

LOW-TEMPERATURE SINTERING AND MICROWAVE DIELECTRIC PROPERTIES OF $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ - CaTiO_3 CERAMICS WITH H_3BO_3 ADDITION

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Low-melting H_3BO_3 , acting as sintering aid, was used to reduce the sintering temperature of 5 wt.% CaTiO_3 -doped $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ ceramics. The sintering behaviors, microstructures and microwave dielectric properties with different amounts of H_3BO_3 addition were investigated. The results showed that H_3BO_3 additive was very effective for lowering the sintering temperature and improving the bulk density during sintering. This was due to the promotion of liquid-phase sintering. In the case of 0.25 wt.% H_3BO_3 addition, fine-grained structure was observed, whereas abnormal grain growth was occurred when 3 wt.% H_3BO_3 was doped. It was found that the addition of H_3BO_3 improved the dielectric constant (ϵ_r) and quality factor ($Q \times f$). When 5 wt.% CaTiO_3 and 3 wt.% H_3BO_3 were added, the $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ ceramics could be sintered at 950~1000°C and showed excellent microwave dielectric properties: $\epsilon_r \approx 20$, $Q \times f > 48000$ GHz (at 8 GHz) and $\tau_f \approx 5$ ppm/°C.

INTRODUCTION

The development of multilayer devices for microwave applications has been paid an increasing attention since multilayer devices have promising applications for reducing the size and the weight of mobile communication components. To meet the requirements of such small sized devices, dielectric materials sintered at low temperature were extensively studied to co-fire with highly conductive metal electrodes, such as silver or copper, which has a low melting point of 961°C and 1064°C, respectively. Most of the well-known commercial microwave dielectric materials exhibit high quality factor (Q) and low temperature coefficient of resonant frequency (τ_f), such as BaTi_4O_9 , $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and MgTiO_3 - CaTiO_3 (MCT). However, they are not compatible with silver or copper electrode due to their high sintering temperatures ($> 1300^\circ\text{C}$) [1-3]. A common method to reduce the sintering temperature of these dielectric materials is adopting low-melting glass additions [4-6]. In another approach, some researches focused on searching for matrix systems with inherent low-sintering temperature, such as BiNbO_4 [7], ZnTiO_3 [8] and so on.

ZnTiO_3 ceramics are well known as one of promising candidates for low temperature co-fired ceramics due to excellent microwave properties: $\epsilon_r \approx 19$, $Q \approx 3000$ at 10 GHz, $\tau_f \approx 55$ ppm/°C and relatively low sintering temperature (about 1100°C) [8]. But when calcined above 945°C, ZnTiO_3 would decompose into TiO_2 and Zn_2TiO_4 that has a very low quality factor. Kim et al.

reported that MgTiO_3 could stabilize ZnTiO_3 phase and single-phase $(\text{Zn}_{1-x}\text{Mg}_x)\text{TiO}_3$ solid solutions were achieved at $x = 0.3\sim 0.4$, but the τ_f values were ranged from -70 to +50 ppm/°C [9]. In our previous research [10], CaTiO_3 with positive τ_f value (≈ 800 ppm/°C) was added to $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ to compensate the negative τ_f and near zero τ_f was obtained by 5 wt.% CaTiO_3 addition. However, 5 wt.% CaTiO_3 -added $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ (noted as ZMCT) ceramics could not be fully densified at sintering temperatures lower than 1150°C. Therefore, this study focused on finding the joint of perfect dielectric properties and low sintering temperature of ZMCT ceramics. In this article, low-melting H_3BO_3 , acting as sintering aid, was used to reduce the sintering temperature of ZMCT ceramics. The microstructures and microwave dielectric properties were also investigated.

EXPERIMENTAL PROCEDURE

$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, ZnO and TiO_2 were mixed according Zn: Mg = 6.5:3.5. The mixtures were milled for 10 h with 2.5 mm diameter zirconia beads in polyethylene jars. Then, the powders were calcined at 900~950°C for 2 h and $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ host material was synthesized. The host materials were doped with 5 wt.% CaTiO_3 and different amounts of H_3BO_3 , and then milled for 20 h, pelleted to 18 mm diameter and 9 mm thick disks. The disks were sintered at 950~1050°C for 2 h in air. The bulk densities of the sintered ceramics were measured using the Archimedes' method. The morphologies of the

microstructures of the as-fired ceramics were observed using a scanning electron microscopy (SEM, S-530 Hitachi). The dielectric constant ϵ_r and the quality values Q at microwave frequencies were measured with a network analyzer (Model Agilent E8363A) using Hakki-Coleman dielectric resonator method [11]. The resonant frequencies at temperatures 20°C (f_{20}) and 80°C (f_{80}) were measured. The temperature coefficient of resonant frequency τ_f was calculated from the formula: $\tau_f = (f_{80} - f_{20}) / (60 \times f_{20}) \times 10^6$ (ppm/°C).

