The low-temperature sintering and microwave dielectric properties of $(Zn_{0.7}Mg_{0.3})TiO_3$ ceramics with H_3BO_3*

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The effects of the addition of H_3BO_3 on the microstructure, phase formation, and microwave dielectric properties of $(Zn_{0.7}Mg_{0.3})TiO_3$ ceramics sintered at temperatures ranging from 890 °C to 950 °C are investigated. H_3BO_3 as a sintering agent can effectively lower the sintering temperature of ZMT ceramics below 950 °C due to the liquid-phase effect. The microwave dielectric properties are found to strongly correlate with the amount of H_3BO_3. With the increase in H_3BO_3 content, the dielectric constant (ε_r) monotonically increases, but the quality factor ($Q \times f$) reaches a maximum at 1 wt% H_3BO_3, and the apparent density of ZMT ceramics with $H_3BO_3 \geq 1$ wt% gradually decreases. At 950 °C, the ZMT ceramics with 1% H_3BO_3 exhibit excellent microwave dielectric properties: $\varepsilon_r = 19.8$, and $Q \times f = 43800$ GHz (8.94 GHz).

Keywords: ZMT ceramics, LTCC, H_3BO_3

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1. Introduction

With high permittivity (ε_r), a high quality factor ($Q \times f$) and a near zero temperature coefficient of the resonant frequency (τ_f), low-temperature co-fired ceramics (LTCCs) have been widely used in microwave communication devices such as resonators, filters, and oscillators.[1] However, to be co-fired with Ag internal electrodes, the sintering temperature of the dielectric for LTCCs must be below 961 °C.[2,3] Even though several types of dielectric materials with good microwave dielectric properties have been reported, most of them can only be sintered well from 1200 °C to 1500 °C to obtain a high density and good properties. Hence, the decrease in sintering temperature is a key problem in the application of LTCCs in the fabrication of dielectric devices such as resonators, filters, and duplexers.[4,5]

Zinc titanate ($ZnTiO_3$)-based systems exhibit good microwave dielectric properties of a high dielectric constant (~ 20) and good quality factor ($Q \times f = 33000$ GHz), and $\tau_f \approx -55$ ppm/°C.[6–8] Therefore, $ZnTiO_3$ ceramics have been developed and used as microwave materials for LTCCs.[9–11] However, there are some difficulties in obtaining single-phase hexagonal $ZnTiO_3$. Owing to the second-phase cubic Zn_2TiO_4, ZMT ceramics have a rather low quality factor at above 945 °C.[12] With the purpose of overcoming the above limitation in the sintering temperature, a (Zn, Mg)TiO_3 system has been developed because the substitution of Mg for Zn can suppress the decomposition of $ZnTiO_3$ at higher temperatures.[13–15] In order to reduce the sintering temperature, Li *et al.*[16] added $BiVO_4$ to reduce the sintering temperature of $(Zn_{0.65}Mg_{0.35})TiO_3$. Besides, Li *et al.*[17] also found that the addition of CaO–B_2O_3–SiO_2 significantly improved the sintering ability of (Zn, Mg)TiO_3. To reduce the sintering temperature of (Zn, Mg)TiO_3, Kim *et al.*[8] investigated low-fired (Zn, Mg)TiO_3 microwave ceramics via the semichemical synthesis route. Recently, many investigations have been performed on the influences of the glass frit (e.g. Zn–B_2O_3–SiO_2 systems) and low melting point compound (e.g. Bi_2O_3, V_2O_5, B_2O_3–V_2O_5,) on the microstructure and microwave properties of $ZnTiO_3$ and (Zn, Mg)TiO_3 dielectrics.[18–27]

In the present paper, H_3BO_3 is selected as a sintering aid to lower the sintering temperature of the ZMT ceramic. The influences of the addition of H_3BO_3 on the microstructure, densification, X-ray diffraction patterns, and the microwave dielectric properties of ZMT are investigated.

2. Experimental procedure

Reagent-grade raw oxide powders of 99.9% purity: ZnO, MgO, TiO_2 were prepared by the conventional solid-state reaction method as original materials. The raw powders were weighed according to the mol ratio of ZnO:MgO:TiO_2 =0.7:0.3:1, and mixed with zirconia balls for 12 h in distilled water. The obtained powders were calcined at 850 °C for 3 h in air. Then, the calcined powders were milled for 12 h, respectively, with an addition of x wt% H_3BO_3 ($x = 0.5$, 1.0, 1.5, 2.0) with purities higher than 98%, and the mixed powders were ground with a suitable amount of polyvinyl alcohol as the binder and formed into disks (12 mm in diameter and

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7 mm in thickness) under 5 MPa. The disks were sintered at 890 °C–950 °C for 3 h.

