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Short communication

Low firing and microwave dielectric properties of $BaTi_4O_9$ with B_2O_3–ZnO–La_2O_3 glass addition

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Abstract

A high-Q low firing ceramics material was fabricated from a composite of 80 wt% of $BaTi_4O_9$ powder and 20 wt% of B_2O_3–ZnO–La_2O_3 glass flux. The sample sintered at 900 °C for 3 h had the maximum bulk density. B_2O_3–ZnO–La_2O_3 glass was found to act as the sintering aid. The material sintered at 900 °C for 3 h consists of $BaTi_4O_9$, $LaBO_3$, an unidentified crystal phase and residual glass phase, and possesses excellent microwave dielectric properties: permittivity $k \approx 27$, quality factor $Q \times f \approx 20{,}000$ GHz, temperature coefficient of resonant frequency $\tau_f \approx 6.5$ ppm/°C.

Keywords: LTCCs; B_2O_3–ZnO–La_2O_3 glass; $BaTi_4O_9$

1. Introduction

Low-temperature co-fired ceramics (LTCCs) have been widely investigated due to their applications for the multilayer microwave components which can miniaturize the microwave devices. In the multilayer structures, the sintering temperature of the dielectric materials has to be reduced to or below 900 °C so as to co-fire with highly conductive embedded electrode such as Ag (the melting point of Ag is about 961 °C).

Generally speaking, adding low softening temperature glass is an effective, cheap approach to lower the densification temperature of ceramics [1–4]. Several researches including BaO–TiO_2–WO_3 with ZnO–B_2O_3 glass addition [5], $BaTi_4O_9$/$Ba_2Ti_9O_{20}$ with MgO–CaO–SiO_2–Al_2O_3 glass addition [6], $Ba_2Ti_9O_{20}$ with 3ZnO–B_2O_3 glass addition [7] have been studied; however, the sintering temperature of the composites was generally higher than 900 °C which is still high for co-firing of Ag inner electrodes. BaO–Nd_2O_3–TiO_2 ceramic with La_2O_3–B_2O_3–TiO_2 glass addition has also been investigated by Jung et al. [8], although temperature of densification could be lowered below 900 °C, the fraction of glass additive was as high as 60 wt%, which certainly will influence the microwave properties of $BaNd_2Ti_5O_{14}$ greatly. To weaken the destructive effect of the glass additives on the intrinsic microwave properties of the ceramics, researchers have to find good glass flux which could decrease the sintering temperature greatly with smaller amount addition but not influence the microwave properties of the host material too much.

B_2O_3–ZnO–La_2O_3 (BZL) glass is used as optical glass with high refractive index. It has not been found reported the literature as a sintering aid for LTCCs applications. In present study, we found the B_2O_3–ZnO–La_2O_3 glass was available as sintering aid in reducing the sintering temperature of the $BaTi_4O_9$-based composites, and the sintering process and the microwave dielectric properties of the sintered composites were also investigated.

2. Experiments

B_2O_3–ZnO–La_2O_3 glass with the composition of B_2O_3 60 mol%, ZnO 30 mol%, La_2O_3 10 mol% was prepared using reagent grade H_3BO_3, ZnO and La_2O_3 as the raw materials. The mixture was melted in a platinum crucible at 1100 °C for 1 h and the glass was quenched in water into fragments which were then pulverized and screened through a 80 mesh sieve to become the BZL glass powder. The $BaTi_4O_9$ was synthesized by conventional solid-state-reaction method using reagent grade $BaCO_3$ and TiO_2 as starting powders. $BaCO_3$ and TiO_2,

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with molar ratio of 1:4, were mixed in a plastic bottle with distilled water and ZrO_2 balls for 5 h. The mixture was then dried and calcined at 1180 °C for 2 h to form $BaTi_4O_9$ phase.