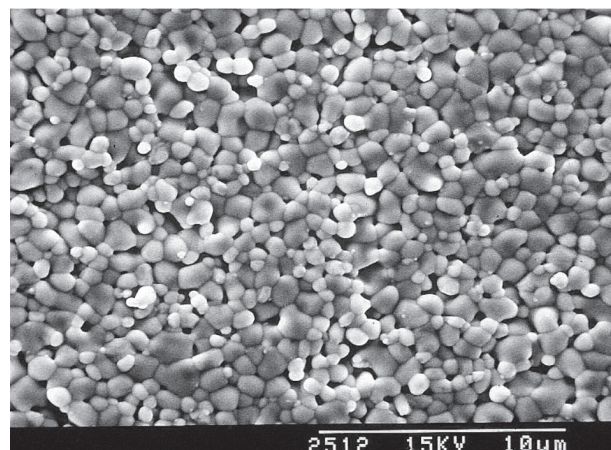
RESULTS AND DISCUSSION

Mg^{2+} was selected as a substitute for Zn^{2+} due to the same valence charge and small ionic size difference. The ionic radius of Mg^{2+} and Zn^{2+} in six-fold coordination is 0.72 Å and 0.75 Å, respectively. Moreover, the crystal structures of $ZnTiO_3$ and $MgTiO_3$ are the same ilmenite structure with rhombohedral symmetry. The lattice parameters of $ZnTiO_3$ and $MgTiO_3$ are $a = 5.0787$ Å, $c = 13.9271$ Å, and $a = 5.054$ Å, $c = 13.898$ Å, respectively. Therefore, solid solutions of zinc magnesium titanate were easily formed. The decomposition of $ZnTiO_3$ is effectively inhibited by the substitution of Zn with 35 mol% Mg, as reported in our previous researches [10] when $(Zn_{0.65}Mg_{0.35})TiO_3$ powders were calcined at 850°C ~ 1000°C. In our previous study, 5 wt.% $CaTiO_3$ -doped $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics without sintering aid must be sintered higher than 1150°C with microwave dielectric properties: $\epsilon \approx 24$, $Q \times f > 45000$ GHz (at 8 GHz) and $\tau_f \approx 10$ ppm/°C. To lower the sintering temperature, H_3BO_3 acting as sintering aid was added to ZMCT ceramics.

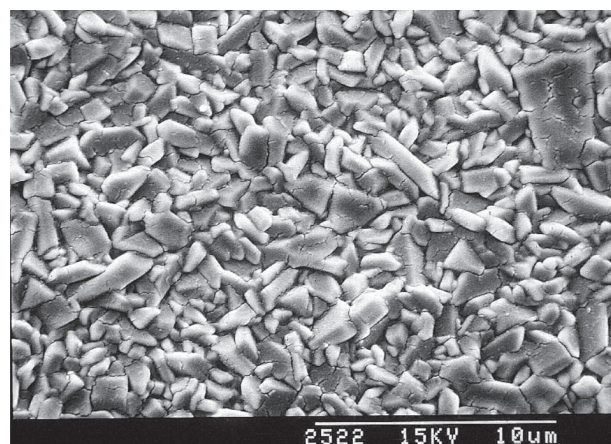
Typical SEM microstructures obtained for doped- $(Zn_{0.65}Mg_{0.35})TiO_3$ sintered at 950°C for 2 h are illustrated in Figure 1. These samples were doped with 5 wt.% $CaTiO_3$ and various amounts of H_3BO_3 . As shown in Figure 1a, fine grains (~ 1µm) were obtained in the specimen doped with 0.25 wt.% H_3BO_3 and many voids existed in grain boundaries and triple points. In this study, H_3BO_3 would decompose to a well known liquid former B_2O_3 at 300°C, which was often employed for a low-temperature sintering of microwave dielectrics due to its very low melting temperature around 450°C [12, 13]. The ZMCT grains were surrounded by B_2O_3 liquid glass phase during sintering so that the grain growth was inhibited. With 1 wt.% H_3BO_3 addition, the pores were almost eliminated and elongated grains were observed (Figure 1b). This is attributed to the fact that liquid fills grain junctions with sufficient H_3BO_3 addition and removes pores on firing. From Figure 1c, coarsened grains embedded in vast glass phase were observed with an addition of 3 wt.% H_3BO_3 , as a result of over adding sintering aid H_3BO_3 .

