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Low-firing $Li_2ZnTi_3O_8$ microwave dielectric ceramics with $BaCu(B_2O_5)$ additive

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Abstract. Phase purity, microstructure, sinterability and microwave dielectric properties of $BaCu(B_2O_5)$-added $Li_2ZnTi_3O_8$ ceramics and their cofireability with Ag electrode were investigated. A small amount of BaCu (B_2O_5) can effectively reduce the sintering temperature from 1075°C to 925°C, and it does not induce much degradation of the microwave dielectric properties. Microwave dielectric properties of $\varepsilon_r = 23{\cdot}1$, $Q \times f = 22{,}732$ GHz and $\tau_f = -17{\cdot}6$ ppm/°C were obtained for $Li_2ZnTi_3O_8$ ceramic with 1·5 wt% $BaCu(B_2O_5)$ sintered at 925°C for 4 h. The $Li_2ZnTi_3O_8$ +BCB ceramics can be compatible with Ag electrode, which makes it a promising microwave dielectric material for low-temperature co-fired ceramic technology application.

Keywords. Microwave ceramics; XRD; SEM; dielectric properties; LTCC.

1. Introduction

To achieve the miniaturization of microwave (MW) components for wireless communication, low-temperature co-fired ceramic (LTCC) technology becomes an important method because of its predominance in enabling the fabrication of three-dimensional ceramic modules with low dielectric loss and co-fired metal electrodes. In order to use the most common electrode silver, the ceramic must have a low sintering temperature below 960°C and chemical compatibility with Ag (Sebastian 2008; Sebastian and Jantunen 2008).

Most of the known commercial dielectric materials for the high frequency applications have good MW dielectric properties, but they cannot be co-fired with Ag electrode because of high sintering temperatures (Nenasheva *et al* 2003; Surendran and Sebastian 2005; Chen and Huang 2010). The addition of sintering aids, such as low-melting glasses and compounds, is most oftenly used to lower the sintering temperatures (Li *et al* 2002; Wee *et al* 2004; Kim and Kim 2009). Besides this, considerable attention has been paid recently to developing new MW dielectrics with low cost raw materials and low sintering temperature (Feteira and Sinclair 2008; Liang and Lu 2009; Pang and Zhou 2010). More recently, George and Sebastian (2010a) reported that $Li_2ZnTi_3O_8$ (LZT) ceramics exhibited good MW dielectric properties and low cost raw materials. However, the sintering temperature is too high (>1000°C) to be co-fired with Ag electrode. As far as we know, there are rarely reports focused on low temperature co-fired LZT ceramics (George and Sebastian 2010b). It has been verified that BaCu (B_2O_5) (BCB) addition often makes it possible to decrease the sintering temperature of many materials (Kim *et al* 2006; Lim *et al* 2007; Zhou *et al* 2009, 2010). In the present study, BCB additive was added to LZT ceramics in order to investigate the possibility of using it as a low-temperature sintering additive. Furthermore, the phase structure, sinterability, and MW dielectric properties of LZT with BCB and their cofireability with Ag electrode were investigated.

2. Experimental

$Li_2ZnTi_3O_8$ (LZT) ceramic samples were prepared by the solid-state reaction method. High-purity Li_2CO_3, ZnO and TiO_2 (99·9+%, Sigma Aldrich, UK) were used as the starting materials. Stoichiometric amounts of the powder samples were mixed and ball milled using zirconia balls in ethanol medium for 24 h. The resultant slurry was then dried. The final LZT ceramic powders were calcined at 900°C for 4 h. The BCB powder was prepared according to the literature (Zhou *et al* 2009). After subsequent ball-milling of LZT with 0·5–3 wt% BCB, followed by drying, pellets, 10 mm in diameter and ~5 mm thick, were prepared by uniaxial pressure of about 100 MPa, and subsequently sintered for 4 h in air at 925°C.

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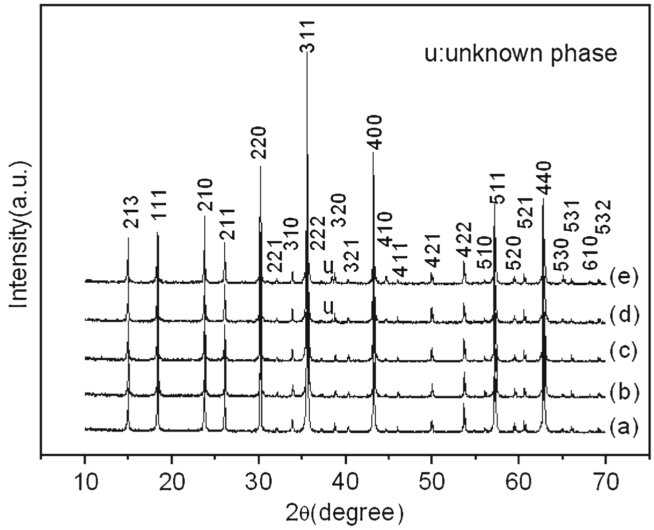