The crystalline phases of the sintered ceramics were identified by X-ray diffraction (XRD) using Cu K_α radiation, and microstructure observations of the sintered surfaces were studied using scanning electron microscopy (SEM). The bulk density was measured by the Archimedes method, and the microwave dielectric properties of the sintered samples were evaluated in terms of the Hakki–Coleman method and using an Agilent N52030A (300 MHz–20 GHz) network analyzer in a resonant cavity. The temperature coefficient resonant frequency (τ_f) was also measured in the same way by changing the temperature mainly from 20 °C to 80 °C, and calculated from the following equation: $\tau_f = (f_{80} - f_{20})/(60 \times 20) \times 10^6$ (ppm/ °C), where f_{80} and f_{20} represent the resonant frequencies at 80 °C and 20 °C, respectively.

3. Results and discussion

Figure 1 shows the XRD patterns of $Zn_{0.7}Mg_{0.3}TiO_3$ ceramics with x wt% H_3BO_3 ($x = 0$, 0.5, 1, 1.5, 2) sintered at 950 °C. The patterns show $ZnTiO_3$ as the major crystalline phase, which matches very well with the ICDD card of 85-0547. Moreover, XRD peaks belonging to the $MgTiO_3$ phase are not presented for all the samples, which indicates that the Mg ions can easily substitute the zinc ions and form the ($Zn_{0.7}Mg_{0.3}TiO_3$) solid solution. This is because $MgTiO_3$ has a similar ilmenite structure to $ZnTiO_3$ and a smaller ionic radius of Mg^{2+} (0.66 Å) than of Zn^{2+} (0.74 Å). In addition, the peaks of the chemical composition of H_3BO_3 are not present in these XRD patterns, nor the extra peaks due to other second phases for ZMT ceramics without H_3BO_3 addition. But with the H_3BO_3 added, the perovskite structure is identified with the second phase Zn_2TiO_4 for all compositions tested in the experiment. However, the strength of the Zn_2TiO_4 peak is weak and has no significant change. The forming of the second phase Zn_2TiO_4, which will affect the dielectric properties of the ZMT ceramics, might be due to the doped B^{3+}. In general, this phenomenon reveals that the addition of H_3BO_3 almost forms the single-phase $ZnTiO_3$ completely, except for a small amount of Zn_2TiO_4 at 950 °C.

The SEM images of ZMT ceramics with various values of H_3BO_3 content, sintered at 950 °C, are illustrated in Fig. 2. As the grains have not grown, the pure ZMT ceramic in Fig. 2(a) sintered at 950 °C is porous and exhibits a uniform microstructure with fine grains. With the addition of H_3BO_3 as the temperature agent, the specimen shows abnormal grain-growth, and the grain size increases gradually with the further increase in H_3BO_3 content and reaches a maximum value at $x = 1$. This result indicates that the H_3BO_3 addition has an obvious influence on the grain growth behavior of ZMT. Moreover, a secondary phase of Zn_2TiO_4 is also observed, owing to the addition of H_3BO_3. With the H_3BO_3 content increasing to 1 wt%, the specimen reaches the maximal densification and fewer pores are observed between the grains in Fig. 2(c). It can be worked out that small amounts of B^{3+} can be dissolved in the ZMT phase, which promotes the abnormal growth of ZMT ceramic grains. When the H_3BO_3 content further increases to 1.5 wt%, the sizes of the grains in Fig. 2(d) are smaller than those in Fig. 2(c) and a small amount of the second phase is observed, which influences the microwave dielectric properties of the ZMT ceramic. Moreover, for the sample doped with 2 wt% H_3BO_3, the grains of the ZMT matrix are elongated, and many pores are observed between the grains compared with Fig. 2(c). The results are consistent with those observed from Fig. 3.

