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Effects of the Bi_2O_3-SiO_2 addition on the sintering behavior and microwave dielectric properties of $Zn_{1.8}SiO_{3.8}$ ceramics

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ABSTRACT

The effects of Bi_2O_3-SiO_2 addition (denoted as BS) on the microstructure and microwave dielectric properties of $Zn_{1.8}SiO_{3.8}$ (denoted as ZS) ceramics have been investigated. It's proved that the addition of BS not only decreases the densification temperature effectively, but also contributes to the well microwave dielectric properties of ZS ceramics by the formation of $Bi_4(SiO_4)_3$ phase at a low sintering temperature. In particular, when BS content was 20.0 wt%, the BS-added ceramics sintered at 875 °C for 2 h exhibited a low dielectric constant(ε_r) of 6.78, a high quality factor($Q\times f$) of 28,742 GHz (at 15.7 GHz) and the temperature coefficient(τ_f) of the resonant frequency of −22.6 ppm/°C, which demonstrated a potential candidate for application of LTCC multilayer technology in millimeters and THz range.

1. Introduction

The fast development of modern communication technology, such as high density, high RF and fast digital applications requiring hermetical packaging and good thermal management, has pushed the continuing miniaturization of microwave devices. Low temperature co-fired ceramics(LTCC) multilayer devices have been intensively investigated in recent years to reduce device size by enabling a significant number of circuit components to be integrated within a module in a multilayer substrate [1,2]. In LTCC, a low sintering temperature lower than the melting point of metal electrodes (961 °C for silver, 1083 °C for copper) [3] is critical instead of using more expensive electrodes such as Ag-Pd binary or Pt-Pd-Au ternary alloys. Unfortunately, most of well-known microwave ceramics with excellent dielectric properties in the microwave range need high sintering temperatures, which put it a constraint on LTCC application.

On the other hand, the utilizable frequency region has been expanded to millimeterwaves and even extends to THz band for the shortage of conventional frequency regions. Therefore, in the millimeterwave region or THz band, the permittivity (ε_r) value is expected to be small for no need for miniaturization and reducing time delay. Among the low ε_r materials, Zn_2SiO_4 ceramics belonging to the orthosilicates [4], are particularly promising candidates [5,6] because of the high quality factor ($Q\times f$) value and adjustable temperature coefficient of resonant frequency. But they were produced by the cold isostatic press (CIP)method, which is not suitable for mass production and the high sintering temperature (~1300 °C) is another limitation for its wide applications in LTCC technology. Therefore, B_2O_3 [7–9]and B_2O_3-containing glass [10–16] have been widely used for lowering the sintering temperature of Zn_2SiO_4 ceramics by solid-state reaction method. However, as an important glass former [17] at low temperature sintering process, B_2O_3 and some boron containing compounds have great influence in LTCC technological process, which would react with the binder such as PVA in LTCC [18–20]. Thus, in this paper, Bi_2O_3-SiO_2 addition without containing boron was chosen as sintering aid with a molar ratio of $ZnO/SiO_2 = 1.8/1$. Thus, the microstructures evolution and microwave dielectric properties of willemite ceramics with different BS contents and sintering temperature were investigated. Additionally, we managed to produce nominal composition $Zn_{1.8}SiO_{3.8}$ ceramics with low permittivity value ($\varepsilon_r \cong 6.8$ at 15.6 GHz) and ultra-low loss ($Q\times f > 20{,}000$ GHz) in the microwave range by solid-state reaction at relatively low temperature range (below 950 °C).

