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Low temperature sintering of $Zn_{1.8}SiO_{3.8}$ dielectric ceramics containing $3ZnO-2B_2O_3$ glass

Hongtao Yu [a,*], Lei He [a], Mengshi Zeng [a], Jingsong Liu [a], Enzhu Li [b], Xiaohua Zhou [b], Shuren Zhang [b]

[a] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] State Key Laboratory of Electronic Thin films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China

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ABSTRACT

In this work, the effects of $\mathbf{3ZnO\text{-}2B_2O_3}$ glass on sintering temperature, phase composition, microstructure and dielectric properties of $\mathbf{Zn_{1.8}SiO_{3.8}}$ ceramics were investigated. The x-ray diffraction results showed that there no reaction between the glass and the ceramic during the sintering process. A mechanism of densification and microstructure evolution of the ceramics with glass was provided based on the x-ray, density and scanning electronic microscopy results. The study on the dielectric properties showed strong dependences of glass content and sintering temperature. At last, the compact ceramic with 20 wt% glass content, exhibited a dielectric constant of 6.5 and a low loss of 0.001, after sintering at 920 °C.

1. Introduction

Low temperature co-fired ceramic (LTCC) devices have been widely available in electronics industry. In general, the dielectrics used in LTCCs are composed of a ceramic filler material and a glass matrix. The choice of filler depends on the dielectric demands of microelectronic device. The most commonly used filler such as alumina, mullite, cordierite, and silica are applied to achieve specific properties [1]. As one kind of important low permittivity materials, $ZnO\text{-}SiO_2$ ceramic systems have been studied widely in recent years for possible applications in microwave communication field due to its low dielectric constant and high quality factor [2]. Guo et al. synthesized willemite-type Zn_2SiO_4 ceramics with a low dielectric constant value of 6.6 and a high $Q \times f$ value of 219,000 GHz using cold isostatic pressing (CIP) [3]. Park et al. investigated the effect of different Zn contents in Zn_2SiO_4, and found that $Zn_{1.8}SiO_{3.8}$ (ZS) exhibited better microwave dielectric properties of $\varepsilon_r = 6.6$, $Q \times f = 147{,}000$ GHz, $\tau_f = -22$ ppm/°C than stoichiometric Zn_2SiO_4 [4]. However, the high sintering temperature ($\sim$1300 °C) is a limitation for its applications in LTCC technology. Zinc borate glasses are of technological interest owing to their application in different fields of electronic products since they are known to have low melting temperatures [5–10].

Thus, the microstructure evolution and the dielectric properties of willemite ceramics with zinc borate glass were investigated in the work.

2. Experiment

Appropriate highly pure ($>99\%$) ZnO and SiO_2 powders were mixed and ball milled for 12 h according to the chemical formula of $Zn_{1.8}SiO_{3.8}$ (ZS), and calcined at 1150 °C for 3 h. $3ZnO\text{-}2B_2O_3$ glass (ZB) was prepared using solid state melting method which was reported in our previous work [10]. The ZS powder was mixed with different ZB glass contents (10, 15, 20 and 25 wt%) and ball-milled for 20 h. After mixing with 5 wt% PVA as binder, the mixed powders were pressed uniaxially into pellets (Φ $12 \times 2 \pm 0.2$ mm). The green pellets were sintered in the different temperatures for 30 min after de-binding.

The crystalline phases of the sintered samples were identified by X-ray diffraction (XRD). The sintered densities were measured by Archimedes method. The microstructure characteristics of the sintered compacts were examined using a scanning electron microscope (SEM) (TM-1000, Hitachi). The dielectric properties were measured using an Impedance Analyzer (4294A, Agilent).

* Corresponding author.
E-mail address: yuhongtao@swust.edu.cn (H. Yu).

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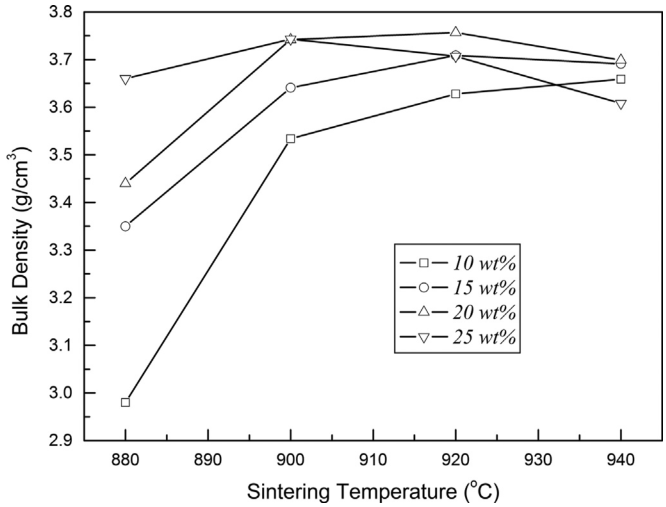

Fig. 1. Bulk densities as a function of sintering temperature for the willemite with different glass contents.

