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Effect of B_2O_3 addition on the sintering temperature and microwave dielectric properties of Zn_2SiO_4 ceramics

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Abstract

B_2O_3 (25.0 mol%) was added to $Zn_{2-x}SiO_{4-x}$ ceramics ($0.0 \leq x \leq 0.5$) to decrease the sintering temperature. Specimens with $0.0 \leq x \leq 0.3$ sintered at 900 °C were well sintered with a high density due to the formation of a B_2O_3 or B_2O_3–SiO_2 liquid phase. The $Q \times f$ value of the Zn_2SiO_4 ceramic was relatively low, 32,000 GHz, most likely due to the presence of a ZnO second phase. A maximum $Q \times f$ value of 70,000 GHz was obtained for the specimens with $x = 0.2$–0.3, and their ε_r and τ_f values were approximately 6.0 and −21.9 ppm/°C, respectively. Ag metal did not interact with the 25.0 mol% B_2O_3-added $Zn_{1.8}SiO_{3.8}$ ceramic, indicating that $Zn_{2-x}SiO_{4-x}$ ceramics containing B_2O_3 are a good candidate materials for low temperature co-fired ceramic devices.

Keywords: Sintering; Microwave dielectric properties; Zn_2SiO_4

1. Introduction

The ongoing development of mobile systems, such as laptop computers and cellular phones has pushed the continuing miniaturization of microwave devices. This miniaturization can be achieved using low temperature co-fired ceramic (LTCC) multilayer devices. LTCC multilayer devices are composed of alternating dielectric ceramics and internal metallic electrode layers.[1] Ag is generally used as the metallic electrode layer on account of its high conductivity and low cost. Therefore, microwave dielectric ceramics with a low sintering temperature need to be developed for co-firing with the Ag electrode whose melting temperature is low, approximately 961 °C.

A large amount of glass is generally used to decrease the sintering temperature of microwave dielectric materials for application to LTCC multilayer devices.[2–5] However, the added glass exists as an amorphous phase in the specimens, which deteriorates the $Q \times f$ value of the specimens.[6–11] Although some materials have a high $Q \times f$ value, they generally show a large negative temperature coefficient of the resonant frequency (τ_f). Moreover, special production techniques, such as the cold isostatic press (CIP), are needed to produce specimens with a high $Q \times f$ value.[12–14] Therefore, new materials with a low ε_r, high $Q \times f$ and almost zero τ_f, as well as the ability to be sintered at low temperatures (≤900 °C), are needed for application to LTCC devices.

Zn_2SiO_4 ceramic synthesized by CIP exhibited a low ε_r value and a high $Q \times f$ value of 6.6 and 219,000 GHz, respectively.[15] However, a Zn_2SiO_4 ceramic recently synthesized without CIP showed a low $Q \times f$ due to the presence of a ZnO second phase.[16] A small amount of ZnO was removed from the Zn_2SiO_4 ceramic to increase the $Q \times f$ value and the $Zn_{1.8}SiO_{3.8}$ ceramic sintered at 1300 °C showed the improved microwave dielectric properties of $\varepsilon_r = 6.6$, $Q \times f = 147{,}000$ GHz, and $\tau_f = -22$ ppm/°C.[16] However, the sintering temperature of the $Zn_{1.8}SiO_{3.8}$ ceramics was high and needs to be decreased before they can be considered for use as LTCC devices. B_2O_3 was used to decrease the sintering temperature of the $Zn_{1.8}SiO_{3.8}$ cearmics.[17] However, no systematic research has been carried out on the effect of B_2O_3 addition on the sintering temperature and microwave dielectric properties of $Zn_{2-x}SiO_{4-x}$ ceramics with $0.0 \leq x \leq 0.5$. In particular, the compatibility of these ceramics with Ag metal has not been investigated.

In this study, 25.0 mol% B_2O_3 was added to the $Zn_{2-x}SiO_{4-x}$ ceramics ($0.0 \leq x \leq 0.5$) to reduce their sintering temperature. The microwave dielectric properties, shrinkage behavior and

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compatibility with the Ag electrode of the resulting ceramics were examined.

2. Experimental procedure

Using the method of conventional solid-state synthesis, $Zn_{2-x}SiO_{4-x}$ ceramics with $0.0 \leq x \leq 0.5$ were prepared from high purity (>99%) oxides. For the synthesis of these materials, ZnO and SiO_2 (High Purity Chemicals, >99%) powders were ball-milled in a nylon jar with zirconia balls for 24 h. After drying, the mixed $Zn_{2-x}SiO_{4-x}$ powders ($0.0 \leq x \leq 0.5$) were calcined at 1150 °C for 3 h. After re-milling with 25.0 mol% B_2O_3 additive, the powders were dried and pressed into discs under a pressure of 9.8 MPa and sintered at 875–900 °C for 2 h. The structural properties of the specimens were examined by X-ray diffraction (XRD: Rigaku D/max-RC, Japan) and scanning electron microscopy (SEM: Hitachi S-4300, Japan). Composition analysis was performed using energy dispersive spectroscopy (EDS: Horiba EMAX, Japan). Shrinkage of the specimens during heating was measured using a horizontal loading heating microscope (HM: Okdu Co. Ltd., Korea). The densities of the sintered bodies were measured using Archimedes' principle. The microwave dielectric properties of the samples were measured using the dielectric resonator technique suggested by Hakki–Coleman and Courtney.[18,19] The τ_f values of the samples were measured at temperatures ranging from 25 to 90 °C.