2. Experimental procedure

The BS addition was directly mixed with high-purity oxides (the mole ratio of Bi_2O_3 to SiO_2 is 0.35:0.65), Bi_2O_3 (99%), SiO_2(99%) from

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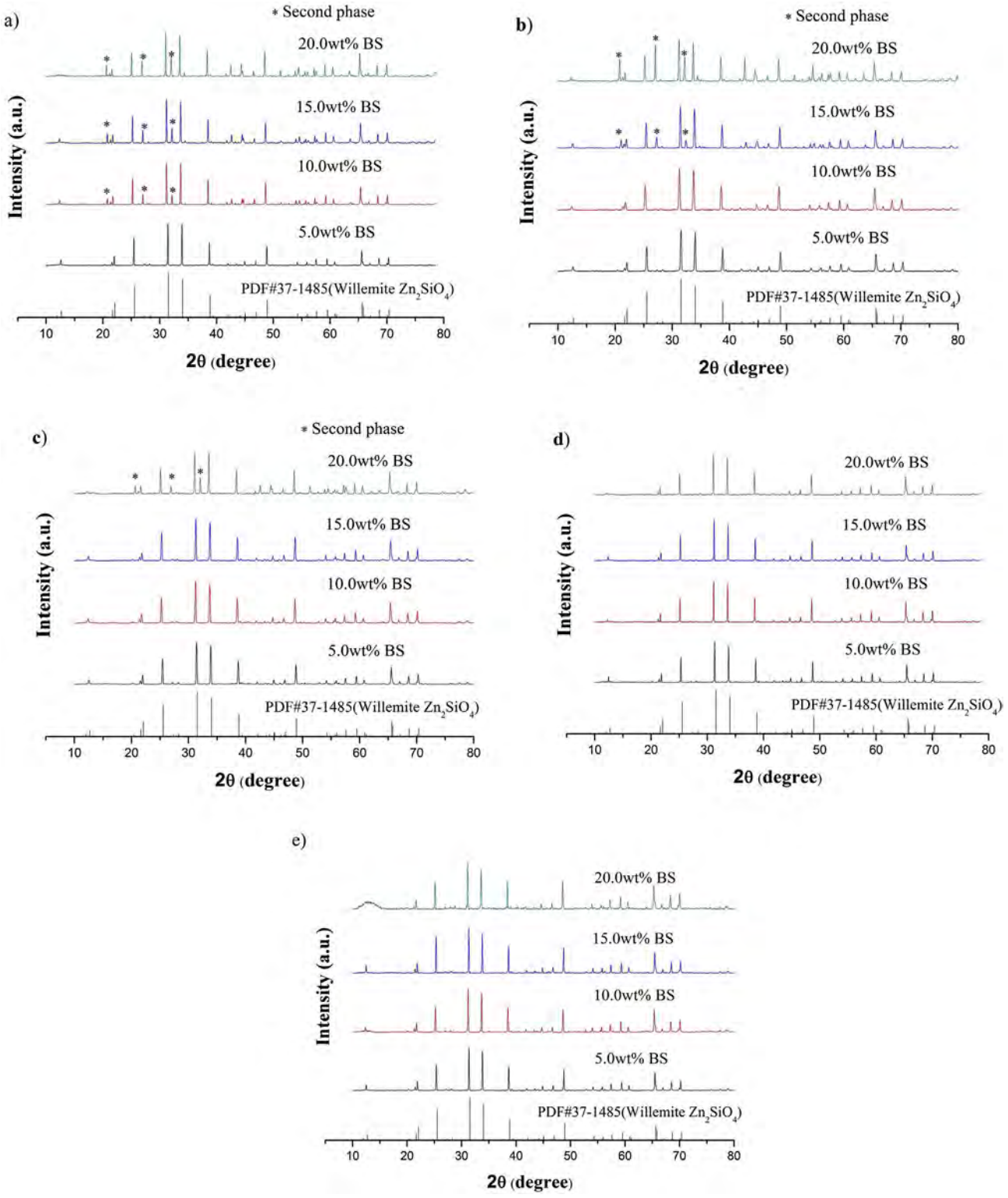

Fig. 1. XRD patterns of the ZS+*x*wt%BS ceramics with $5.0 \leq x \leq 20.0$, sintered at various temperatures: (a)875 °C, (b)925 °C, (c)975 °C, (d)1025 °C and (e)1075 °C for 2 h.

