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Fabrication and microwave dielectric properties of $CuO-B_2O_3-Li_2O$ glass-ceramic with ultra-low sintering temperature

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ABSTRACT

$CuO-B_2O_3-Li_2O$ (CBL) glass-ceramic with a composition of 32 wt% CuO – 63 wt% B_2O_3 – 5 wt% Li_2O was prepared through conventional glass-ceramic route. The CBL glass-ceramic could be densified well by sintering at 625 °C for 30 min. The X-Ray diffraction (XRD) and transmission electron microscopy (TEM) analysis indicated that the CuB_2O_4 phase was dominated in the sintered glass-ceramic, which showed excellent microwave dielectric properties with ε_r = 5.84, $Q\times f$ = 10120 GHz (at 13.44 GHz), and τ_f = −33 ppm/°C. Furthermore, the CBL material is chemically compatible with both silver (Ag) and aluminum (Al) electrodes at their sintering temperatures. These properties indicate that the CBL glass-ceramic might be a promising ultra-low temperature co-fired ceramic (ULTCC) material for packaging substrate applications.

1. Introduction

Low temperature co-fired ceramics (LTCC) with low dielectric constants (low-K, ε_r = 4–10) have been successfully used to make ceramic multilayer packaging substrates for millimeter-wave communications and high density integrated devices [1,2]. In recent years, the studies of new LTCC materials with ultra-low sintering temperatures (< 650 °C, ULTCC) have attracted much interest, since there are demands for LTCC technology to directly integrate with ICs or even organic electronics [3]. In such cases, the electrode materials such as aluminum or nano silver ink can be used with sintering temperature less than 650 °C and 400 °C, respectively [4].

The reported ULTCC materials with low-K are generally based on tellurates, molybdates, vanadates, and tungstates of Bi, K, Na, Ag, Li, Ba, *etc*. [4]. Most of them have intrinsic ultra-low sintering temperatures and present good dielectric properties. However, it's a little difficult for these crystallized materials to match the co-firing process with the metal electrodes [5,6]. Since the commercially available LTCC materials are either glass-ceramic or glass + ceramic systems [7,8], it should be favorable to search ULTCC materials in glass-ceramic systems. Compared to the widely-used silicate or borate-silicate glasses in the traditional LTCC materials, borate glasses have a relatively low soften temperature and crystallization temperature [9,10]. Yu et al. reported that $3ZnO–2B_2O_3$ glass-ceramic sintered at 650 °C for 30 min with a dielectric constant ε_r = 7.5 and $\tan\delta = 6\times10^4$ at 10 MHz. The $ZnO–B_2O_3$ based glass-ceramics do not react with silver electrode and are promising candidates for ULTCC applications [11]. Nevertheless, the dielectric properties at microwave frequency regime have not been reported in details. To the best of our knowledge, except for $3ZnO–2B_2O_3$ glass-ceramic, no other glass-ceramic ULTCC materials have been reported up to now.

The ion substitutions with low polarizability for Zn in $3ZnO–2B_2O_3$ glass-ceramic could obtain new ULTCC systems, such as Cu. Because the dielectric polarizability is associated with the ionic radius, and the ionic radius of Cu^{2+} (0.73 Å) is very close to that of Zn^{2+} (0.74 Å) [12]. CuB_2O_4 has a tetragonal structure with space group I_42d and lattice parameters $a = b$ = 11.528 Å, and c = 5.607 Å [13,14]. The CuB_2O_4 single crystal has been reported to present low-K (~6) and low loss ($\tan\delta \le 1\times10^{-3}$) at 1 kHz [15,16]. In addition, the crystallization temperature of CuB_2O_4 from $CuO-B_2O_3-Li_2O$ (CBL) glass-ceramic was about 650 °C [17]. These reports indicate that the glass-ceramic with CuB_2O_4 as the main crystallization phase could be a potential ULTCC material.

In present paper, CBL glass-ceramics with CuB_2O_4 as main crystallization phase were fabricated. The sintering behaviors, microstructures and the microwave dielectric properties of the CBL glass-ceramics

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were studied, and the compatibility of co-firing with Ag and Al metallic electrodes were also investigated.

