

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/ $^\circ\text{C}$, 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.

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1. Introduction

The ongoing development of mobile systems, such as lap-top 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 iso-

static 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 ($\leq 900^\circ\text{C}$), 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 $\epsilon_r=6.6$, $Q \times f=147,000$ GHz, and $\tau_f=-22$ ppm/ $^\circ\text{C}$.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 $Zn_{1.8}SiO_{3.8}$ ceramics.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, $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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 $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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 $875\text{--}900^\circ\text{C}$ 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 $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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

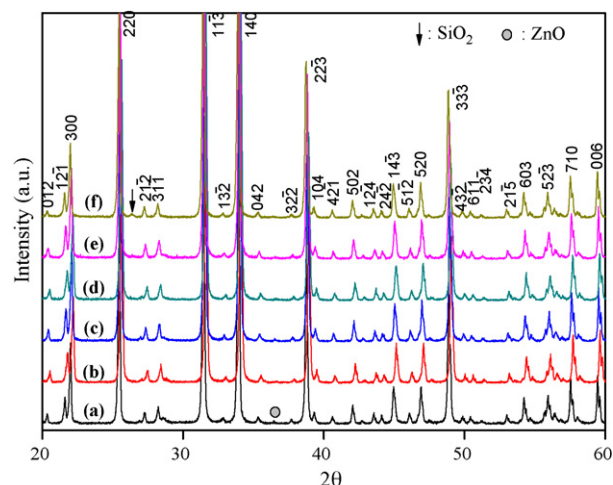


Fig. 2. XRD patterns of 25.0 mol% B_2O_3 -added $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramics with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) $x = 0.5$ sintered at 900°C for 2 h.

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. 2(a)–(f) shows the XRD patterns of the 25.0 mol% B_2O_3 -added $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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 $\text{B}_2\text{O}_3\text{--SiO}_2$ 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 $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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 $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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 $\text{Zn}_{2-x}\text{SiO}_{4-x}$ 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 $\geq 95\%$ of the theoretical density, which was attributed to the liquid phase sintering induced by the presence of the B_2O_3 or $\text{B}_2\text{O}_3\text{--SiO}_2$ 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-

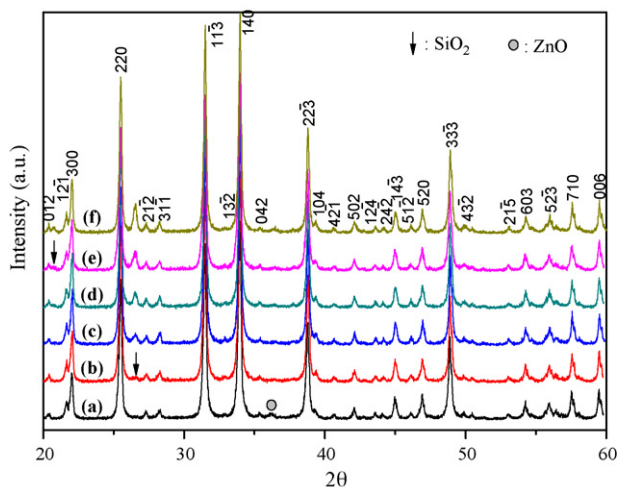


Fig. 1. XRD patterns of the $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powders with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) $x = 0.5$ calcined at 1150°C for 3 h.

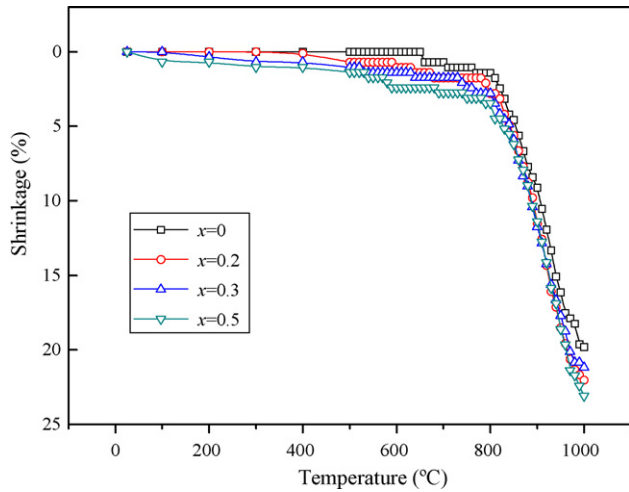


Fig. 3. Shrinkage behavior of the 25.0 mol% B₂O₃-added Zn_{2-x}SiO_{4-x} ceramics with $0.0 \leq x \leq 0.5$.

