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Influence of Li_2O–B_2O_3–SiO_2 glass on the sintering behavior and microwave dielectric properties of BaO–0.15ZnO–4TiO_2 ceramics

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Abstract

This paper reports the investigation of the performance of Li_2O–B_2O_3–SiO_2 (LBS) glass as a sintering aid to lower the sintering temperature of BaO–0.15ZnO–4TiO_2 (BZT) ceramics, as well as the detailed study on the sintering behavior, phase evolution, microstructure and microwave dielectric properties of the resulting BZT ceramics. The addition of LBS glass significantly lowers the sintering temperature of the BZT ceramics from 1150 °C to 875–925 °C. Small amount of LBS glass promotes the densification of BZT ceramic and improves the dielectric properties. However, excessive LBS addition leads to the precipitation of glass phase and growth of abnormal grain, deteriorating the dielectric properties of the BZT ceramic. The BZT ceramic with 5 wt% LBS addition sintered at 900 °C shows excellent microwave dielectric properties: $\varepsilon_r = 27.88$, $Q \times f = 14{,}795$ GHz.

Keywords: BaO–0.15ZnO–4TiO_2; LTCC; Li_2O–B_2O_3–SiO_2 (LBS); Microwave dielectric ceramics

1. Introduction

Low temperature cofired ceramic (LTCC) technology enables to cofire active layers, electrodes and substrates together at a temperature below the melting points of these main components [1]. Thus, this technology supports passive integration and system-on-a-package (SOP), and plays an important role in the fabrication and integration of miniaturized modern microwave circuits [2]. For the miniaturization of devices, three parameters of the ceramic component should be taken into account: (1) The medium to high relative permittivity ε_r ($20 < \varepsilon_r < 80$) of materials ensures the small size of components, because the size is inversely proportional to the square root of ε_r. (2) The quality factor of materials, defined as $Q \times f$, (where Q is proportional to 1/tan δ and f is the resonant frequency), should be as high as possible. (3) The temperature coefficient of the ceramics at the resonant frequency τ_f should close to zero to maintain the temperature stability of components [3]. TiO_2-rich region of the BaO–TiO_2 ceramics, (such as $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, and $BaTi_5O_{11}$), show desirable microwave dielectric properties, [4–6] but the high sintering temperature and the large positive τ_f limit their applications in the LTCC industry. ZnO can effectively lower the sintering temperature and improve the microwave dielectric properties of the BaO–TiO_2 ceramic [7–11]. For example, $BaZn_2Ti_4O_{11}$ sinters at 1200 °C with microwave dielectric properties: $\varepsilon_r = 30$, $Q \times f = 68{,}000$ GHz, and $\tau_f = -30$ ppm/°C [9], and it may be added to offset the positive τ_f of some BaO–TiO_2 ceramics such as $BaTi_4O_9$ and $BaTi_5O_{11}$. However, a sintering temperature of less than 950 °C is generally required in LTCC technology, considering the melting temperature of Ag (961 °C) that is usually used as the internal electrode. A common method to reduce the sintering temperature is adding the sintering aid with low melting points, such as glasses or oxides [12]. Many kinds of sintering aids, such as ZnO–B_2O_3–SiO_2 glass [13,14], Li_2O–ZnO–B_2O_3 glass [15], B_2O_3–ZnO–La_2O_3 glass [16,17], BaO–ZnO–B_2O_3 glass [18], Li_2O–B_2O_3–SiO_2 glass [19], CuB_2O_4, $BaCu(B_2O_5)$ [20–23], BaO–ZnO–B_2O_3–SiO_2 glass [24] have been used to decrease the sintering temperature successfully, among which Li_2O–B_2O_3–SiO_2

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(LBS) glass is one of the widely used sintering aids [25–27]. For instance, Young-Jin Choi et al. used 10 wt% Li_2O–B_2O_3–SiO_2 glass to decrease the sintering temperature of $BaTi_4O_9$ to 875 °C, and the microwave dielectric properties of the resulting ceramic are $\varepsilon_r = 32$, $Q \times f = 9000$ GHz and $\tau_f = 10$ ppm/°C [19]. Dong Zou et al. have reported that the $Ba_5Ti_3Nb_4O_{18}$ ceramics with 1.5 wt% $MnCO_3$–CuO and 0.5 wt% LBS glass can be well sintered at 900 °C for 2 h, giving ceramics with good dielectric properties: $\varepsilon_r \sim 41$, $Q \times f \sim$ 15,000 GHz and $\tau_f = 4$ ppm/°C [28]. In this study, LBS glass was chosen as the sintering aid of BaO–0.15ZnO–4TiO_2 (BZT) ceramic. The low-temperature sintering behavior with the assistance of the LBS glass and the relevant microwave dielectric properties has been studied in detail.