Figure 1. XRD patterns of LZT ceramics with different BCB contents sintered at 925°C for 4 h: (**a**) 0·5 wt%, (**b**) 1 wt%, (**c**) 1·5 wt%, (**d**) 2 wt% and (**e**) 3 wt%.

The crystal structures were investigated by X-ray diffraction (XRD) using CuKα radiation (Philips PW1710). The bulk density was measured by the Archimedes method. The microstructure of the sintered and thermally etched samples was studied via scanning electron microscope (JEOL JSM-6400, Japan). MW dielectric properties were measured using a vector network analyser (Advantest R3767CH, Japan). The temperature coefficient of the resonant frequency (τ_f) was measured in the range 20°–80°C. To check the chemical compatibility of LZT+BCB ceramic with the silver powder, the ceramic powder was mixed with silver and pressed into pellet and sintered at 925°C for 4 h. In addition to the XRD analysis, microstructural study was carried out using scanning electron microscopy.

3. Results and discussion

XRD patterns of LZT ceramics with BCB fired at 925°C for 4 h are shown in figure 1. All the diffraction peaks of LZT ceramics with 0·5–1·5 wt% BCB could be indexed

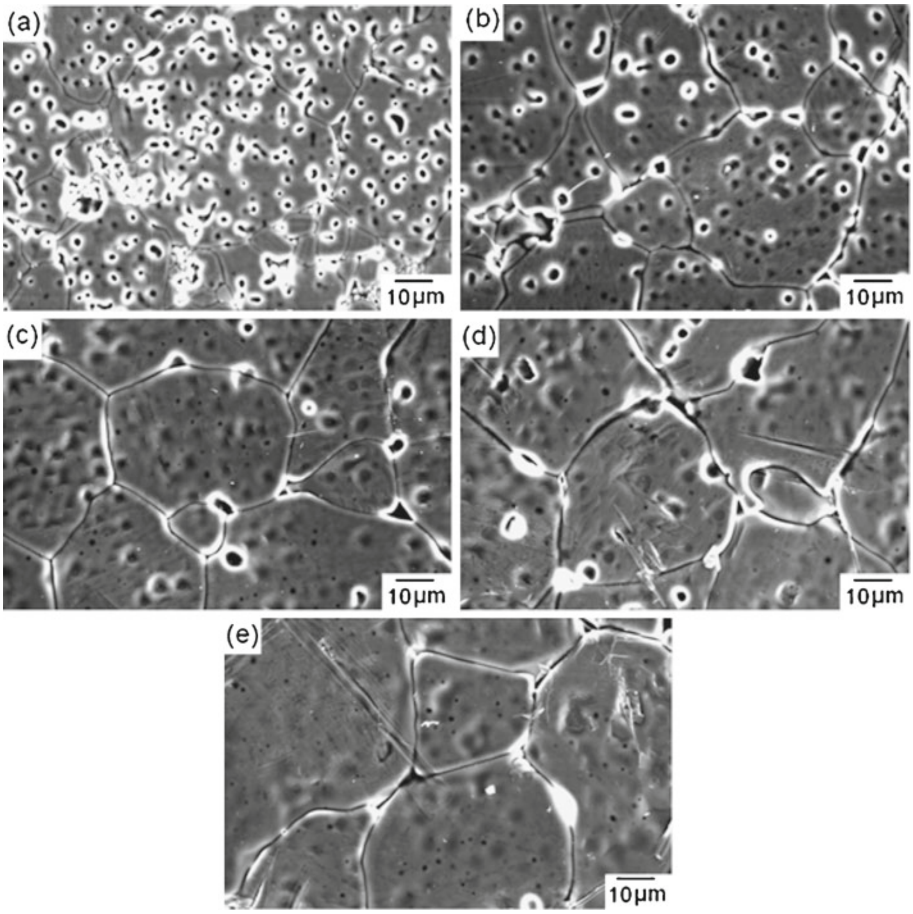

Figure 2. SEM micrographs of polished surface of LZT ceramics with different BCB contents sintered at 925°C for 4 h: (**a**) 0·5 wt%, (**b**) 1 wt%, (**c**) 1·5 wt%, (**d**) 2 wt% and (**e**) 3 wt%.

as a cubic structure $Li_2ZnTi_3O_8$ (PDF 86–1512) without secondary phase, which agreed well with the result reported by Kawai *et al* (1998). When BCB content exceeds 1·5 wt%, a small amount of unknown secondary phase occurred, as shown in figures 1(d)–(e).