2. Experimental procedure

The starting materials, including CuO (≥99.0%), H_3BO_3 (≥99.5%), and Li_2CO_3 (≥98.0%) (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), were first mixed according to the CBL glass-ceramic with 32 wt% CuO, 63 wt% B_2O_3 and 5 wt% Li_2O, then melted at 1050 °C for 2 h. The molten solution was quenched into de-ionized water to form glass slag. The resultant dark blue samples exhibited typical glassy appearance with lustrous and smooth fracture surfaces, which are similar to the previous report [17]. Then the obtained glass was crushed and ball milled for 12 h in ethanol. The dried glass powders were then pressed into pellets with a diameter of 13 mm and a height of 6–7 mm, under 2 MPa pressure, and sintered at 550–650 °C for 30 min in air, with a heating rate of 5 °C/min.

The thermal behavior of the CBL glasses was investigated by differential thermal analysis (DTA, Netzsch STA 449 C, Germany) using a heating rate of 10 °C/min in air, and alumina was used as the reference material. The phase structure of glass-ceramics was performed using the X-ray diffraction analysis (XRD, Rigaku D/MAX 2550V, Japan). The scanning electron microscope (SEM, JEOL JSM6700F, Tokyo, Japan) and transmission electron microscope (TEM, JEOL JEM-2100F, Tokyo, Japan) equipped with energy dispersion spectroscopy (EDS) were used for observing the microstructures of the sintered samples and the compatibility of co-firing with Ag and Al electrodes.

Density (ρ) of the sintered samples was measured using the Archimedes method. The microwave dielectric properties of the samples were measured at a frequency range of 13–14 GHz by using Hakki-Coleman method on a network analyzer (Agilent, E8363A PNA Series, California, USA) [18]. The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range of 25–85 °C, and calculated using the formula $\tau_f = (f_T - f_0)/f_0(T - T_0)$ where f_T, f_0 were the resonant frequencies at the measuring temperature T and T_0 (25 °C), respectively.

3. Results and discussion

The DTA curve and XRD pattern of the CBL glass powders are shown in Fig. 1. The wide diffraction peak at about 25° reveals that the sample is non-crystallized glass. The DTA analysis indicates that glass transition temperature (T_g) of CBL glass is 468 °C. A sharp exothermic peak observed at a temperature of 633 °C is related to the crystallization of the glass. The following XRD analysis demonstrates that the crystalline phase is CuB_2O_4. As heating continued, the endothermic peak at 797 °C can be observed, which represents the melting temperature of CBL glass.

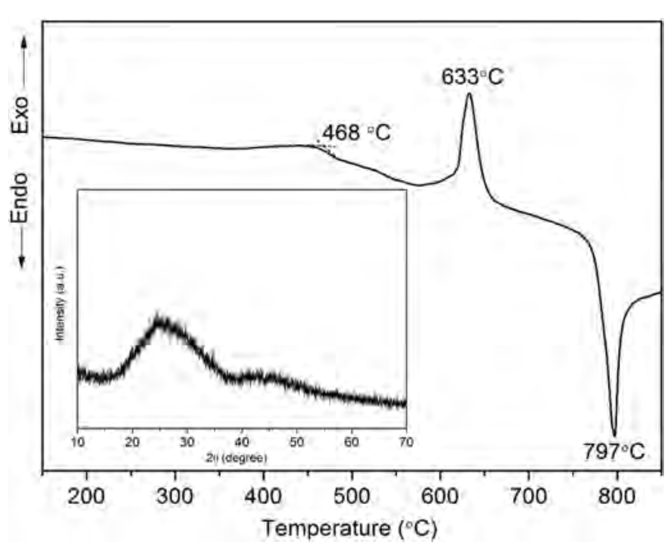

Fig. 1. DTA curve of CBL glass powders, and insert shows the XRD pattern of CBL glass.

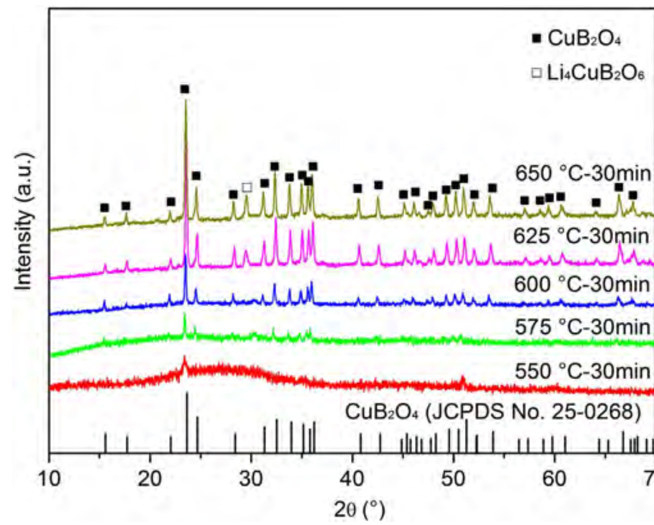

Fig. 2. XRD patterns of CBL glass sintered from 550 to 650 °C.