the West Long Chemical Co., Ltd., Guangdong, China. High-purity oxide powders(>99.99%) of ZnO, SiO_2 were used as starting materials. They were mixed according to the nominal composition of $Zn_{1.8}SiO_{3.8}$, and ball-milled in a polyethylene bottle with agate balls using distilled water as a medium. The mixture was then dried and calcined at 1150 °C for 2 h. The calcined powders were re-milled for 4 h with different contents(5 wt%, 10.0 wt%, 15 wt% and 20 wt%) of BS addition. The powder mixture, with poly vinyl alcohol (PVA) as an organic binder(0.70 wt%) and granulated was subsequently uniaxially pressed into cylindrical compacts 13 mm in diameter and 5.2–6.8 mm in thickness using a uniaxial press(200 MPa). The green tapes were heated up to 600 °C at 1.5 °C/min and held for 1 h

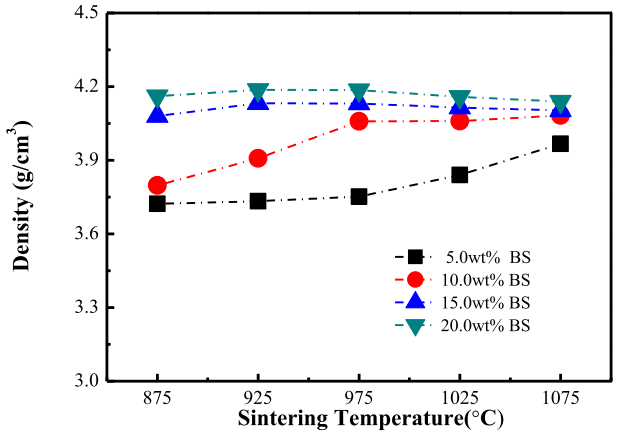

Fig. 2. Bulk density of ZS ceramics with different BS contents as a function of sintering temperature.

to totally remove the PVA binder. The samples were sintered at 875–1075 °C for 2 h with a heating rate of 5 °C/min in air after debinding, and then cooled to room temperature.

The bulk density of the sintered samples was measured by the Archimedes' method using distilled water as the immersion medium. The crystalline phase and microstructure of sintered disks were determined by X-ray diffraction(XRD). Two-theta scans between 10° and 80° were determined by 0.02° per steps on a Bruker-AxsD8 diffractometer using Cu-Kα radiation, operated at 40 kV and 40 mA. The microstructure observation and an energy dispersive spectra (EDS) of the prepared specimens were performed by scanning electron microscopy (SEM; Hitachi SU70, Japan).

The dielectric constants and unloaded *Q* values were measured in the TE_{011} mode using the Hakki and Coleman method [21], where a cylindrically shaped specimen is positioned between two silver plates. An E8362B network analyzer was used as the measuring system. The temperature coefficient of frequency (τ_f) values were calculated by the following equations in the temperature range between 20 and 80 °C:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times 60} \times 10^6 (\mathrm{ppm/^\circ C}); \quad (1)$$

where *f* represent the resonant frequency. Subscripts of 20 and 80 are referred to the testing temperature, respectively.