Eighty weight percent of $BaTi_4O_9$ and 20 wt% BZL glass powders were mixed and milled with ZrO_2 balls and deionized water for 24 h. After drying, the mixture was granulated by adding 7 wt% polyvinyl alcohol (PVA) solution. Then the pellets 15 mm in diameter and 9 mm in thickness were fabricated by uniaxial pressing at 1000 kg/cm^2, followed by sintering between 880 and 940 °C for 3 h in air with a heating rate of 5 °C/min. The bulk densities of the sintered pellets were measured by the Archimedes method. The crystal phases present in samples were identified by X-ray diffraction analysis (XRD, *D*/max 2550 V Rigaku, Japan). Polished and HF-etched surface of sintered sample was observed by scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS: model INCA, Oxford Instruments, Bucks, UK). The microwave dielectric properties of sintered samples were measured among the frequency range of 5–6 GHz by network analyzer (HP8363A, Agilent, USA), the temperature coefficient of resonant frequency (τ_f) was measured within the range from −25 °C to 85 °C, and τ_f was defined by $(f(85) - f(-25))/(f(25) \times 110)$, where $f(85)$, $f(-25)$ and $f(25)$ are the resonant frequencies at 85, −25 and 25 °C, respectively.

3. Results and discussion

3.1. Sintering process and microstructure

The bulk density of the pellets sintered between 880 and 940 °C is shown in Fig. 1. It was found that the sample sintered at 880 °C had a bulk density of only 3.0 g/cm^3, whereas the one sintered at 900 °C for 3 h had already reached the maximum value of 4.3 g/cm^3, and kept almost unchanged at 920 °C. It shows that the sample could be well-densified at and above 900 °C. It was believed that the B_2O_3–ZnO–La_2O_3 glass plays a crucial role in facilitating the densification of the composites. This result also indicated that the original B_2O_3–ZnO–La_2O_3 glass creates a large liquid phase at about 900 °C but not at or below 880 °C.

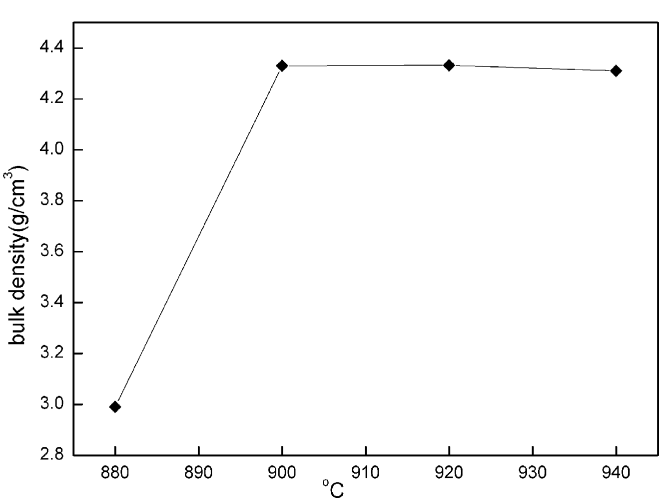

Fig. 1. Bulk density of the composites as a function of sintering temperature with dwell time for 3 h.

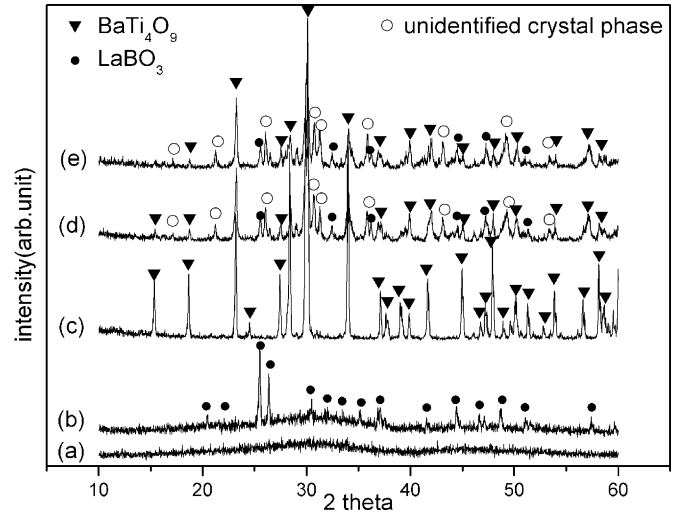

Fig. 2. X-ray diffraction patterns of (a) quenched BZL glass, (b) BZL glass heat treated at 900 °C, (c) calcined $BaTi_4O_9$ powder at 1180 °C, the composites sintered at (d) 900 °C and (e) 920 °C for 3 h.