Fig. 2 shows the XRD patterns of CBL glass sintered at 550, 575, 600, 625, and 650 °C for 30 min, respectively. The peaks of CuB_2O_4 phase (JCPDS No. 25–0268) emerge in the 550 °C sintered sample, and the intensity of diffraction peaks increases as the sintering temperature increased. This suggests that the amount of CuB_2O_4 phase and degree of crystallinity of CuB_2O_4 phase increased. In addition, the second phase $Li_4CuB_2O_6$ can be observed from the sample sintered at 625 °C. Since the Li_2O addition is only 5 wt%, the peak intensity of $Li_4CuB_2O_6$ phase is not strong even sintered at 650 °C.

The bulk density and microwave dielectric properties of CBL glass-ceramics sintered at different temperatures are list in Table 1. The sample sintered at 550 °C exhibits a low bulk density of about 2.12 g/cm^3, implying that it is not densified. With further increase of sintering temperature, the bulk density of glass-ceramics increased and reached its maximum value of 3.13 g/cm^3 at 625 °C. When the sintering temperature increased to 650 °C, the density decreases to 3.08 g/cm^3. The decrease of density should be the result of over-sintering [19,20].

The dependence of ε_r of CBL glass-ceramics on sintering temperature has a tendency similar to that of the bulk density. The microwave dielectric properties of CBL glass-ceramics sintered at 550 °C and 575 °C could not be measured because of their low density. ε_r and Q×f of CBL glass-ceramic sintered at 625 °C could reached their maximum of 5.84 and 10,120 GHz (at 13.44 GHz), respectively. The τ_f value of CBL glass-ceramics varies slightly from −38 to −31 ppm/°C in the sintering temperature ranging from 600 to 650 °C. These results suggest that the sintering temperature of 625 °C is sufficient for the densification of CBL glass-ceramics. Although trace amount of the

Table 1
Bulk density and microwave dielectric properties of CBL glass-ceramics obtained at different sintering temperatures.

Sintering Temperature (°C)	ρ (g/cm^3)	f (GHz)	ε_r	Q×f (GHz)	τ_f (ppm/°C)
550	2.12	–	–	–	–
575	2.53	–	–	–	–
600	2.92	13.29	5.75	8053	−38
625	3.13	13.44	5.84	10,120	−33
650	3.08	13.51	5.81	9897	−31