3. Results and discussion

Fig. 1 shows the X-ray patterns of ZS ceramics with different BS contents sintered at various temperatures for 2 h. It is clearly observed that the peaks of all the samples annealed at various temperatures are in good match with the standard ICSD card for Zn_2SiO_4 (no.37–1485, willemite). Peaks without corresponding to a rhombohedral crystal structure in space group *R*-3 (no. 148) may belong to the new phase indicated by the asterisk formed by the reaction between Bi_2O_3 and excess SiO_2. On the basis of XRD patterns, the diffraction peak intensity of second phases decreased with increasing the sintering temperature, which suggests that they are probably Bi-Si-rich low-melting phases. Additionally, it is obviously observed that the unknown phase disappeared at a higher sintering temperature shown in Fig. 1(d) (e), which are probably because of a part of the second phases melt and changed into Bi-Si-based glass. Furthermore, the second phase could be observed clearly when the samples were sintered at 875 °C, 925 °C and 975 °C with a minimum BS content of 10.0 wt%, 15.0 wt% and 20.0 wt%, respectively. According to the Bi_2O_3-SiO_2 phase diagram [22], $Bi_4(SiO_4)_3$ and SiO_2 phase coexist on the SiO_2-rich side. Hence, one possible candidate of the second phase could be $Bi_4(SiO_4)_3$ phase with the three main peak also matched well with JCPDS card No.01-080-1596 33–215 for $Bi_4(SiO_4)_3$. Finally, the $Bi_4(SiO_4)_3$ phase fused and disappeared with further increase of the sintering temperature.

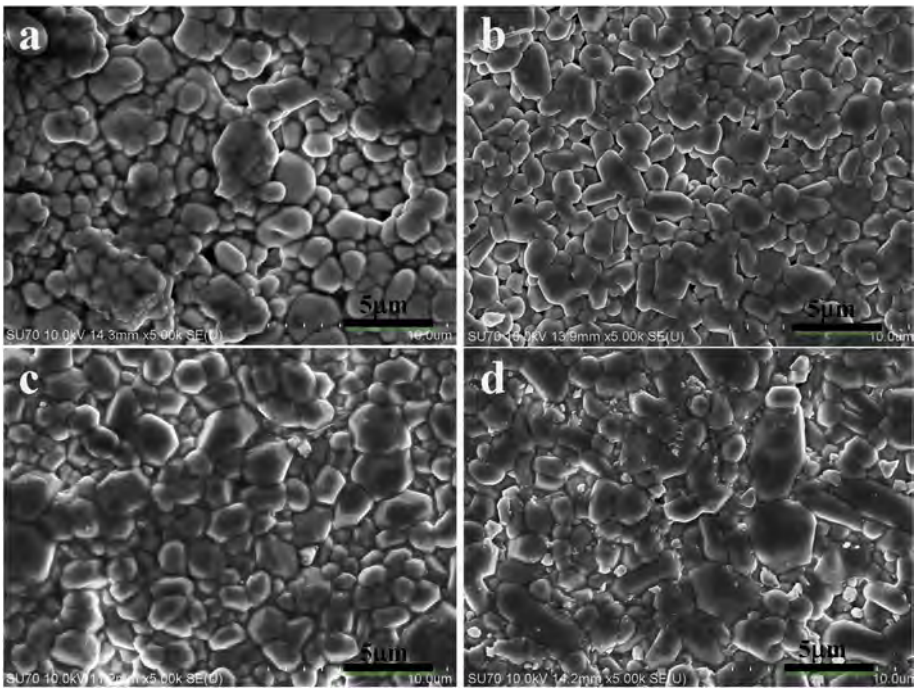

Fig. 3. Scanning electron microscopy images of the surface microstructures for ZS+*x*wt%BS ceramics as a function of sintering temperature and amount of BS addition: (a)x = 20, 875°C/2 h, (b)x = 15, 925°C/2 h, (c) x = 10, 975°C/2 h, (d)x = 5, 1025°C/2 h.