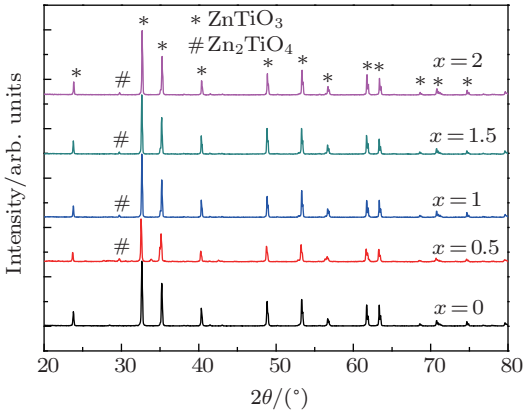


Fig. 1. (color online) XRD patterns of ZMT samples with different values of H_3BO_3 content, sintered at 950 °C.

Figure 3 shows the bulk densities of ZMT ceramics with the addition of H_3BO_3 sintered at temperatures ranging from 890 °C to 950 °C. It can be easily observed that the sintering temperature is significantly lowered by the H_3BO_3 addition, thereby enhancing the densification of the sample. The density of the ZMT ceramic gradually increases with increasing sintering temperature and then reaches a saturation value, which indicates that an H_3BO_3-related liquid phase is formed and that the liquid phase can lower the sintering temperature effectively. In fact, H_3BO_3 could form the liquid phase at temperatures more than 450 °C. However, the more HBO_3 ($\geq$ 1.5 wt%) cannot further reduce the sintering temperature, and the density of the sample gradually drops off in general. This is because there are some smaller grains and more pores, which are clearly observed from Figs. 2(d) and 2(e). In addition, the density of the ceramic material is usually enhanced with increasing sintering temperature. Nonetheless, the decrement of density might result from over-firing. From the above results, it can be considered that a significant reduction in the sintering temperature of the ZMT ceramic is possible, owing to the addition of H_3BO_3.

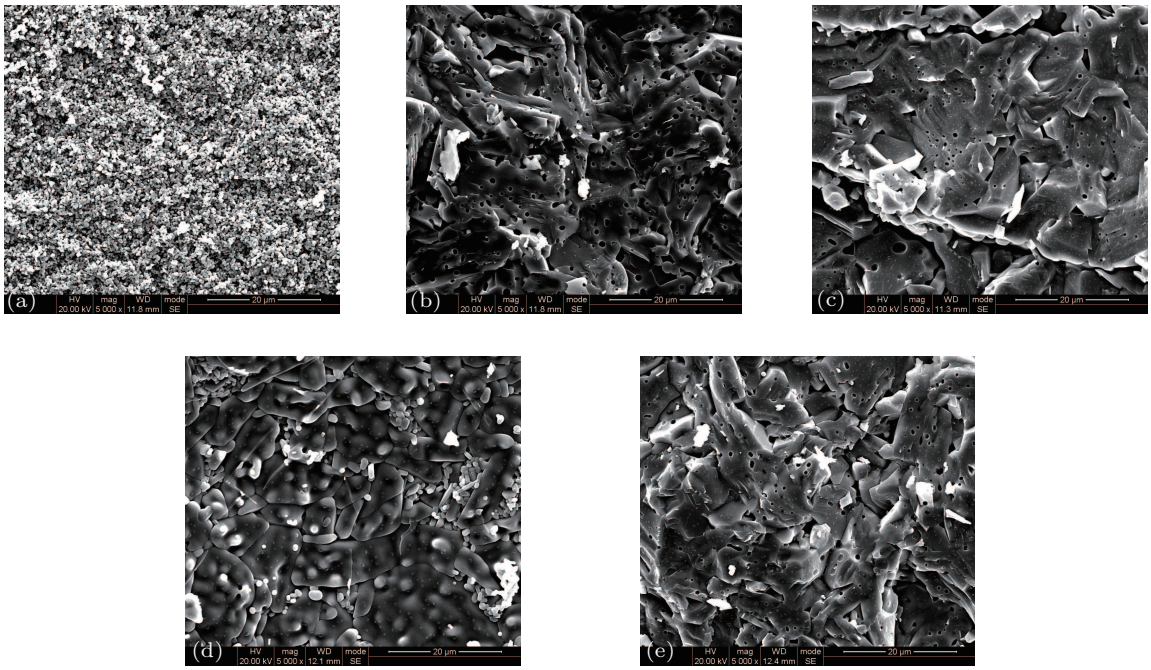


Fig. 2. SEM photographs of ZMT samples doped with x wt% H_3BO_3 additions, sintered at 950 °C, where $x = 0$ (a), 0.5 (b), 1 (c), 1.5 (d), and 2 (e).