Figure 2 presents the bulk density of ZMCT ceramics as functions of sintering temperature and the content of H_3BO_3 . Generally, ZMCT ceramics without additives

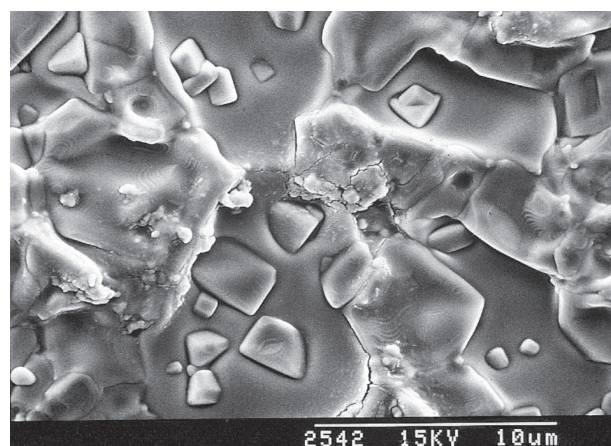
are known to be sintered only at 1150°C and above. The addition of H_3BO_3 markedly enhanced the sinterability of ZMCT ceramics. With the addition of H_3BO_3 , the bulk density initially increased as the sintering temperature increased, and then decreased. In the case of H_3BO_3 concentration ≤ 2 wt.%, the turning point is 1000°C. On the other hand, in samples doped with 3 wt.% H_3BO_3 ,



a)



b)



c)

Figure 1. SEM micrographs of $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics doped with 5 wt.% $CaTiO_3$ and different amounts of H_3BO_3 (sintered at 1000°C): a) 0.25 wt.%, b) 1 wt.%, c) 3 wt.%.

the density began to decrease above 1030°C. A saturated density of approximately 3.83 g/cm³ was obtained for ZMCT ceramics with 3 wt.% H_3BO_3 addition and sintered at 1000°C for 2 h. Moreover, the density increased with increasing the amount of H_3BO_3 addition. This is compatible with the SEM results that voids were removed by sufficient H_3BO_3 substitution. Previous studies have reported that glass phase surrounding the particles on sintering improves particle rearrangement and promotes the densification by liquid phase sintering [12-14]. However, over sintering would cause abnormal grain growth and lots of pores existed between coarsened grains, resulted in a decrease in density.

Figure 3 shows the microwave dielectric properties of ZMCT ceramics sintered at 950°C for 2 h when various amounts H_3BO_3 were added. The dielectric constant ϵ_r increased with an increase of H_3BO_3 amount, exhibiting the same trend as that of the bulk density since that dense ceramics had less pores (air, $\epsilon = 1$) to decay the ϵ value. The $Q \times f$ value is an important index for the application of dielectric ceramics at microwave frequencies since higher $Q \times f$ value means lower loss. ZMCT ceramics have relatively high sintering temperatures (~ 1150°C), so that ZMCT ceramics could not be well sintered with lower amounts of H_3BO_3 addition at 950°C. It revealed that the $Q \times f$ value increased with an increase of H_3BO_3 content. A maximum $Q \times f$ value of 53330 (at 8 GHz) was achieved for 3 wt.% H_3BO_3 -doped ZMCT ceramics, attributed to the highest density obtained in these samples. The τ_f values varied from 4.37 to 6.89 ppm/°C, which was acceptable in microwave devices.

The dielectric constant and $Q \times f$ value as functions of sintering temperature for ZMCT ceramics doped with 3 wt.% H_3BO_3 are illustrated in Figure 4. It suggested that excellent microwave dielectric properties were obtained when the ceramics were sintered at 950 ~ 1000°C for 2 h: $\epsilon \approx 20$, $Q \times f > 48000$ GHz (at 8 GHz).

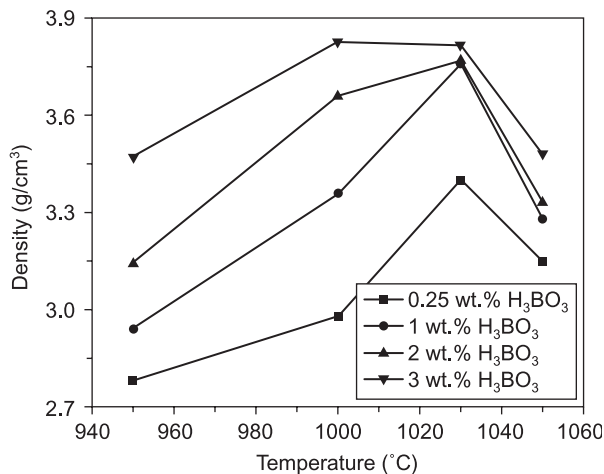


Figure 2. Bulk density as functions of sintering temperature and the content of H_3BO_3 .

CONCLUSIONS

Hexagonal single-phase $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ powders could be synthesized when the powders were calcined at 900°C by solid-state reaction process. 5 wt.% CaTiO_3 doped $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ ceramics exhibited good microwave dielectric properties ($\epsilon_r \approx 24$, $Q \times f > 45000$ GHz).

