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Microwave dielectric properties of LBBS glass added $(Zn_{0.95}Co_{0.05})_2SiO_4$ for LTCC technology

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ABSTRACT

The effects of Li_2O–B_2O_3–Bi_2O_3–SiO_2 (LBBS) glass on the sintering characteristics and microwave dielectric properties of $(Zn_{0.95}Co_{0.05})_2SiO_4$ were investigated in this study. $(Zn_{0.95}Co_{0.05})_2SiO_4$ powders were fabricated by traditional solid-state preparation, and LBBS glass was synthesised by quenching method. The LBBS glass can effectively reduce the sintering temperature of $(Zn_{0.95}Co_{0.05})_2SiO_4$ from 1300 °C to 900 °C and thus promote the densification and uniformity of the specimens. XRD patterns indicated that no other secondary phases existed in our doping range (0–2 wt%). To obtain the highest sintering density and a uniform microstructure when the samples were sintered at 900 °C, the optimal doping content was set to be 1.5 wt%. The sample also demonstrated the following excellent microwave dielectric properties: ε_r=6.16, Qf=33,000 GHz and τ_f= −59 ppm/°C.

1. Introduction

Microwave devices and microwave dielectric materials with low dielectric constant (ε_r) and minimal loss should be miniaturised to intensively develop the wireless communication systems [1,2]. Given the co-firing among active layers, electrodes and substrates, low-temperature co-fired ceramics (LTCC) have emerged in recent decades as an ideal technology to miniaturise microwave devices. To date, several microwave dielectric ceramics have been promoted for applications in LTCC with low melting point oxides and glasses to decrease the temperature designed for co-firing with an electrode. Generally, Ag is used as a metallic electrode in LTCC because of its high conductivity and low cost [3,4]. Hence, the sintering temperature of all microwave dielectric materials must be decreased to approximately 900 °C or lower to co-fire with the Ag electrode without significantly affecting their dielectric properties. Glass addition is a traditional approach to aid sintering [5,6]. However, this method may lead to poor microwave dielectric properties or crack formation during soldering because of the different thermal expansion coefficients between glasses and ceramics [7–8]. Therefore, the selection of a proper glass with less influence on the material dielectric properties is of critical importance. Furthermore, low permittivity and high Q value are extremely significant for ceramic substrates in microwave applications. As important low-ε_r materials, Zn_2SiO_4 ceramics synthesised by conventional solid-state reaction exhibited the following excellent dielectric properties: ε_r=6.6, Qf=219,000 GHz and τ_f= −61 ppm/°C [9,10]. Such materials have been widely studied for potential LTCC applications. In addition, B_2O_3 has been used to reduce the sintering temperature of $Zn_{1-x}SiO_{4-x}$ ceramics(x=0–0.5), and the Qf value increased to a maximum of 7000 GHz when x=0.3. However, 25% B_2O_3 addition can make the material difficult to cast as a film [11]. Consequently, BaO–B_2O_3 was selected as a sintering aid to increase the sintering temperature to 900 °C. The optimum microwave dielectric properties were exhibited as follows: Qf=26,000 GHz, ε_r=6.4 and τ_f= −40 ppm/°C. However, the addition of 10 wt% BaO–B_2O_3 deteriorated the microwave dielectric properties [12].

In the present work, we used Li_2O–B_2O_3–Bi_2O_3–SiO_2 (LBBS) glass as a sintering aid and systematically investigated the effects of this glass on the sintering behaviour and microwave dielectric properties of $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramics.

2. Experimental procedure

A $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramic composed of $(ZnO)_{1.9}(Co_2O_3)_{0.05}(SiO_2)_1$ was prepared by conventional solid-state reaction. Analytical grade ZnO, SiO_2 and Co_2O_3 were weighed according to formula

