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Sintering and microwave dielectric properties of LTCC-zinc titanate multilayers

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Abstract

The effects of $ZnO–B_2O_3–SiO_2$ (ZBS) on the sintering behavior and microwave dielectric properties of $ZnO–TiO_2$ system were investigated as a function of ZBS content and sintering temperature. Densities of the specimens were enhanced with an increase of ZBS up to 2 wt.% and then decreased. X-ray diffractometry analyses results indicated that the phase stability region of the hexagonal $ZnTiO_3$ extended to lower temperatures as the amount of ZBS increased. The dielectric properties of $ZnO–TiO_2$ system with ZBS are strongly dependent on the sintering conditions, especially near the phase decomposition temperature. The sintering temperature of the specimens could be reduced to 900 °C without the degradation of the microwave dielectric properties. From 900 °C, the temperature compensation characteristics occurred as the phase composition changed from $ZnTiO_3$ to two phases: Zn_2TiO_4 and rutile. The dielectric constant (ε_r) increased and Q×f value decreased due to the phase decomposition. The ε_r value of 27, Q×f value of 19,396 (at 6 GHz) and τ_f value of 2 ppm/°C were obtained for $ZnO–TiO_2$ ceramics with 2.0 wt.% ZBS sintered at 900 °C for 3 h. The low-temperature sintering ceramics powders were suitable for the tape casting process. Also, the material is compatible with Ag electrodes and, therefore, is suitable for LTCC application.

Keywords: Microwave dielectric properties; Liquid phase sintering; Microwave ceramics; Multilayer device structure

1. Introduction

Over the past decade, RF multilayer device structures have been developed in order to induce the device size, for which a low melting point flux is frequently added to co-fire the dielectric ceramics with high conductive internal-electrode metal such as silver or copper. Although several types of dielectric materials with good microwave dielectric properties have been reported, they usually needed to be sintered at high sintering temperatures. Therefore, it is necessary to lower the sintering temperature of the dielectric ceramics in order to process the ceramics along with electrode material. Low-temperature sintering of dielectric materials with glass addition have been successfully developed in the several microwave dielectric systems, e.g. (Zr, Sn) TiO_4, $BaO–TiO_2$, $ZnO–Nb_2O_5–TiO_2$, (Ca, Mg) TiO_3, $BaO–Nd_2O_3–TiO_2$, et al. [1–9]. However, the majority of the ceramics systems with glass and/or a mixture of additives offer relatively inferior dielectrical performances relative to those of the high-temperature firing systems.

Golovchanshi et al. reported that hexagonal $ZnTiO_3$ ceramics as a microwave dielectric material could be sintered at relatively low temperature (1100 °C). The dielectric constant (ε_r) of 19, the quality factor (Q×f) of 30,000 GHz, and the temperature coefficients of the resonant frequency (τ_f) of −55 ppm/°C were obtained. They pointed out that $ZnTiO_3$ ceramics could be a good candidate for low firing microwave dielectric ceramics [10]. Kim et al. demonstrated that the additions of 1–5 wt.% B_2O_3 were effective in reducing the sintering temperature of the $ZnTiO_3$ ceramics from 1100 to 875 °C without degradation of microwave dielectric properties [11]. However, our previous work found that addition B_2O_3 in the ceramics

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was unsuitable for the tape casting process due to its very large viscosity caused by the free B_2O_3 reacted with the solvents, and the surface of ceramics green tape was rough due to precipitation of the free B_2O_3 out of the solvent.

In this study, the microwave dielectric ceramics based on $ZnTiO_3$ was chosen as the host material. To compensate the τ_f value, TiO_2 with positive τ_f value (+450 ppm/°C)[12] was added to form a composition of $ZnTiO_3$+0.2TiO_2 ceramics. Instead of B_2O_3, ZnO–B_2O_3–SiO_2 (ZBS) was used as an additive to promote the sintering of $ZnTiO_3$ ceramics. The sintering behavior and microwave dielectrics with different amount of ZBS addition were investigated. Relationships among crystalline phase, sintering temperature, and the amount of ZBS addition were also discussed. The properties of ceramics slurry and green tape and the chemical compatibility of silver electrodes and the low-fired samples have also been investigated.