From XRD patterns in Fig. 2(d and e), it was found that the composites sintered between 900 and 920 °C consisted of three crystalline phases: $BaTi_4O_9$ phase, $LaBO_3$ phase and an unidentified crystal phase. Fig. 2 also shows that the original glass was almost amorphous according to the dome outline of the XRD and $LaBO_3$ come from the crystallization of the B_2O_3–ZnO–La_2O_3 glass at about 900 °C. Because the raw materials were $BaTi_4O_9$ and the BZL glass, the unidentified crystal phase should be formed as the product of the interreaction between the glass flux and the $BaTi_4O_9$ phase. Due to the formation of the unknown phase, the sintering process obviously belonged to reactive sintering. Therefore, it was believed that dynamic mechanism of the chemical reaction was also one of the factors in facilitating the sintering process.

In the backscattered electron image (Fig. 3.) of the sample sintered at 900 °C for 3 h, three different areas were found in the picture: the grey area, the white area and the dark area. The white area and the grey area were confirmed by EDS as $LaBO_3$ and $BaTi_4O_9$, respectively, and the dark area consisted of the elements of Ba, Zn, Ti and O as shown in Table 1. From both Figs. 2 and 3, we know the $BaTi_4O_9$ phase was the majority phase of the composite. Combining with Fig. 2, we could deduce that the dark area corresponded to the unidentified phase in Fig. 2(d and e). Unfortunately, the unknown phase could not be identified by existing XRD data base. To identify the unknown phase, further investigations will be needed.

3.2. Microwave dielectric properties

Fig. 4 shows the permittivity (k) and quality factor ($Q \times f$) of the samples as a function of sintering temperature. As shown in Fig. 1, the bulk density of the sample increased rapidly from 880 to 900 °C, and remained unchanged from 900 to 920 °C. A little decrease in the bulk density of the sample appeared at 940 °C. Permittivity and quality factor of the samples exhibited

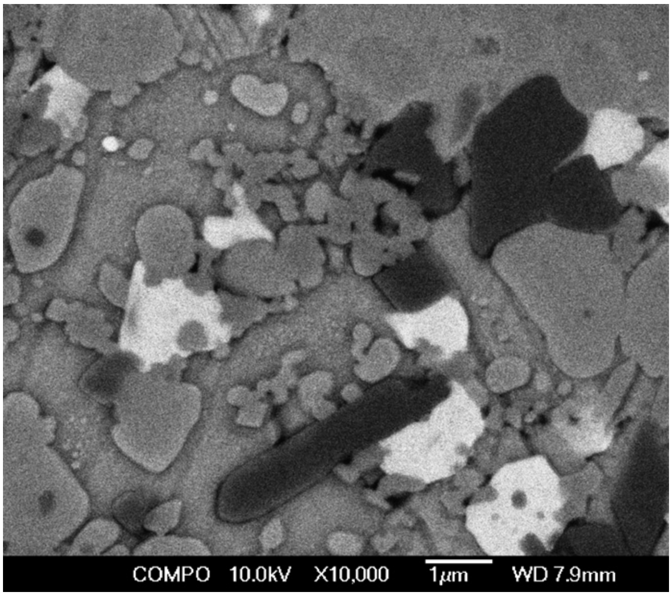

Fig. 3. Backscattered electron image of the sample sintered at 900 °C for 3 h.

similar trend of change to that of bulk density with increasing sintering temperature. At 880 °C, due to the high porosity, the composite had low permittivity and quality factor. While at 900 °C, due to high densification, the sample exhibited great enhancement of permittivity and quality factor. The decrease in the permittivity and quality factor of the sample sintered at 940 °C is probably due to a little over-sintering of the sample. Generally speaking, the $Q \times f$ value of glass is much lower than pure microwave dielectric ceramic. In the present study probably because of the smaller amount of glass addition, the sample sintered at 900 °C for 3 h exhibited a permittivity k of 27 and quality factor $Q \times f$ value of near 20,000 GHz. This is an excellent quality factor value compared with most LTCCs materials.