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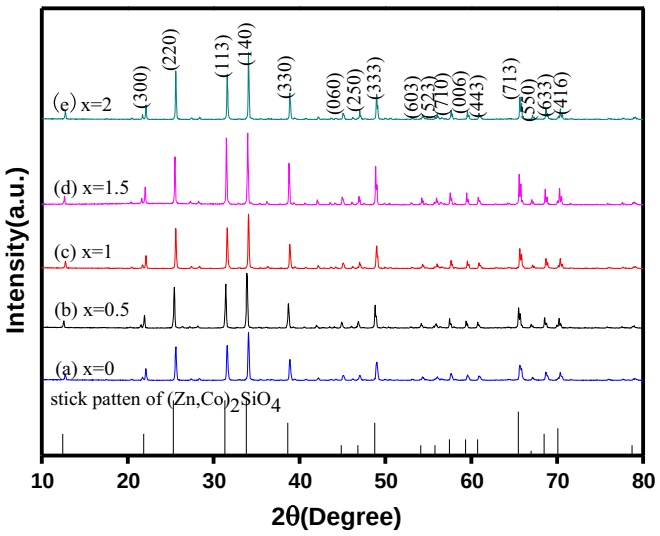

Fig. 1. XRD diffraction patterns of $(Zn_{0.95}Co_{0.05})_2SiO_4$ with x wt% LBBS: (a) $x=0$, (b) $x=0.5$, (c) $x=1$, (d) $x=1.5$, and (e) $x=2$.

and mixed in a ball mill. After drying, ceramic powder was calcined at 1200 °C for 3 h to obtain pre-sintered powders. Different amounts of LBBS glass, between 0 wt% and 2 wt%, were added to the pre-sintered powders, and the mixtures were further milled in ball mills. After the addition of PVA, the milled powders were granulated and pressed into cylindrical samples, which were finally sintered at 850 °C to 950 °C. To prepare the LBBS glass, high-purity Li_2CO_3, B_2O_3, Bi_2O_3 and SiO_2 were weighed at the ratio of 2:2:1:1. The powders were mixed, dried and melted at 1200 °C for 3 h. Subsequently, the melt was quenched in water to form the LBBS glass.

Phase compositions of the sintered samples were identified by X-ray diffraction (XRD: DX-2700) with Cu K_α radiation. The microstructure was examined by scanning electron microscopy (SEM: INCA penta FETX3 oxford). Bulk densities of the sintered samples were measured using the Archimedes' method. The microwave dielectric properties were evaluated using an Agilent N5230A network analyser in a resonant cavity. The quality factor was measured by the transmission cavity method, and the relative ε_r was detected using the Hakki–Coleman method. The temperature coefficient resonant frequency (τ_f) was measured from the invar cavity at the temperature range of 20 °C to 80 °C.