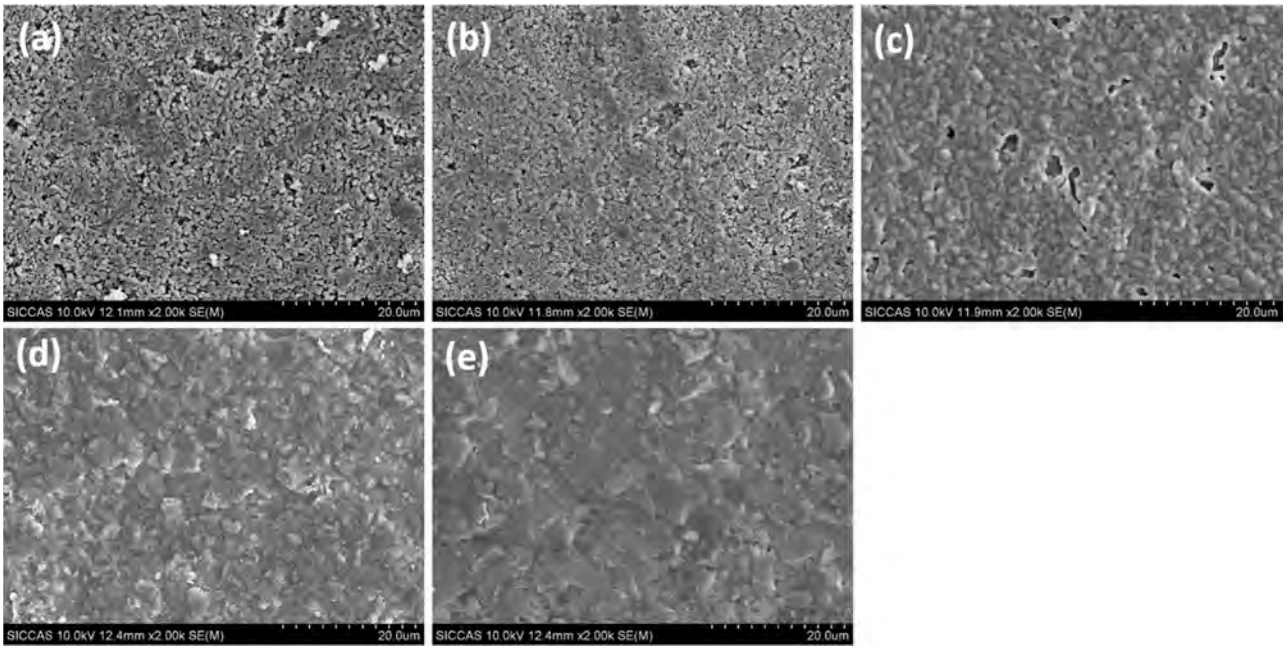

Fig. 3. SEM images of the natural surface of CBL glass-ceramics sintered at different temperatures (a) 550 °C; (b) 575 °C; (c) 600 °C; (d) 625 °C; (e) 650 °C for 30 min.

secondary phase $Li_4CuB_2O_6$ appeared from CBL glass-ceramic, no obvious effect of the secondary phase on the dielectric constant was observed. Since the low dielectric polarizabilities of boron and the strong covalent bonds in trigonal planar BO_3 or tetrahedral BO_4 structural units in the borates result in the low dielectric constant of borates, the $Li_4CuB_2O_6$ phase should also have a low dielectric constant. Furthermore, the crystal structure of $Li_4CuB_2O_6$ is similar to that of $Li_3AlB_2O_6$, which was reported to be a low dielectric constant of 4.2 and a $Q\times f$ value of 13027 GHz sintered at 675 °C [21]. Thus, the microwave dielectric properties of the secondary phase $Li_4CuB_2O_6$ in the CBL glass-ceramic are very likely to be close to the main phase CuB_2O_4 and would have no obvious effect on the dielectric properties.

Fig. 3 shows the SEM images of the natural surface of CBL glass-ceramics sintered at different temperatures. It can be seen that the surface of the sample sintered at 550 °C is porous, implying that it has low density, which is consistent with bulk density measurements. As sintering temperature increased, reduction in porosity and uniform grain growth are observed. The well-densified CBL glass-ceramics can be obtained at sintering temperatures of 625–650 °C, as shown in Fig. 3d and e.

The microstructure of the CBL glass-ceramic was further investigated by TEM. Fig. 4a shows a typical TEM image of the CBL glass-ceramic sample sintered at 625 °C for 30 min. It can be observed that there is a grain (mark 3) surrounded by the glass matrix (mark 1). Cu and O elements with the atomic ratio of about 1:4 can be identified from the EDS analysis of mark 3, as shown in the insert of Fig. 4a. Nanosized grains were observed from the high-resolution transmission electron microscopy (HRTEM) image. These grains may be the crystal phase precipitated from the glass matrix, which is confirmed by the selected area electron diffraction (SAED) patterns of mark 1, as shown in Fig. 4b. It is known that the SAED patterns of pure glass are halos. However, the SAED patterns extracting from these nanosized grains showed that amorphous halos were accompanied by crystal electron-diffraction spots. This revealed that there were crystallized phases formed in the glass matrix. Fig. 4c shows the HRTEM image of the boundary (mark 2) between the grains and glass matrix. The crystalline and amorphous regions are observed. The crystalline lattice can be clearly seen in the grain. The interplanar distance is about 0.505 nm, which is corresponding to the (1 0 1) plane of CuB_2O_4 (JCPDS No. 25–0268). The SAED pattern of the region with fringes shown in the insert of Fig. 4c also reveals that these regions are composed of tetragonal CuB_2O_4 phase.

For LTCC application of a new glass-ceramic system with ultra-low sintering temperature, its chemical compatibility with silver or aluminum electrodes is very important. Fig. 5 shows the XRD results, backscattered electron (BSE) images of the as-fired surface and EDS analysis of CBL glass-ceramic co-fired with 20 wt% Ag and 20 wt% Al powders at 625 °C for 30 min, respectively. In the XRD patterns, the main peaks of CuB_2O_4 and the respective metals can be seen without any intermediate phases. In the BSE images of the silver co-fired sample, the marked grains with bright color can be identified as silver, which is confirmed by EDS analysis. The grains with dark color in the aluminum co-fired sample are found to be pure aluminum, which is also confirmed by the corresponding EDS analysis. Combined with the XRD results, it can be concluded that the CBL glass-ceramic does not react with either silver or aluminum at the sintering temperature of 625 °C. The desired the chemical compatibility between CuB_2O_4 and silver/aluminum powders suggests that the CBL glass-ceramic could be a promising ULTCC material.

