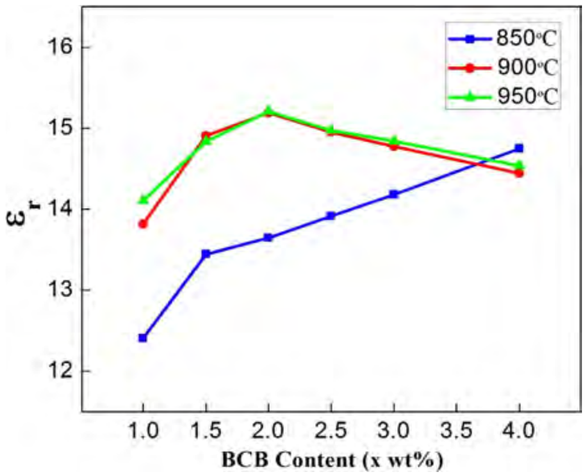

Fig. 4. Dielectric constant of Li_2TiO_3 ceramics with x wt% BCB sintered at 850 °C to 950 °C.

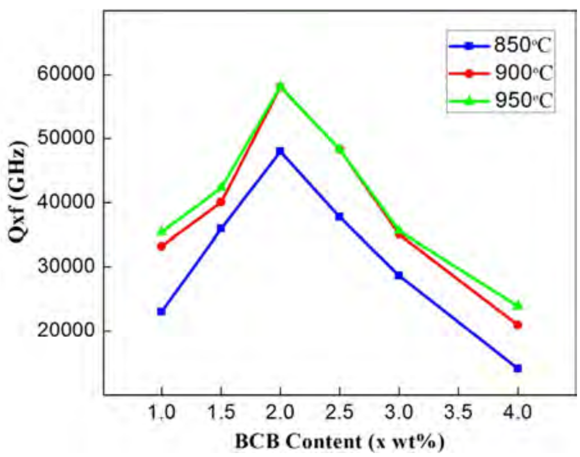

Fig. 5. *Qf* values of Li_2TiO_3 with x wt% BCB.

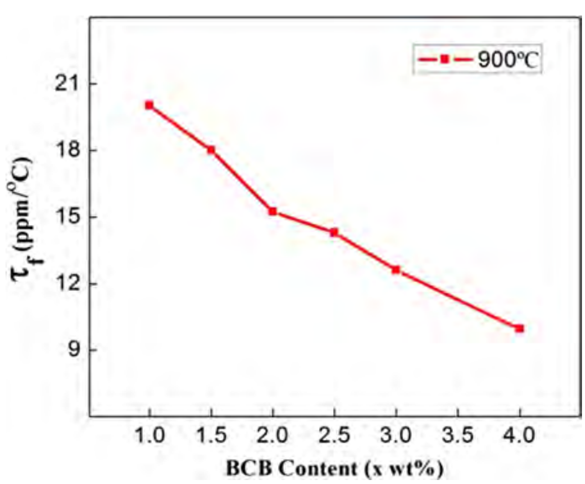

Fig. 6. τ_f values of Li_2TiO_3 ceramics with x wt% BCB and sintered at 900 °C.

of the bulk and theoretical densities. The microwave dielectric properties were measured with the Hakki–Coleman method and Agilent N5230A network analyzer, and using the transmission cavity method to get the quality factor. The samples with Ag were analysed through X-ray diffraction (XRD), backscattered-electron diffraction (BSED) image and energy dispersive X-ray spectroscopy (EDX).

The temperature coefficients of resonant frequency (τ_f) were obtained in a temperature range of 20–80 °C. The values were

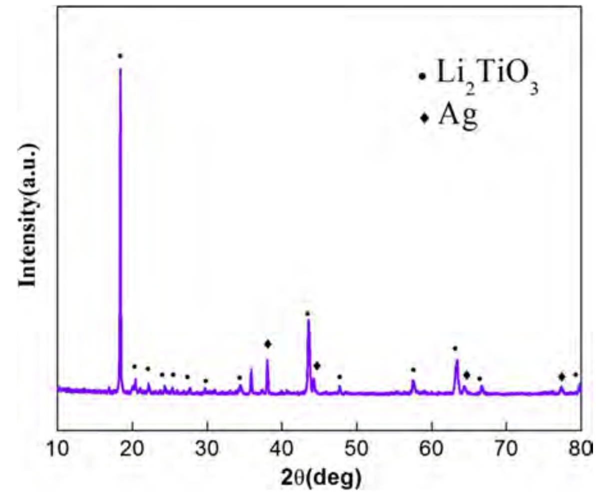

Fig. 7. XRD patterns of Li_2TiO_3 mixed with 30 wt% Ag powders and sintered at 900 °C for 3 h in air.

calculated from the following formula:

$$\tau_f = \frac{f_T - f_0}{f_0(80 - 20)}$$

where f_T and f_0 are the resonant frequencies at 80 °C and 20 °C, respectively [16].