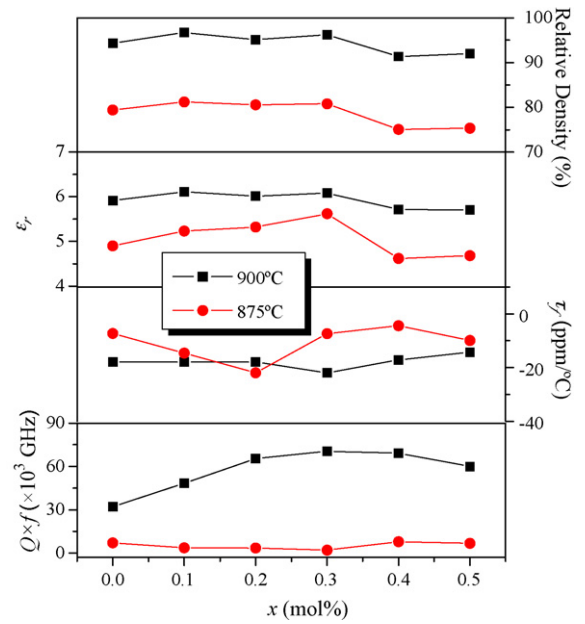


Fig. 4. Relative density, ϵ_r , τ_f and $Q \times f$ values of the 25.0 mol% B₂O₃-added Zn_{2-x}SiO_{4-x} ceramics with $0.0 \leq x \leq 0.5$, sintered at 900 and 875 °C for 2 h.

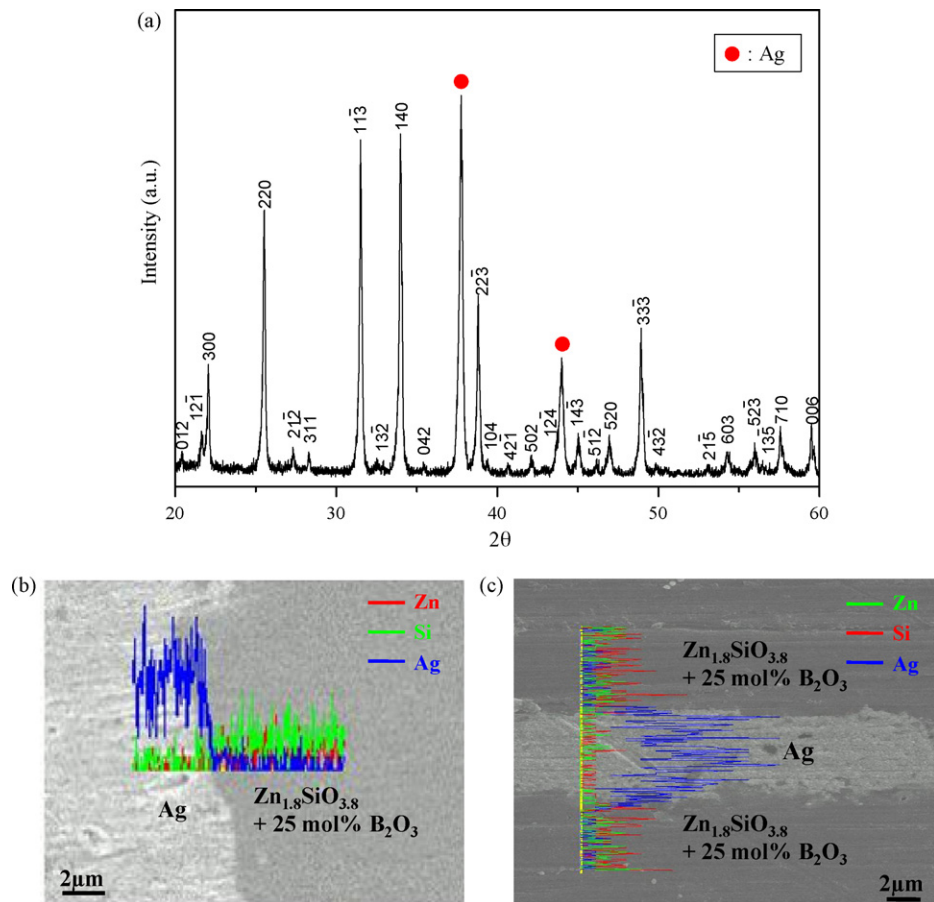


Fig. 5. (a) XRD pattern of the 25.0 mol% B₂O₃-added Zn_{1.8}SiO_{3.8} ceramic sintered with Ag metal at 900 °C for 2 h. SEM image and EDS line scan of the interface between the 25.0 mol% B₂O₃-added Zn_{1.8}SiO_{3.8} ceramic and the Ag metal: (b) bulk and (c) multilayers.