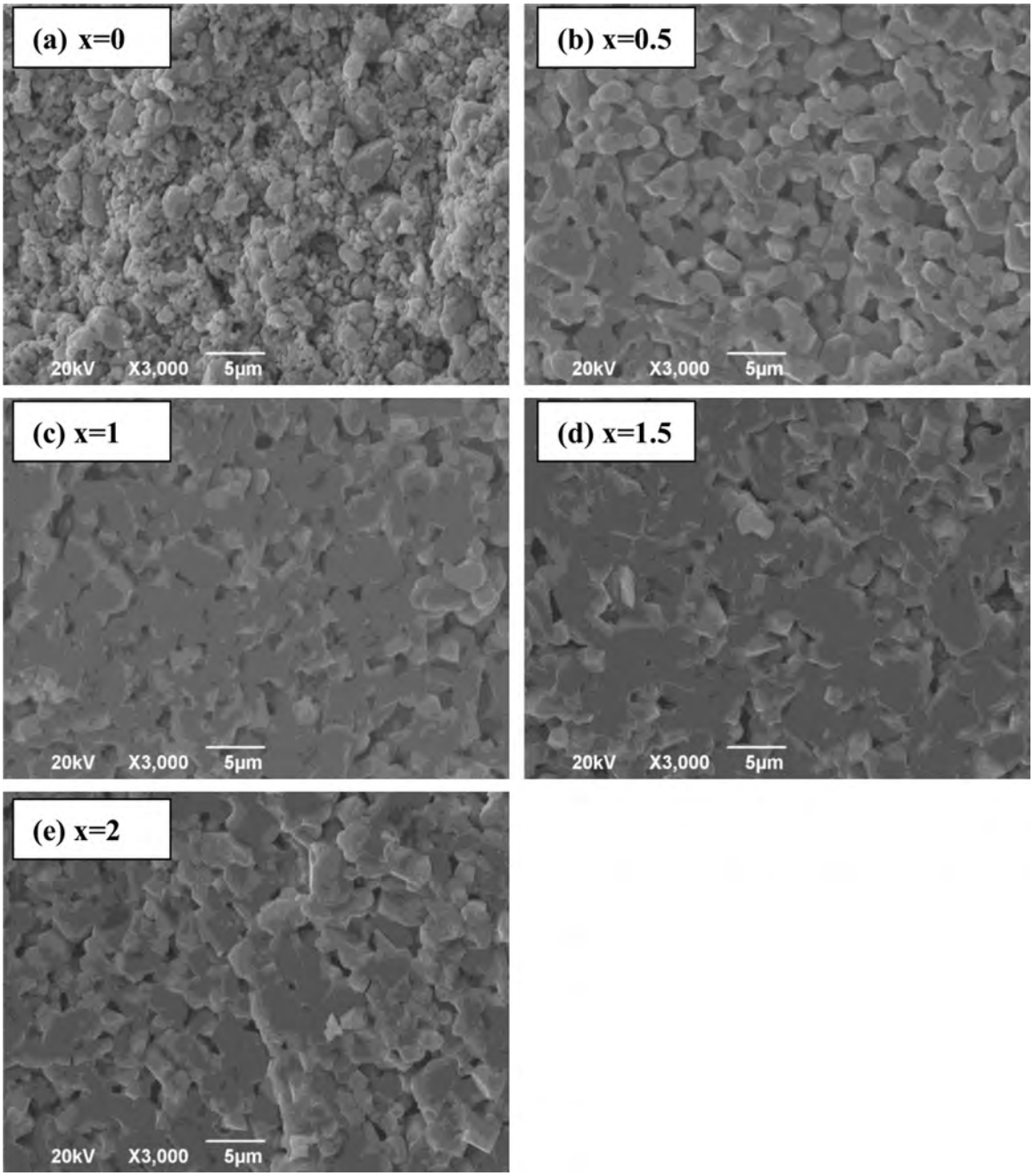

Fig. 2. SEM micrographs of $(Zn_{0.95}Co_{0.05})_2SiO_4$ with x wt% LBBS: (a) $x=0$, (b) $x=0.5$, (c) $x=1$, (d) $x=1.5$, and (e) $x=2$.

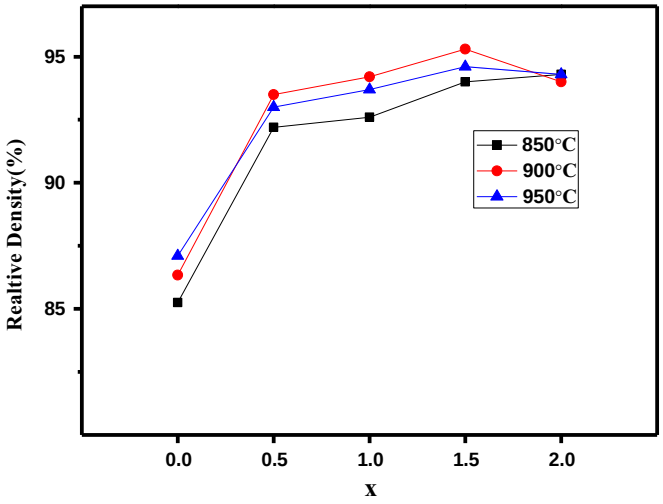

Fig. 3. Relative density values of $(Zn_{0.95}Co_{0.05})_2SiO_4$ with x wt% LBBS.

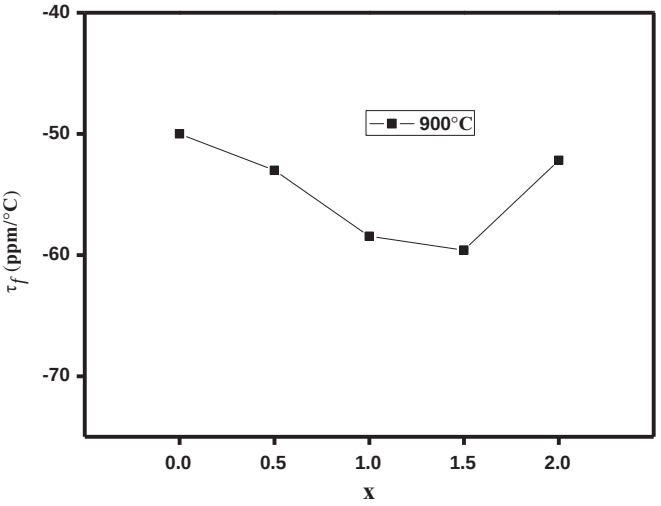

Fig. 6. τ_f values of $(Zn_{0.95}Co_{0.05})_2SiO_4$ with different amounts of LBBS.