3. Results and discussion

Fig. 1 shows the XRD patterns of Li_2TiO_3 added with different amounts of BCB and sintered at 900 °C for 3 h. A pure Li_2TiO_3 phase was observed, and no trace of the impurity phase existed, thus indicating the absence of a chemical reaction between Li_2TiO_3 and BCB. Although the amount of BCB increased, the BCB phase did not show any peaks. This result might be due to the inability of the BCB liquid phase to crystallise in the Li_2TiO_3 ceramics when cooling and remaining amorphous [17,18].

Fig. 2 presents the SEM micrographs of the Li_2TiO_3 ceramics doped with (a) 1.0 wt%, (b) 1.5 wt%, (c) 2.0 wt%, (d) 2.5 wt%, (e) 3.0 wt% and (f) 4.0 wt% BCB and sintered at 900 °C for 3 h. The samples with low BCB content (1.0 wt%) showed numerous pores (Fig. 2(a)). With the increase in the BCB content, some grains slowly grew, and the intergranular pores slowly reduced in size (Fig. 2(a)–(c)) because of the liquid phase effect. The melted BCB could facilitate sintering process (the melting point of BCB is around 850 °C), thus benefitting the decrease in porosity and the growth of grains. When x was 2.0 wt%, the microstructure become compact and grain sizes became uniform. However, when 2.5 wt% of BCB was added, the microstructure did not become compact, and the sizes of the grains were nearly the same because the grain growth was inhibited by the high surface energy [19,20]. As the BCB content continued to increase, part of the grains grew abnormally and even fused together (Fig. 2(d)–(e)) mainly because of the excessive liquid phase of BCB.

The resulting relative densities of Li_2TiO_3 ceramics sintered at 850, 900 and 950 °C with different amounts of BCB are shown in Fig. 3. The curve of relative densities showed a similar trend at different sintering temperatures of 900 and 950 °C. The relative density increased rapidly with increasing x up to 2.0 wt% because the melted BCB promoted sample densification when Li_2TiO_3 was sintered. The melted BCB decreased the sintering temperature and decreased the pores, similar to the SEM images shown in Fig. 2(a)–(c). When x was between 2.0 wt % and 3.0 wt%, the relative density stayed almost balanced at 900 and 950 °C because the amount of BCB was adequate for the sintering of the Li_2TiO_3 ceramics. With x up to 4.0 wt%, the relative density slightly increased. According to the tests, the density of BCB (~ 4.3 g/cm^3) is

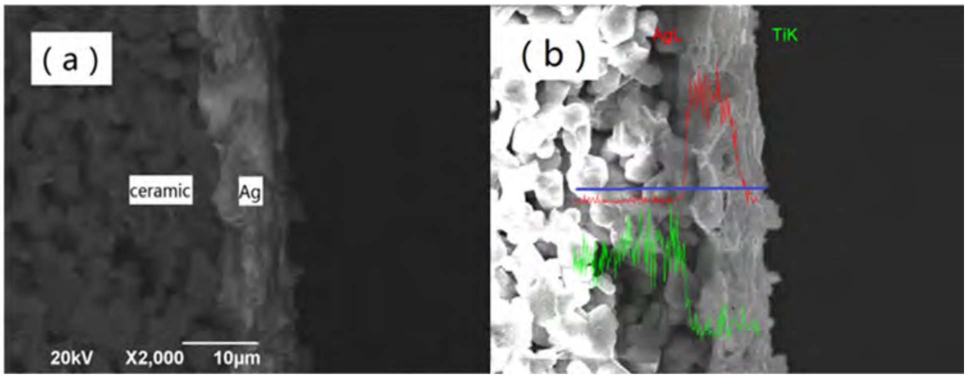

Fig. 8. BSED image and EDX line scanning analysis of Li_2TiO_3 ceramic doped with 2.0 wt% BCB and co-fired with Ag electrode at 900 °C for 3 h in air.

greater than that of Li_2TiO_3 (~ 3.4 g/cm^3). With the increase of BCB content, the increase of actual density and theoretical density of samples is the same. Therefore, the ratio of actual density and theoretical density increased. This may cause the relative density increasing slighting. However, the curve of relative densities monotonically increased at 850 °C; the same was not observed in the curves at 900 and 950 °C because 4 wt% BCB was not sufficient to densify the samples sintered at 850 °C.

Fig. 4 shows the dielectric constant of Li_2TiO_3 with different BCB contents and sintered at different temperatures. The dielectric constant increased monotonously at 850 °C as the BCB content increased. A consistent variation was observed in the relative density during sintering, and it indicated that the dielectric was mainly influenced by density at 850 °C. However, the samples with 2.0 wt% BCB peaked with dielectric constants of 15.19 and 15.21 sintered at 900 and 950 °C and then decreased possibly because of two factors. The first one is the density, which was confirmed by the curve of relative density in Fig. 3 before the BCB content reached 2.0 wt%. Although the relative densities of Li_2TiO_3 ceramics reached approximately 97%, some pores remained in the ceramic samples and thus decreased the dielectric constants. The second factor is the low dielectric constant of BCB. The dielectric constant of BCB is reported to be 7.4, which is much lower than that of Li_2TiO_3 [13,14]. These two factors caused the dielectric constant of the samples to be lower than that of pure Li_2TiO_3 (ε_r = 22). When BCB was more than 2.0 wt%, the dielectric constant of Li_2TiO_3 decreased slowly mainly because of the lower dielectric constant of BCB.