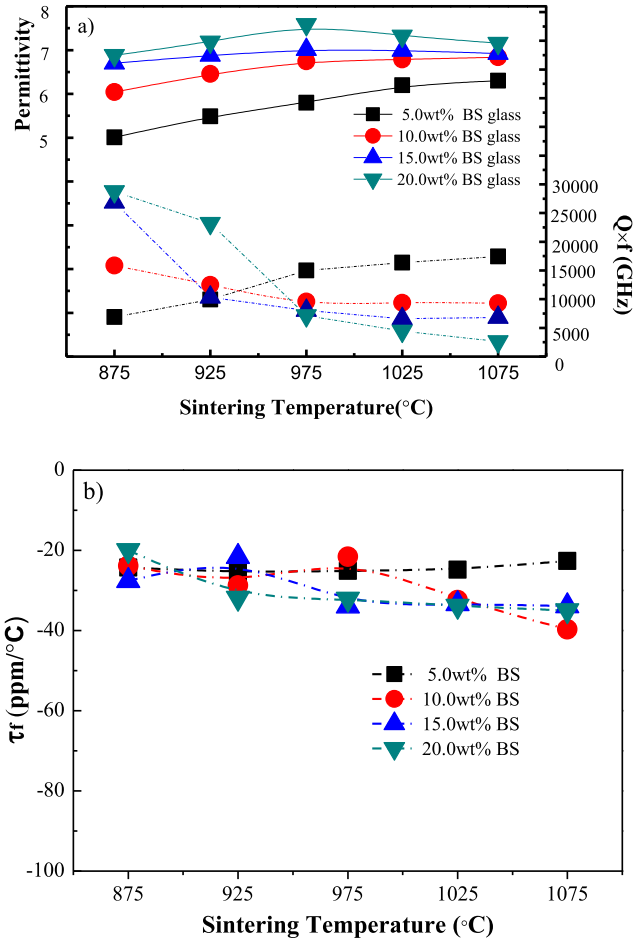

Fig. 4. Variation of microwave dielectric properties of ZS ceramics with different BS contents as a function of various sintering temperatures (a) dielectric constant(ε_r) and quality factor($Q\times f$), (b) temperature coefficient of the resonant frequency(τ_f).

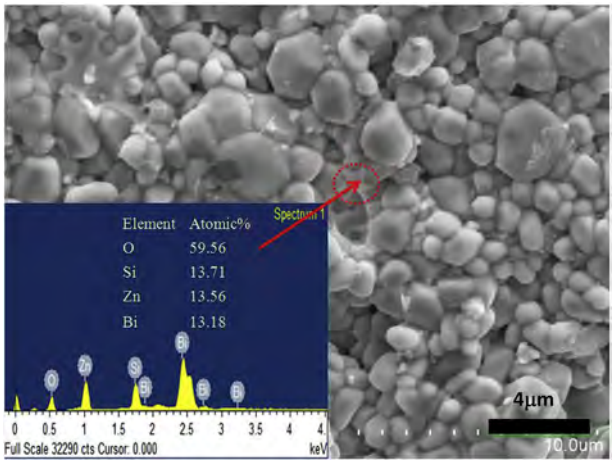

Fig. 5. SEM photographs and EDS analysis of ZS+20 wt%BS ceramic sintered at 875 °C for 2 h.

Fig. 2 shows the relation between the bulk density of ZS+*x*wt% BS ceramics with $5.0 \le x \le 20.0$ and the sintering temperature. It appears that the density of samples with relatively high content of addition ($10.0 \le x \le 20.0$) initially increased, subsequently decreased with the increase of sintering temperature. Moreover, the density of ZS+5 wt%BS ceramics increased monotonically with the increase of sintering temperature. The densification mechanism of the ceramics/glass composites can be summarized as follows [23,24]. BS liquid-phase is uniformly dispersed in the glass phase matrix for the well wettability with ZS ceramic powder, which could act as lubrication during sintering process, wetting solid particles, and providing capillary pressure between them, thus resulting in a faster grain growth of ceramics [25]. However, the excessive grain growth would preclude the pore venting process as further increase of sintering temperature and eventually decrease the density in ceramics. In addition, other factors [26] such as a bimodal grain growth, the spreading of the liquid phase at high temperatures and high amount of BS can be also responsible for such reduction of the densification. From Fig. 2 it can be deduced that the densification temperature of ZS+*x*wt%BS (x = 15,20) was around 875–925 °C, while that of ZS+10.0 wt%BS and ZS+5.0 wt% BS were around 975 °C and 1075 °C respectively. SEM images in Fig. 3 demonstrate that these specimens sintered at the densification temperature have dense microstructures with low pore density and uniform grain size distribution. The dense structure of samples prepared at the densification temperature is beneficial for microwave performances of ZS ceramics.