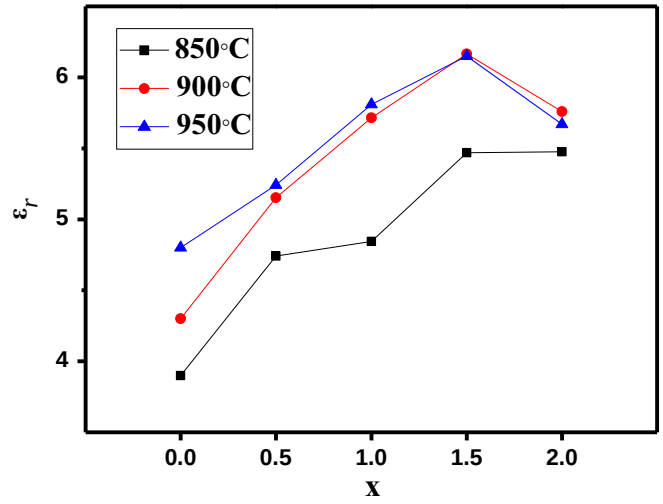

Fig. 4. ε_r of $(Zn_{0.95}Co_{0.05})_2SiO_4$ with x wt% LBBS.

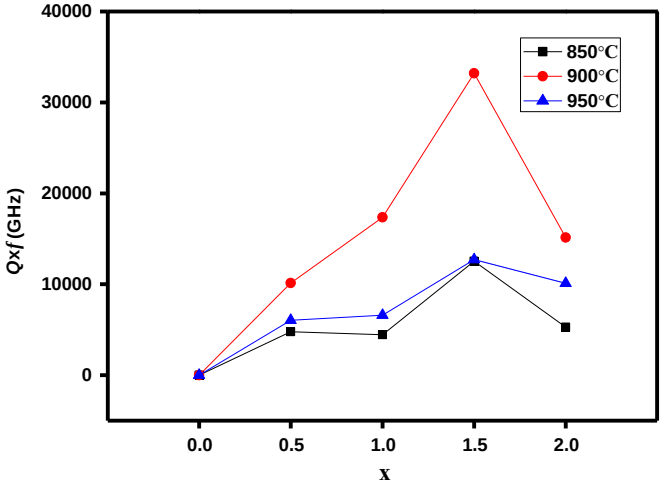

Fig. 5. Qf values of $(Zn_{0.95}Co_{0.05})_2SiO_4$ with different values of LBBS glass.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples with x wt% LBBS (x=0, 0.5, 1, 1.5, and 2) and sintered at 900 °C. All the compounds exclusively contained the diffraction peaks of $(Zn, Co)_2SiO_4$ (ICDD-PDF 46-1316), which implied that no other secondary phases existed. XRD results showed that no chemical reaction occurred between $(Zn_{0.95}Co_{0.05})_2SiO_4$ and the LBBS glass. The diffraction peak intensities evidently showed that the increasing proportion of the LBBS glass enhanced the growth of Willemite crystals (Fig. 1 (a)–(d)), but excessive amounts of LBBS weakened this effect (Fig. 1 (e)).

Fig. 2 presents the SEM micrographs of the samples with x wt% LBBS glass and sintered at 900 °C. A porous and non-homogenous microstructure is observed in Fig. 2(a), which indicated that only $(Zn_{0.95}Co_{0.05})_2SiO_4$ cannot be densely sintered at 900 °C. With increasing LBBS addition, microstructures with decreased porosity and increased grain size can be observed in Fig. 2(a)–(d). The LBBS glass increased the densification via liquid-phase sintering effect. However, the microstructure with numerous pores (Fig. 2(e)) indicated that excessive amounts of glass may hinder the densification of the ceramic and consequently deteriorate the microwave dielectric properties.