Fig. 5 shows the *Qf* values of Li_2TiO_3 ceramics with different amounts of BCB sintered at 850, 900 and 950 °C. The *Qf* values steeply increased to the maximum value with 2.0 wt% BCB and then decreased when the BCB content was more than 2.0 wt%. Microwave dielectric loss includes not only intrinsic losses mainly contributed by lattice vibrational modes but also extrinsic losses caused by densification, porosity, secondary phases and grain sizes [21,22]. Given the absence of secondary phases in the Li_2TiO_3 ceramic samples, densification, porosity and grain sizes in particular were investigated. Before BCB was increased to 2.0 wt%, the samples were mainly affected by sample density. The increase in density decreased the microwave dielectric loss of the samples. Therefore, the *Qf* value increased. When the amount of BCB exceeded 2.0 wt%, the microwave dielectric loss was caused mainly by BCB and not the density. The sample density increased during sintering at 850 °C with 2.5 wt% to 4.0 wt% BCB. This result confirmed that the negative influence of increased BCB on dielectric loss exceeded the positive influence of increased density on dielectric loss. In addition, the excess BCB caused part of the grains to grow abnormally, thereby causing an increase in porosity and poor grain uniformity, as shown in Fig. 2(d)–(f). These factors caused the microwave loss to increase when the amount of BCB exceeded 2.0 wt%. The best *Qf* values of the Li_2TiO_3 ceramics were 58,084 GHz at 900 °C and 58,143 GHz at 950 °C. The higher *Qf* value of the samples sintered at 950 °C was due to the higher density of the samples sintered at 950 °C.

The τ_f values of Li_2TiO_3 ceramics doped with BCB and sintered at 900 °C are shown in Fig. 6. According to the reports, the τ_f value can be tuned by the formation of a solid solution or mixtures of dielectrics with an opposite τ_f value [23]. Li_2TiO_3 is known to have a positive τ_f (~ +22.3 ppm/°C), whereas BCB is known to have a negative τ_f (~ −32 ppm/°C). Fig. 6 illustrates that the τ_f values of the samples decreased as the BCB content increased. When the BCB content was 2.0 wt%, the τ_f value was 15.23 ppm/°C. With BCB increasing up to 4.0 wt%, the τ_f value was 9.95 ppm/°C. This result clearly confirmed that BCB was effective in reducing the τ_f value of Li_2TiO_3. However, excess BCB increased the microwave dielectric loss rapidly, thus indicating the significance of establishing a balance between *Qf* and τ_f in practical applications.

Two experiments were performed to evaluate the chemical compatibility of the Li_2TiO_3 ceramic with Ag. Firstly, the 2.0 wt% BCB-doped Li_2TiO_3 powders with 30% Ag powders were mixed and sintered in air at 900 °C for 3 h. Fig. 7 shows the XRD pattern of the co-fired powders. The XRD pattern only showed Li_2TiO_3 and Ag phases, which proved that no chemical reaction occurred between Li_2TiO_3 and Ag. Secondly, the 2.0 wt % BCB-doped Li_2TiO_3 ceramic sample with Ag electrode coating was sintered in air at 900 °C for 3 h to detect interactions between the ceramic and the Ag electrode. Fig. 8 shows the backscattered-electron diffraction (BSED) image and EDX line scanning analysis of the fracture surface. A clear dividing line between the ceramic and the Ag electrode was observed in the BSED image, and this line indicated the good combination of the Li_2TiO_3 ceramic and Ag electrode. The EDX line scanning analysis indicated different levels of elements on both sides of the dividing line. Obviously, Ag and Ti changed rapidly at the dividing line. Both BSED and EDX revealed that Ag did not diffuse into the Li_2TiO_3 ceramic after co-firing at 900 °C for 3 h. Therefore, the 2.0 wt% BCB-doped Li_2TiO_3 ceramic was deemed compatible with the Ag electrode.

4. Conclusion

In this work, BCB was added to Li_2TiO_3 LTCC to reduce its sintering temperature and tune its τ_f. The 2.0 wt% BCB reduced the sintering temperature and formed dense microstructures with uniform grain sizes under sintering at 900 and 950 °C. The samples also presented the following optimum dielectric properties: ε_r = 15.19 and *Qf* = 58,084 GHz at 900 °C; ε_r = 15.21 and *Qf* = 58,143 GHz. Furthermore, BCB was effective in reducing the τ_f value of Li_2TiO_3, that is, τ_f = 15.23 ppm/°C with 2.0 wt% BCB and τ_f = 9.95 ppm/°C with 4.0 wt% BCB. All the results and the chemical compatibility of the Li_2TiO_3 ceramic with Ag indicated that Li_2TiO_3 doped with BCB is suitable for LTCC applications.

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