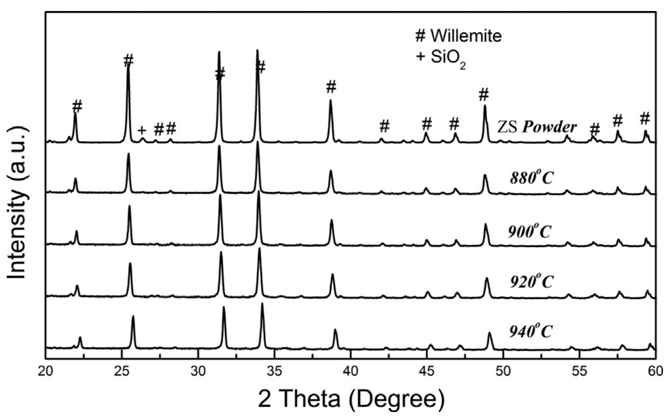

Fig. 2. XRD patterns of 20 wt% glass-willemite ceramics sintered at different temperatures and ZS powder.

3. Results and discussions

Fig. 1 illustrates the bulk density of the willemite ceramics with different ZB glass contents. Although the composition of the sample is different, the bulk density curve has a similar tendency with sintering temperature. The glass content has a strong dependence on the sintering temperature. As can been seen, when the content of glass is less than 20 wt%, the density increases with the sintering temperature elevating, no largest density value can be obtained during the sintering procedure. At the level of 20 and 25 wt%, a tiny reduction on the curve indicates that the ceramics are excessively sintered. This may have been caused by the increase in porosity due to the coalescence of neighboring pores and excessive melting of glass matrix above an optimum sintering temperature [11]. It is obvious that glass content and sintering temperature are two important factors in the densification process of composites. To confirm phase evolution, the X-ray diffraction was used to investigate the phase development of the ceramics.

Fig. 2 shows the X-ray diffraction patterns of ZS ceramics with 20 wt% glass sintered at different temperatures and ZS powder calcined at 1150 °C for 3 h. There are two crystalline phases in the ZS powder, SiO_2 and willemite, which is in accord with the found by Park [4], whereas only a willemite-type crystalline phase can be found in each sample for all sintering temperatures. Thus it can be proposed that the SiO_2 phase is dissolved in the glass during the sintering procedure. The same phase compositions are found in other ZS ceramics with different glass contents.

Fig. 3 shows the SEM of the cross section of 20 wt% ZB-willemite ceramics sintered at different temperatures. Big separate lumps with few small grain inclusions and a large amount of pores are observed in the samples sintered at 880 °C (Fig. 3(a)). These lumps result from the softening and coalescence of the glass particles. At 900 °C, glass lumps coalesce to form a continuous phase, and the pores decrease. After sintering at 920 °C, the glass forms a completely continuous phase and encapsulates all grains and fewer pores left (Fig. 3(c)). More pores can be observed at 940 °C, due to the more liquid phase with relatively low viscosity under the high temperature.

Based on the investigations of bulk densities, XRD and SEM results, the densification and microstructure evolution may be attributed to a nonreactive type during the sintering process. It was reported that the densification of ceramic with a relatively large amount of glass can be described by conventional three-stage liquid phase sintering process, consisting of particle rearrangement, dissolution and precipitation, and solid state sintering [12]. For the investigations, a high glass content of the glass + ceramic composites is chosen to prevent direct contact between the filler particles in the early stage of sintering. Therefore, no significant solid-state sintering can be expected. As the sintering mechanism is of the nonreactive type which was discussed in the phase analysis, thus, the composite is densified by a nonreactive liquid-phase sintering which is presented by Ewsuk and colleagues [13]. This sintering model is achieved by three-stage sintering process, consisting of glass redistribution and grains rearrangement, closure of pores, and viscous flow.

The variations of dielectric properties with respect to glass content are shown in Fig. 4. It is clear that the dielectric properties strongly depend on the glass content and the sintering temperature. It is well known that the microstructure characteristics, such as porosity and glass phase have heavy influences on the dielectric properties of ceramics [14]. At the same sintering temperature, the highest dielectric constant and the lowest dielectric loss corresponds to the highest bulk density, which means the variations in the dielectric properties have a similar tendency to the bulk density with glass content and sintering temperature. For low glass contents (10 and 15 wt%), the dielectric constant increases from 5.35 to 6.4 and 5.9–6.5 respectively accompanied with a reduction in the dielectric loss (Fig. 4(b)) during the whole sintering temperature ranges. However, the dielectric constant reaches a maximum value after sintered at 920 °C for the high glass content (20 and 25 wt%), and decreases a little at 940 °C.

At the sintering temperature of 920 °C, the dielectric constant increases when the glass content increases from 10 to 20 wt%, and decreases at the level of 25 wt%, whereas the dielectric loss decreases from 0.014 to 0.0007 and increases to 0.016. According to the SEM results, for the samples with 10 and 15 wt% glass contents, some pores are found, leading to the reduction of bulk density, and the liquid phase was obvious in the sample with 25 wt% glass content. Both reasons result in the enhancement of the dielectric loss and the reduction of the dielectric constant.

4. Conclusions

In this work the dielectric properties of newly suggested LTCC compositions, which were based on $Zn_{1.8}SiO_{3.8}$ ceramic with $3ZnO\text{-}2B_2O_3$ glass, are strongly depended on the glass content and sintering temperature. During the sintering process, SiO_2 might dissolve in the zinc borate glass, only a crystal phase of willemite could be found. The densification and the microstructure evolution could be attributed to a nonreactive type where the glass played a binder role during the sintering process. At the glass level of 20 wt%, the sample exhibited a low dielectric constant of 6.5 and a