Table 1
The compositional data in Fig. 3 by EDS analysis

Three different areas	The compositional elements	Crystal phase
The grey area	Ba, Ti, O	$BaTi_4O_9$
The white area	La, B, O	$LaBO_3$
The dark area	Ba, Zn, Ti and O	Unknown phase

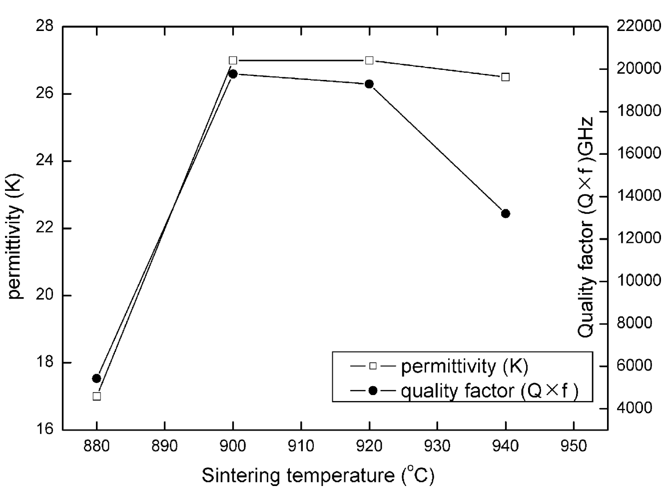

Fig. 4. Permittivity k and quality factor of the composites as a function of sintering temperature.

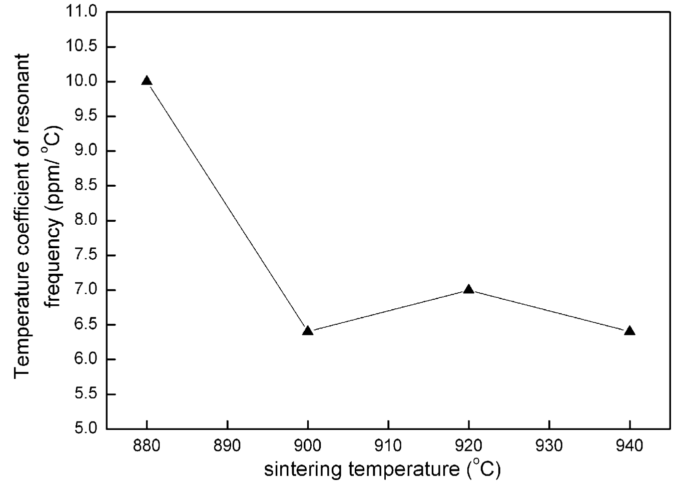

Fig. 5. The temperature coefficient of resonant frequency τ_f of the composites as a function of sintering temperature.

The temperature coefficient of resonant frequency τ_f was measured from the samples sintered at different temperatures for 3 h, and the result is shown in Fig. 5. A very good τ_f value of 6.5 ppm/°C was obtained for the sample sintered at 900 °C. The ceramics obtained in this work had a very complicated phase composition. Besides the main phase $BaTi_4O_9$, the samples contained the $LaBO_3$ phase precipitated from the BZL glass flux, the unidentified crystal phase and the residual glass phase. Although the τ_f value of $LaBO_3$ and $BaTi_4O_9$ have been reported to be 670 [9] and 16 ppm/°C [10], respectively, the τ_f value of the other two phases are not clear at present from the existing literature. Because the temperature coefficient of resonant frequency τ_f is determined by the collective effects of all phases [11], it could be only speculated that the τ_f value of the Ba–Zn–Ti–O crystal phase is negative which would offset the positive τ_f of $LaBO_3$ and $BaTi_4O_9$ to obtain the final smaller τ_f 6.5 ppm/°C of the composite sintered at 900 °C. To better understand the behavior of the τ_f of the materials, further investigation on the nature of individual crystal phase and the residual glass will be necessary.

4. Conclusion

A high-Q low firing ceramics material was fabricated from a composite of 80 wt% of $BaTi_4O_9$ and 20 wt% of B_2O_3–ZnO–La_2O_3 glass flux. The B_2O_3–ZnO–La_2O_3 glass could be promising sintering aid in LTCCs.

The composite could be well-densified at 900 °C for 3 h; the B_2O_3–ZnO–La_2O_3 glass played crucial role in low-temperature sintering. The ceramics obtained in this work had a very complicated phase composition. Besides the main phase $BaTi_4O_9$, three other phases existed. They are the $LaBO_3$ phase which precipitated from the BZL glass flux, the unidentified crystal phase which was formed as the product of interreaction between glass flux and $BaTi_4O_9$, and the residual glass phase.

The composite sintered at 900 °C for 3 h obtained the maximum bulk density and possessed excellent microwave dielectric properties: permittivity k of 27, quality factor $Q \times f$ of near 20,000 GHz and temperature coefficient of resonant frequency τ_f of 6.5 ppm/°C.

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