Fig. 4 shows the ε_r, $Q\times f$, and τ_f values of the ZS ceramics sintered at various temperatures for 2 h. It is readily observed that the dielectric properties strongly depend on the BS content and the sintering temperature. The ε_r value of ZS ceramics with 5.0 wt%BS increased monotonically with the increase of sintering temperature, and that with x = 10, 15 and 20 increased firstly, subsequently decreased with the increase of sintering temperature. The density and dielectric constant of specimens with low BS content (x = 5,10) displayed the similar tendency with the sintering temperature. However, the deviation of the trend between the density and dielectric constant for specimens with high BS content (x = 15, 20) probably accounts for the formation of a large amount of liquid phase at high sintering temperature (above 925 °C). On the other hand, the ε_r values of the specimens with higher BS contents were higher than that with the lower BS contents, due to the presence of secondary possible phases such as Bi_2O_3, $Bi_4(SiO_4)_3$ and $Bi_{12}SiO_{20}$ whose ε_r values are 18.2, 13.9 and 37.6, respectively, which are much higher than that of ZS ceramic($\varepsilon_r = 6.6$) [27,28]. According to Fig. 4(a), $Q\times f$ values of the sample (x = 20) reached the maximum(28,742 GHz at 15.7 GHz) when the sintering temperature was 875 °C and decreased monotonically with increasing sintering temperature. Similar trend was obtained for the specimens with x = 10, 15. Moreover, the $Q\times f$ values of the sample doped with low BS content (x = 5) increased monotonically with increasing sintering temperature. Generally, the sintering process, including glass redistribution and ceramic grains rearrangement, dissolution and precipitation, and viscous flow is the deciding factor in the liquid phase sintering process of glass/ceramics composites. Herein the high content (≥10.0 wt%) of BS addition is more favorable for low temperature sintering effect of ZS ceramics.

Moreover, many factors are commonly believed to decide the microwave dielectric properties and can be divided into two parts: the intrinsic loss and the extrinsic loss. Intrinsic loss is mainly caused by lattice vibration modes while extrinsic loss is dominated by various factors such as lattice defect, crystallinity, cation ordering, impurities, oxygen vacancies, internal stress, and densification. In ZS-BS system, it's not doubt that the second phase plays crucial role in sintering process, and thus affects the microstructure and microwave properties for large amounts of BS addition. According to Kim's work [27], the $Q\times f$ value of secondary phase $Bi_4(SiO_4)_3$ (about 34,179 GHz) is much higher than that of $Bi_{12}SiO_{20}$ (8,100 GHz) [28], which may account for not obvious degradation of dielectric properties for ZS ceramics with different BS contents than

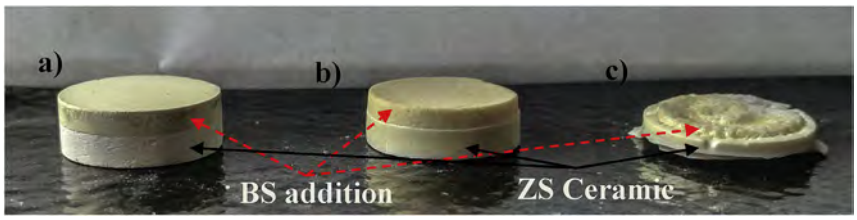

Fig. 6. Compact of BS and ZS (a) before firing, after firing at 875 °C (b) and 925 °C (c) for 2 h.