2. Experimental procedure

Reagent-grade raw materials of ZnO and TiO_2 with purities higher than 99% were used as the starting materials. These powders were appropriately weighed to meet the mol ratio of ZnO/TiO_2=1:1.2, and then milled with ZrO_2 balls for 24 h in ethanol. Mixtures were dried and calcined at 780 °C for 2 h. The ZBS glass with the composition of 60%ZnO, 27%B_2O_3, and 13%SiO_2 (in mol) was prepared by firing in platinum crucible at the temperature of 1200 °C. ZBS glass frit was milled with a mixture of agate balls in different diameters of 7–25 mm to an average particle size of less than 4 μm. The calcined ceramic powders were re-milled for 24 h with the additions of ZBS glass powders, and then the mixed powders were pressed into pellets with 10 mm in diameter and 5 mm in thickness under 1000 kg/cm^2 isostatically. The pellets were sintered for 4 h in air subsequently from 860 to 960 °C. The crystalline phases were analyzed by X-ray powder diffraction (XRD) using Cu-Kα radiation of 2θ from 20 to 80°. The microstructure observation of the ceramics sections was performed under a scanning electron microscope (SEM). The bulk densities of the sintered pellets were measured by the Archimedes method. Microwave dielectric constants ε_r and the quality factor values Q×f at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using an Agilent 8719ET(50 MHz–13.5 GHz) Network Analyzer. Temperature coefficient of resonant frequency τ_f was also measured by the same method with changing temperature mainly from 25 to 80°C and calculated from the equation:

$$\tau_f = (f_{80} - f_{25})/(f_{25} \times 55) \times 10^6(\text{ppm°C}) \quad (1)$$

where f_{80} and f_{25} represent the resonant frequency at 80 and 25°C, respectively.

3. Results and discussion

Fig. 1 shows (a) XRD patterns of ZnO–TiO_2 system with ZBS sintered at 900° for 3 h, and (b) with 2 wt.% ZBS sintered at different temperature for 3 h. For all the specimens sintered at 900° for 3 h, hexagonal $ZnTiO_3$ and rutile (TiO_2) were formed. However, with 5 wt.% ZBS addition, a small amount of unknown phase was detected. The hexagonal $ZnTiO_3$ phase was maintained at the sintering temperature (Ts) ⩽900°C. Zn_2TiO_4 appeared as the main crystalline phase associated with rutile and $ZnTiO_3$ at Ts=920°C. At 940°C, the $ZnTiO_3$ phase completely disappeared. It indicates that the $ZnTiO_3$ phase was decomposed to cubic Zn_2TiO_4 and rutile at Ts >900°C, which is lower than the decomposing temperature of 950°C reported by Kim [13]. These results suggest that ZBS can lower the decomposing temperature of $ZnTiO_3$ phase.

From our studies, pure ZnO–TiO_2 ceramics specimens sintered at 1100°C for 3 h had about 98% theoretical density(TD=5.09 g/cm^3, estimated from the XRD pattern).The bulk densities of ZnO–TiO_2 ceramics with various amount of ZBS addition at different sintering temperature for 3 h are shown in Fig. 2. The ZnO–TiO_2 ceramics with

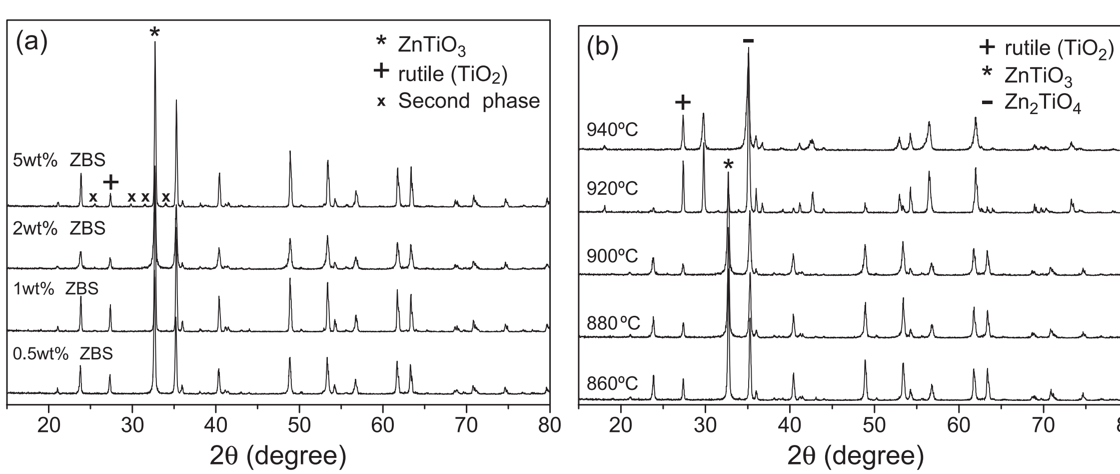

Fig. 1. (a) XRD patterns of ZnO–TiO_2 system with ZBS sintered at 900 °C, and (b) with 2 wt.% ZBS sintered at different temperatures.