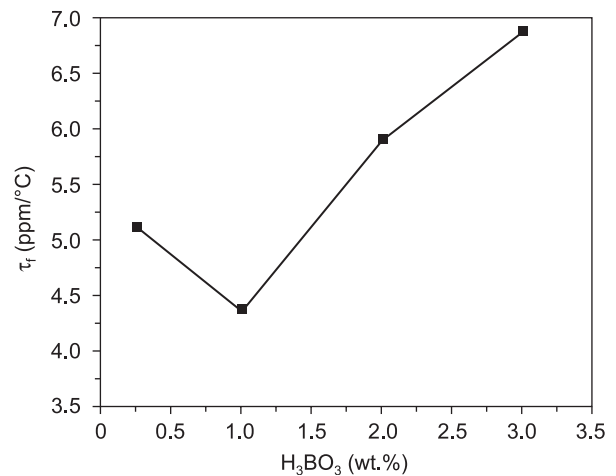
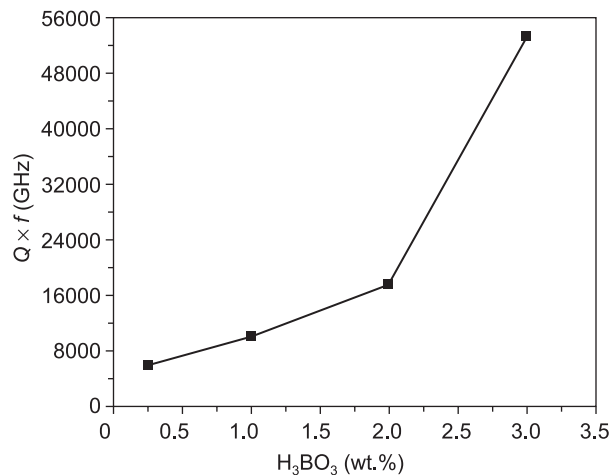
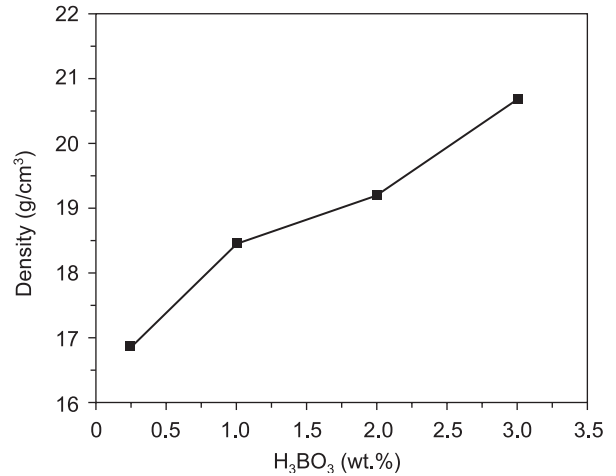


Figure 3. Microwave dielectric properties (at 8 GHz) versus H_3BO_3 amount of 5 wt.% CaTiO_3 -added $(\text{Zn}_{0.65}\text{Mg}_{0.35})\text{TiO}_3$ ceramics sintered at 950°C for 2 h.

(at 8 GHz) and $\tau_f \approx 10$ ppm/°C). However, this system ceramics could not be fully densified at sintering temperatures lower than 1150°C. Low-melting H₃BO₃ additive could significantly reduce the sintering temperature from 1150°C without H₃BO₃ addition to 950°C. With 3 wt.% H₃BO₃ addition, microwave dielectric properties were improved: $\epsilon \approx 20$, $Q \times f > 48000$ GHz (at 8 GHz) and $\tau_f \approx 5$ ppm/°C when the ceramics were sintered at 950 ~1000°C for 2 h.

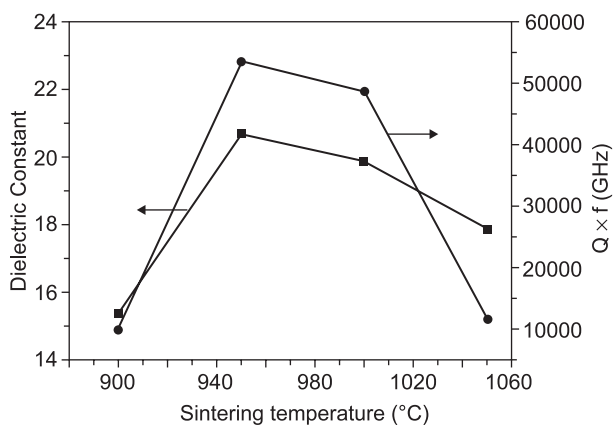


Figure 4. Microwave dielectric properties (at 8 GHz) versus sintering temperature of 5 wt.% CaTiO₃-added (Zn_{0.65}Mg_{0.35}) TiO₃ ceramics with 3 wt.% H₃BO₃ addition.

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