To further verify the influence of the LBBS glass on the densification of $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramics, the relative density values of the sintered samples under 850 °C to 950 °C with different LBBS glass contents were tested (Fig. 3). The relative density first increased with the increasing amount of LBBS glass regardless of the different sintering temperatures. The results agreed well with the SEM micrographs. The relative density peaked with 1.5 wt% LBBS glass when sintered at 900 °C and 950 °C before starting to decrease. By contrast, the relative density monotonously increased with the LBBS content when the samples were sintered at 850 °C. These phenomena implied that 1.5 wt% LBBS glass was enough to obtain the peak relative density when the samples were sintered at 900 °C and 950 °C. For the samples sintered at lower temperatures, a higher content of LBBS glass was necessary to densify the ceramics. The samples without LBBS addition increased by 1.85% as the sintering temperature varied from 850 °C to 950 °C, whereas that significantly increased by 9.05% in the specimen doped with 0.5% LBBS glass. Given the liquid-phase sintering of the LBBS glass, the sintering temperature of $(Zn_{0.95}Co_{0.05})_2SiO_4$, which was approximately 1300 °C, can be reduced to 900 °C, with only a small amount of the LBBS glass required as a sintering aid (1.5 wt%). Thus, the LBBS glass was a highly efficient sintering aid to reduce the sintering temperature of $(Zn_{0.95}Co_{0.05})_2SiO_4$.

Fig. 4 presents the ε_r values of the samples with different LBBS glass contents and sintered under various temperatures. The relationship between ε_r and x revealed almost the same trend as that

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between density and x shown in Fig. 3. This similar tendency indicated that density played a critical role in influencing ε_r [13,14]. Comparatively, ε_r increased with the increasing amount of LBBS glass and reached a maximum value at $x=1.5$. Notably, ε_r increased with the increasing sintering temperature for specimens without LBBS addition. However, in terms of increased range, the influence of LBBS glass was much higher than that of the sintering temperature on the densification and ε_r of the $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramics.

The Qf values of the samples sintered at 850–950 °C are shown in Fig. 5. Generally, the Qf value initially increased and then decreased with the increasing LBBS content. A maximum value of 33,000 GHz was reached when the sample was sintered at 900 °C with 1.5% LBBS doping. As shown in Figs. 3 and 5, the Qf value was also significantly relevant to the density. The microwave dielectric loss includes the intrinsic and extrinsic losses, with the extrinsic losses playing a more important role [15,16]. Thus, the Qf values were highly affected by the densification and grain uniformity. The first increase of Qf ($x=0$–1.5) can be mainly attributed to the promotion of the sintered density. SEM micrographs in Fig. 2(d)–(e) show that, with the increased amount of LBBS glass, an abnormal grain growth occurred, which resulted in the reduction of Qf values when the LBBS content was more than 1.5 wt% [17]. When the samples were sintered at 850 °C, the Qf value decreased when more than 1.5 wt% LBBS glass was used, by contrast, the density increased. Therefore, excessive LBBS doping would deteriorate the dielectric properties of $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramics. Further improvement of the Qf value of a ceramic cannot be achieved by increasing the LBBS content but might be possible by combining 1.5 wt% LBBS glass with other additives.

Fig. 6 shows the τ_f (TCF) values of $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramics added with various LBBS glasses and sintered at 900 °C for 3 h in air. The τ_f of the specimens with 1.5 wt% LBBS was -59 ppm/°C. With increasing LBBS content, TCF did not show any significant variation between -50 ppm/°C and -59 ppm/°C.

4. Conclusion

In this work, the LBBS glass effectively reduced the sintering temperature of $(Zn_{0.95}Co_{0.05})_2SiO_4$ from approximately 1300 °C to 900 °C, thereby achieving excellent microwave dielectric properties. XRD patterns showed that no chemical reactions occurred between $(Zn_{0.95}Co_{0.05})_2SiO_4$ and the LBBS glass. A dense microstructure with a uniform grain size can be obtained with 1.5 wt% LBBS. The sample also presented good dielectric properties as follows: $\varepsilon_r=6.16$, $Qf=33{,}000$ GHz and $\tau_f=-59$ ppm/°C.

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