SEM images of the polished surface of LZT ceramics with 0·5, 1·0, 1·5, 2 and 3 wt% BCB are shown in figure 2. It was evident that the porosity of LZT ceramics decreased with BCB content, as was confirmed by figure 3a, which indicates the dependence of porosity (or relative density) on BCB content. Grain growth had a close connection with the BCB content. The more BCB content, the bigger the grains of the LZT ceramics. It illustrates that the added BCB may accelerate the grain growth due to the liquid phase effect during sintering. It can be deduced that some small grains dissolve in the liquid phase at the sintering temperature while other grains grow up. It was found that some pits existed in the surface of grains, which may arise from the volatilization of constituents such as BCB.

The dependence of BCB content on the relative density, permittivity (ε_r), $Q \times f$ and τ_f values of LZT ceramics sintered at 925°C for 4 h is depicted in figure 3. The ε_r value first increased and then decreased. When BCB $= 1{\cdot}5$ wt%, ε_r reached a maximum value of 23·1. The first increase of ε_r might result from the increase of density (or the decrease of porosity) of the LZT ceramics (Penn *et al* 1997). On further increase of BCB content ($>1{\cdot}5$ wt%), though the relative density slightly increased, the ε_r obviously decreased, which was mainly attributed to the increase of BCB content (low permittivity of 7·4 (Zhou *et al* 2009)) and secondary phase formation (seen in figure 1). From figure 3b, it was observed that the $Q \times f$ value of the ceramics first increased and the maximum $Q \times f$ value of 22,732 GHz was obtained when BCB $= 1{\cdot}5$ wt%. However, the $Q \times f$ value sharply decreased with further increase of BCB content (≥ 2 wt %). It was expected that as the grain size increased, the $Q \times f$ value (or 1/tan δ) would increase because a reduction in the number of grain boundaries per unit volume would result in a material with a lower loss. In fact, the $Q \times f$ value (or 1/tan δ) increased for samples with small grain size and then

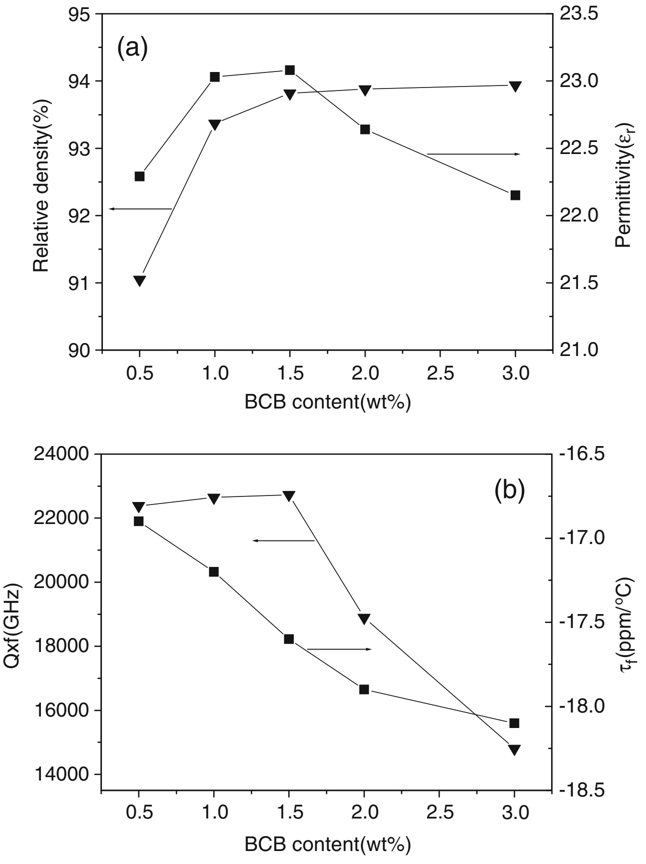

Figure 3. Dependence of BCB content on relative density and permittivity (**a**), on the $Q \times f$ and τ_f value (**b**).