3. Results and discussion

Fig. 1(a)–(f) shows the XRD patterns of the $Zn_{2-x}SiO_{4-x}$ powders with $0.0 \leq x \leq 0.5$, calcined at 1150 °C for 3 h. The peak for the ZnO phase was observed for the specimen with $x = 0.0$. A complete interaction between SiO_2 and ZnO was difficult due to the very stable structure of crystalline SiO_2, resulting in the formation of the ZnO second phase.[16] A SiO_2 second phase was also expected to exist in the Zn_2SiO_4 powder but no peak for this phase was observed; indicating that a very small amount of SiO_2 existed in the Zn_2SiO_4 powder. The ZnO second phase disappeared with increasing x but a SiO_2 phase indicated by the arrow was newly formed in the ZnO-deficient Zn_2SiO_4 powders, as shown in Fig. 1(b)–(f).

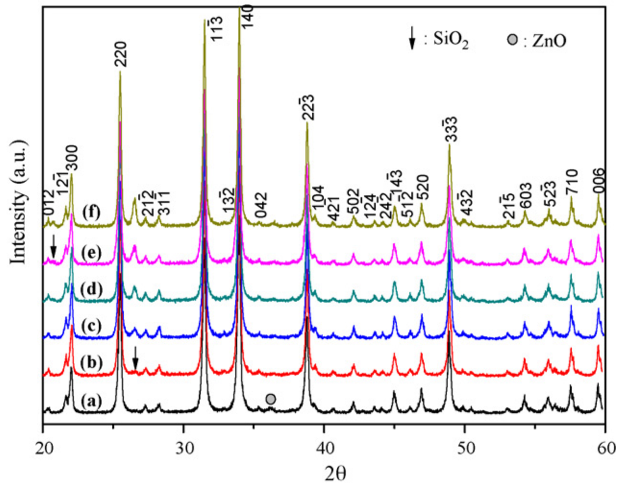

Fig. 1. XRD patterns of the $Zn_{2-x}SiO_{4-x}$ powders with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) $x = 0.5$ calcined at 1150 °C for 3 h.

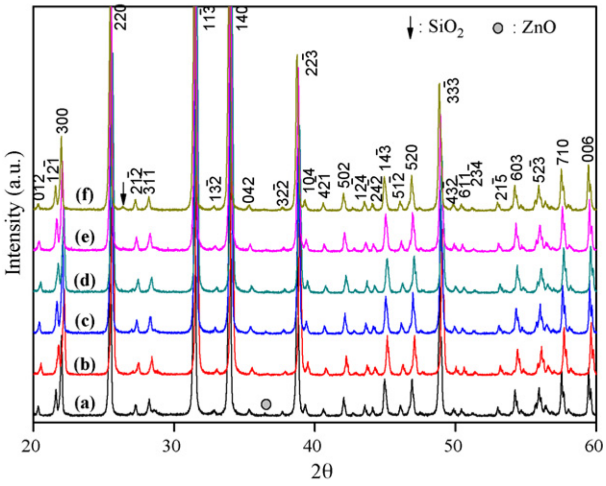

Fig. 2. XRD patterns of 25.0 mol% B_2O_3-added $Zn_{2-x}SiO_{4-x}$ ceramics with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) $x = 0.5$ sintered at 900 °C for 2 h.

Fig. 2(a)–(f) shows the XRD patterns of the 25.0 mol% B_2O_3-added $Zn_{2-x}SiO_{4-x}$ ceramics with $0.0 \leq x \leq 0.5$, sintered at 900 °C for 2 h. The 25.0 mol% B_2O_3-added Zn_2SiO_4 ceramic was well sintered and a ZnO second phase still existed after the sintering without other second phases. Therefore, it is believed that the B_2O_3 melted during the sintering and assisted the densification of the Zn_2SiO_4 ceramic. On the other hand, the ZnO-deficient, Zn_2SiO_4 ceramics were also well sintered at 900 °C and the SiO_2 second phase, which was observed in the ZnO-deficient, Zn_2SiO_4 powders, disappeared after sintering the specimens with $x < 0.4$. Therefore, B_2O_3 was considered to have interacted with the remnant SiO_2 and formed a B_2O_3–SiO_2 related liquid phase, which assisted the densification of the specimens. However, for the specimens with $x \geq 0.4$, the 25.0 mol% B_2O_3 was insufficient to consume the remaining SiO_2 in the ZnO-deficient specimens, resulting in the presence of SiO_2 second phase, as shown in Fig. 2(e) and (f).

Fig. 3 presents the shrinkage behavior of the 25.0 mol% B_2O_3-added $Zn_{2-x}SiO_{4-x}$ ceramics with $0.0 \leq x \leq 0.5$. Shrinkage began at approximately 800 °C for all these ceramics, indicating that B_2O_3 acted as a good low temperature sintering aid for $Zn_{2-x}SiO_{4-x}$ ceramics with $0.0 \leq x \leq 0.5$.

Fig. 4(a)–(d) shows the relative density, ε_r, τ_f and $Q \times f$ values of the 25.0 mol% B_2O_3-added $Zn_{2-x}SiO_{4-x}$ ceramics with $0.0 \leq x \leq 0.5$, sintered at 900 and 875 °C for 2 h. All specimens sintered at 875 °C showed a very low relative density, indicating that densification did not occur at 875 °C. On the other hand, the relative density of the specimens with $0.0 \leq x \leq 0.3$ sintered at 900 °C was ≥95% of the theoretical density, which was attributed to the liquid phase sintering induced by the presence of the B_2O_3 or B_2O_3–SiO_2 related liquid phase. The relative density of the specimens decreased slightly when x exceeded 0.3, probably due to the existence of a large amount of the liq-