4. Conclusions

A new ULTCC material, CBL glass-ceramic with the composition of 32 wt% CuO – 63 wt% B_2O_3 – 5 wt% Li_2O, was introduced. The CBL glass-ceramics can be well-densified at 625 °C for 30 min with a bulk density of 3.13 g/cm^3, and exhibits excellent microwave dielectric properties with ε_r = 5.84, $Q\times f$ = 10,120 GHz (at 13.44 GHz) and τ_f = −33 ppm/°C. CuB_2O_4 is the main crystalline phase in the sintered glass-ceramics. The chemical compatibility with both silver and aluminum electrodes at the sintering temperatures makes CBL glass-ceramic a promising ULTCC material for packaging substrate applications.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

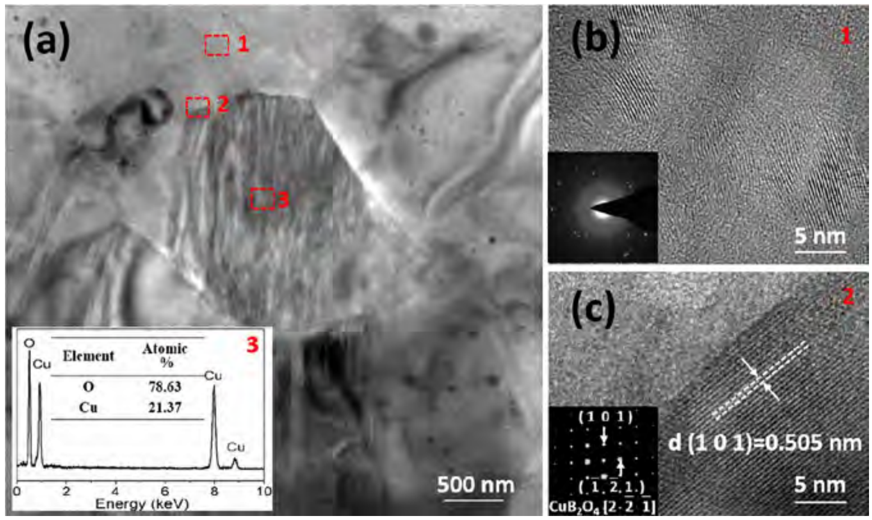

Fig. 4. TEM images of (a) the CBL glass-ceramic sample sintered at 625 °C for 30 min, and insert shows the EDS patterns of mark 3; (b) HRTEM image of mark 1 and insert shows the corresponding SAED patterns; (c) HRTEM image of mark 2 and insert shows the corresponding SAED patterns.

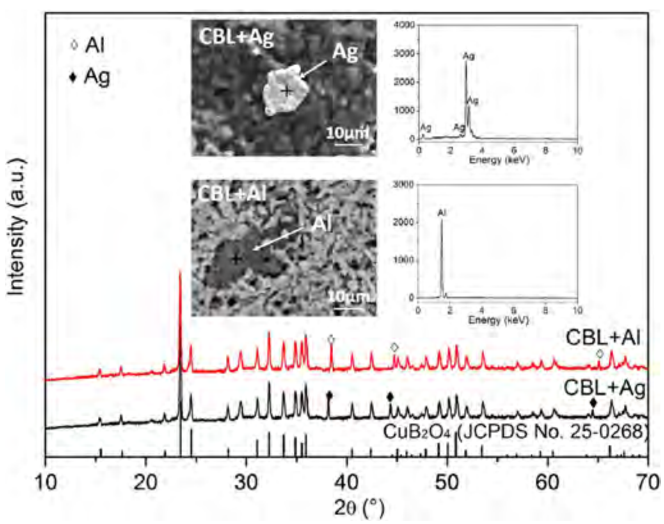

Fig. 5. XRD patterns, BSE images of the as-fired surface and EDS analysis of CBL glass-ceramic co-fired with 20 wt% Ag and 20 wt% Al powders at 625 °C for 30 min, respectively.

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