uid phase and a SiO_2 second phase. The variation of the ε_r value with x was very similar to that of the relative density, indicating that the ε_r value was considerably influenced by the density, but its variation was not significant ranging between 5.7 and 6.1. The variation of the τ_f value with x , ranging between -21.9 and -14.3 ppm/ $^\circ\text{C}$, was not significant. The $Q \times f$ value of the specimens is also shown in Fig. 4. The $Q \times f$ value of the Zn_2SiO_4 ceramic sintered at 900°C was approximately 32,000 GHz and increased with increasing x to 70,000 GHz for the specimen with $x=0.3$, but then decreased slightly when x exceeded 0.3. Although the relative density of the B_2O_3 -added Zn_2SiO_4 ceramic was higher than that of the specimens with $x>0.3$, its $Q \times f$ value was lower than that of the specimens with $x>0.3$. According to the previous work, the presence of a ZnO second phase considerably reduced the $Q \times f$ value of the Zn_2SiO_4 ceramic sintered at high temperature,¹⁶ indicating that the low $Q \times f$ value of the B_2O_3 -added Zn_2SiO_4 ceramic sintered at 900°C can also be explained by the presence of a ZnO second phase.

Ag has generally been used as the electrode in LTCC devices, because of its high conductivity and low cost. Therefore, it is important to study the reaction between the Ag electrode and the B_2O_3 -added $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramic. Fig. 5(a) shows the XRD pattern of the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramic sintered with Ag metal at 900°C . Peaks for the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramic and the Ag metal were observed without any peaks for a second phase. The interface between the Ag metal and the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramic was also studied using SEM and EDS line scan, as shown in Fig. 5(b). This interface was well developed and the silver profile sharply decreased at the interface, indicating that no diffusion of silver occurred into the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramic. Moreover, the very low concentrations of Zn and Si in the Ag metal suggested the absence of any reaction between the Ag metal and the B_2O_3 -added $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramic. The B_2O_3 -added, $\text{Zn}_{1.8}\text{SiO}_{3.8}/\text{Ag}/\text{B}_2\text{O}_3$ -added, $\text{Zn}_{1.8}\text{SiO}_{3.8}$ multilayers were also formed at 900°C and the interface between B_2O_3 -added, $\text{Zn}_{1.8}\text{SiO}_{3.8}$ and Ag was observed using SEM, as shown in Fig. 5(c). A relatively sharp interface was developed without any Ag diffusion into the B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ layer, indicating that the Ag metal did not react with the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramic at 900°C .

4. Conclusion

B_2O_3 (25.0 mol%) was added to the $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramics ($0.0 \leq x \leq 0.5$) to decrease their sintering temperature. Shrinkage started at approximately 800°C for these ceramics, and they were well sintered at 900°C . A ZnO second phase was observed in the B_2O_3 -added Zn_2SiO_4 ceramic, indicating that a liquid phase containing B_2O_3 was responsible for the densification of this specimen. On the other hand, the liquid phase containing B_2O_3 – SiO_2 was responsible for the densification of the $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramics with $0.1 \leq x \leq 0.5$. The relative density of the specimens with $0.0 \leq x \leq 0.3$ sintered at 900°C was high but slightly decreased when x exceeded 0.3, probably due to the presence of a large amount of the liquid phase and a SiO_2

second phase. The variation of the ε_r value with x was very similar to that of the relative density. The $Q \times f$ value of the Zn_2SiO_4 ceramic sintered at 900°C was low, at approximately 32,000 GHz, but increased to a maximum of 70,000 GHz for the specimen with $x=0.3$. The variation of the τ_f value of all the specimens ranged between -21.9 and -14.3 ppm/ $^\circ\text{C}$, was relatively small. The Ag metal did not react with the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramic at 900°C and a chemically sharp interface was formed between the Ag and the 25.0 mol% B_2O_3 -added $\text{Zn}_{1.8}\text{SiO}_{3.8}$ layers.

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