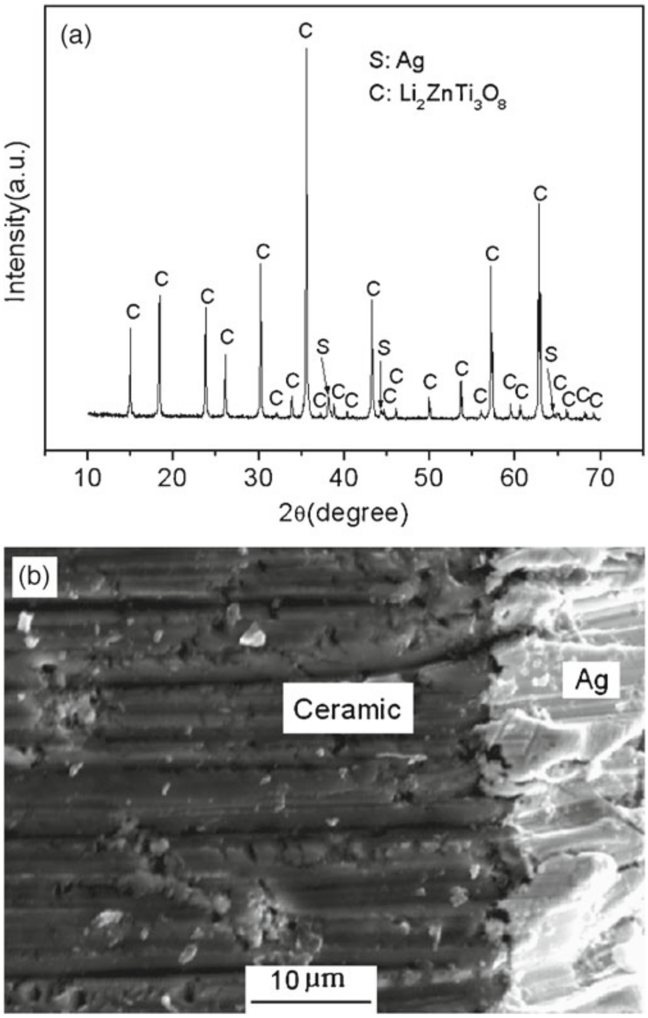

Figure 4. XRD pattern (**a**) and SEM micrograph showing interface between Ag electrode and LZT+1·5 wt% BCB ceramic sintered at 925°C for 4 h (**b**).

decreased rapidly for samples with big grain size, as shown in figures 2 and 3b. This result was not in accordance with other results reported by other researchers (Kim and Yoon 1994; Kucheiko *et al* 1997). It may be that the decrease in $Q \times f$ value seen at larger grain sizes is due to other factors such as secondary phase and liquid phase as well as non-uniform microstructure, which was in agreement with Penn *et al*'s (1997) study. It was apparent that the τ_f value decreased with the increase of BCB content. The pure LZT ceramic has a negative τ_f ($-11{\cdot}2$ ppm/°C) (George and Sebastian 2010a), and BCB also has negative τ_f value (-32 ppm/°C^{-1}) (Zhou *et al* 2009). Therefore, addition of BCB increased the negative τ_f value of the LZT ceramics. The τ_f value of the LZT ceramics ranged from $-16{\cdot}9$ to $-18{\cdot}1$ ppm/°C. The optimum BCB content should be in the range of 1–1·5 wt%. The XRD pattern together with SEM micrograph showing interface between Ag electrode and the LZT+1·5 wt% BCB ceramic is presented in figure 4. It was seen that there were only diffraction peaks of the $Li_2ZnTi_3O_8$ phase and the cubic silver phase (PDF 4–783) in the co-fired ceramic (figure 4a). A good contact between the ceramic and Ag was observed, as shown in figure 4b. It indicates that the ceramic phase did not react with the Ag powders and no other phase was formed when they were co-fired at 925°C for 4 h. This result is tolerable during the LTCC procedures and the BCB-added $Li_2ZnTi_3O_8$ ceramic can be recognized as a promising dielectric material for LTCC application.

4. Conclusions

The addition of BCB to $Li_2ZnTi_3O_8$ ceramic enhances densities, reduces its sintering temperatures significantly to 925°C, and induces only a limited degradation in the $Q \times f$ value. MW dielectric properties of $\varepsilon_r = 23{\cdot}1$, $Q \times f = 22{,}732$ GHz and $\tau_f = -17{\cdot}6$ ppm/°C can be obtained by adding 1·5 wt% BCB in LZT ceramics sintered at 925°C for 4 h. XRD analysis and SEM observation show that BCB added-LZT ceramic can co-fire with the silver electrode, and can be a promising MW dielectric material for LTCC application.

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