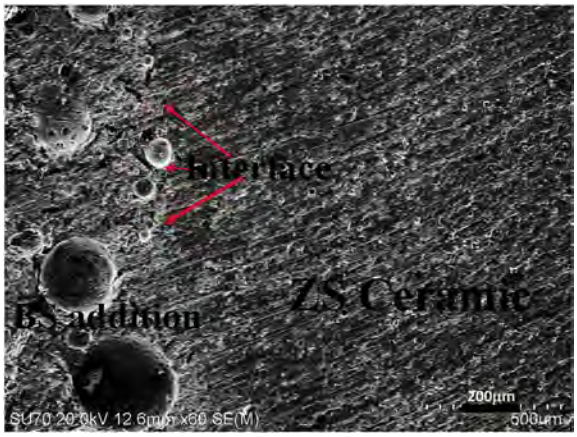

Fig. 7. SEM micrographs of interface between ZS and BS after 925 °C for 2 h.

that for ZS ceramics with different Bi_2O_3 contents. The τ_f values of ZS ceramics with different BS contents sintered at various temperatures are shown in Fig. 4(b). The variation of the τ_f values with different BS content range between −20 and −40 ppm/°C and the τ_f value of specimen with 20.0 wt%BS content sintered at 875 °C was −22.6 ppm/°C.

To investigate the effect of microstructure on dielectric properties and further identify the composition of the second phase, the SEM photographs and EDS analysis of ZS+20 wt%BS ceramic sintered at 875 °C are shown in Fig. 5. From Fig. 5, it was clearly observed that the ZS crystals are distributed throughout the entire BS addition matrix and ZS+20 wt%BS ceramic with good compactness can be readily synthesized in temperature of 875 °C. Hence, the ZS+20 wt%BS ceramics sintered at 875 °C showed excellent microwave properties. According to the semi-quantitative molar ratio of Bi/Si about 1:1, the second phase was probably $Bi_4(SiO_4)_3$. The results of EDX analysis are also confirmed by the X-ray patterns discussed previously.

In order to further evaluated the reactivity between ZS ceramics and BS addition, green tape of BS was stacked on the top of the porous ZS green body under pressure condition of 50 MPa and co-fired at 875 and 925 °C respectively for 2 h in air. Fig. 6 shows the samples before and after firing. The comparison between Fig. 6(b) and (c) confirmed the fact that $Bi_4(SiO_4)_3$ phase formed at 875 °C and liquid phase of BS addition largely formed at sintering temperature of 925 °C, which is consistent with the XRD results. Additionally, BS addition showed nearly nonreactivity with ZS ceramic and an almost negligible interface could be found by cross-sectional SEM images in Fig. 7. The phenomena confirm that the BS addition could be an excellent sintering aid for ZS LTCC. Furthermore, it is obviously observed that sintered BS addition possessed porous structure, which might put constraints on the further improvement for microwave properties of ZS ceramic with a great number of BS addition. This was confirmed by the relationship between the bulk density of ZS+10.0 ≤ x ≤ 20.0 wt%BS ceramics and the sintering temperature in Fig. 2.

4. Summary

The addition of BS can effectively lower the sintering temperature of ZS ceramics from 1300 °C to ≤950 °C. In the meantime, no obvious degradation of the microwave dielectric properties for ZS ceramics was observed. In particular, optimal microwave dielectric properties can be obtained in ZS ceramic with high content of BS addition(20 wt%) sintered at 875 °C, with a permittivity of 6.78, $Q\times f$ value of 28,742 GHz (at 15.7 GHz), and a negative τ_f value of −22.6 ppm/°C. Moreover, the results also show that the BS addition not only decreased the densification temperature of ZS ceramics effectively, but also contributes to the good microwave dielectric properties of ZS ceramics by the formation of $Bi_4(SiO_4)_3$ phase when the high BS addition (≥15.0 wt%) was added at a low sintering temperature. Based on the experimental results of the research, ZS + 20 wt% BS ceramics seem to be an attractive candidate for the low temperature co-fired ceramics technology.

Acknowledgements

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