2. Experimental

To synthesize the BZT powders, $BaCO_3$, ZnO and TiO_2 with purity higher than 99% were weighted as the mole ratio of BaO–0.15ZnO–4TiO_2, and ball-milled with deionized water in a nylon jar using zirconia balls for 3 h. The resulting mixtures were dried and calcined at 1000 °C for 3 h. The LBS glass was fabricated by a conventional glass fabrication process: high-purity powders of Li_2CO_3, H_3BO_3, and SiO_2 were weighed as the raw materials according to the composition of 56.92 wt%, 37.59 wt%, and 5.49 wt%. The batches were dry-milled with zirconia balls for 2 h and then melted in a platinum crucible at 1400 °C for about 2 h. The glass melt was then quickly poured into a copper plate to quench, and then pulverized in a vibration mill for 4 h. The calcined BZT powders and LBS glass powders were weighed with the ratio of BZT-x wt% LBS, where $x = 2$–10, and re-milled with alcohol in a nylon jar using zirconia balls for 3 h. The mixtures were dried and added with acrylic acid to form pellets (15 mm in diameter and 8 mm in height), and then sintered at 875–925 °C for 0.5 h at a heating rate of 5 °C/min in air.

The bulk density of the sintered sample was measured by the Archimedes method. The thermo-gravitometry (TG) and differential scanning calorimetry (DSC) analyses of the as prepared pallets were carried out by using a simultaneous thermal analyzer (NETZSCHSTA449C, Germany) with a heating rate of 5 °C/min. For the experiments of thermomechanical analyses (TMA) (NETZSCH, Germany), samples were fired at a heating rate of 5 °C /min in flowing air. The wetting behavior of LBS glass/BZT was studied by placing a piece of green LBS glass compact on the top of dense BZT substrate and fired at a heating rate of 5 °C /min from room temperature to 900 °C, and the sintering process was observed and recorded through a sintering point testing device with screen display. The phase composition was analyzed by X-ray diffraction (XRD) using CuKα radiation (DX–1000 CSC, Japan). The microstructures of the materials with polished surfaces were determined using scanning electron microscopy (SEM, FEI Inspect F, the United Kingdom). The compositional and elemental analysis was carried out with an energy dispersive spectroscopy (EDS). The microwave dielectric characteristics were measured by the Hakki–Coleman dielectric resonator method in the TE011 mode using a network analyzer (HP83752A, the United States), and the τ_f value was determined from the difference between the resonant frequencies obtained at 25 °C and 85 °C using the equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6 \text{ (ppm/°C)}$$

where f_{25} and f_{85} are the resonant frequencies at 25 °C and 85 °C, respectively.

3. Results and discussion

The DSC and TG curves of the LBS glass are shown in Fig. 1. The endothermic peak at around 147 °C associated with slight weight loss corresponds to the loss of crystallization water, and there is no other obvious mass loss observed in the TG curve. The endothermic peak at around 845 °C is assigned to the melting temperature of the LBS glass.

The linear shrinkages of BZT ceramic with 2–9 wt% LBS glass sintered at different temperatures are shown in Fig. 2. The linear shrinkage increases all along with the increasing

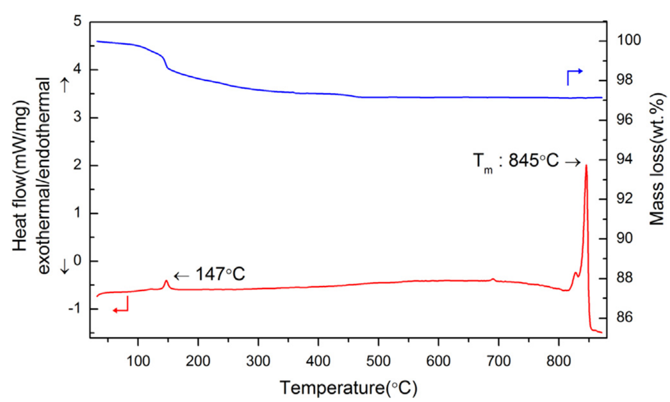

Fig. 1. The DSC and TG curves of the Li_2O–B_2O_3–SiO_2 (LBS) glass.

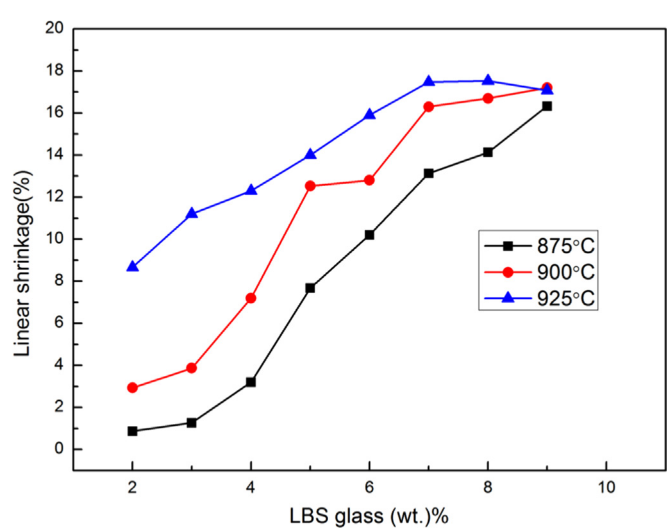

Fig. 2. The linear shrinkages of BZT ceramic with addition of different LBS glass (in the range of 2–9 wt%) sintered at 875, 900 and 925 °C for 0.5 h.