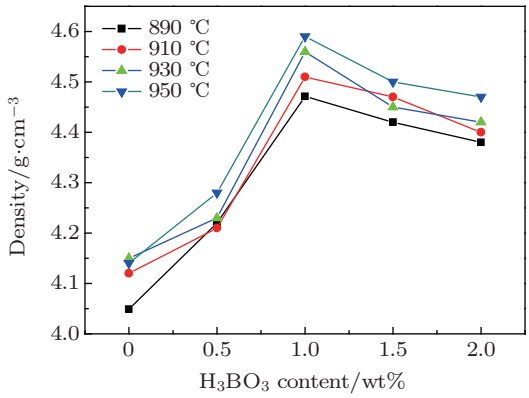


Fig. 3. (color online) The densities of the ZMT ceramics with different values of H_3BO_3 content, sintered at 890 °C–950 °C.

Figure 4 shows the dielectric constants of the ZMT ceramics with different amounts of H_3BO_3, sintered at 890 °C–950 °C. From the experiment, we can conclude that the central frequency is about 9.0 GHz. The relationship between the ε_r value and H_3BO_3 content reveals the same trend as that between the density and H_3BO_3 content since a higher density means a lower porosity. The ε_r value of the H_3BO_3-doped ZMT sample monotonically increases with increasing H_3BO_3 addition, and then reaches a maximum value. This is because the specimen reaches the maximal densification and fewer pores are observed between the grains, which is consistent with the observations from Figs. 2(c) and 3. With the addition of up to 1.5 wt%, the ε_r value begins to decrease with the H_3BO_3 addition increasing, which is surely due to the density and microstructure. Therefore, the ε_r value is generally affected by the morphology of the microwave ceramic, such as the grain size and density.

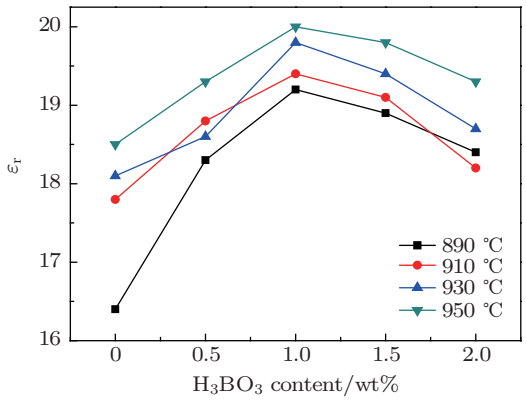


Fig. 4. (color online) The dielectric constants of ZMT ceramics with different values of H_3BO_3 content, sintered at 890 °C–950 °C.

The values of the quality factor ($Q \times f$) of the ZMT ceramics with x wt% H_3BO_3 additions at different temperatures are shown in Fig. 5. It can be seen that the $Q \times f$ values keep increasing as the sintering temperature increases from 890 °C to 950 °C. This is because the $Q \times f$ value is independent of density or porosity for a density higher than the 85% theoretical density of ZMT. Moreover, the grains become large when the sintering temperature increases, which will result in lower dielectric loss, because a large grain could lead to a lower grain boundary and less lattice mismatch. Meanwhile, the $Q \times f$ value reaches a maximal value at 1 wt% of H_3BO_3, and then decreases with increasing H_3BO_3 addition. Thus, a maximum $Q \times f$ value of 43800 GHz could be obtained at 950 °C for 1 wt% H_3BO_3-doped ZMT ceramics.

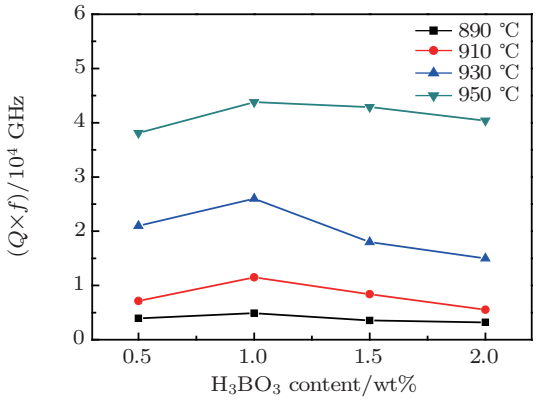


Fig. 5. (color online) The Q×f values of ZMT ceramics with different values of H_3BO_3 content, sintered at 890 °C–950 °C.

The values of τ_f for 1 wt% H_3BO_3-doped ZMTs sintered at 950 °C are shown in Fig. 6. The τ_f value for the ZMT ceramic depends on the crystalline structure. According to the mixing rule, the τ_f of a composite material can be expressed as $\tau_f = v_1\tau_1 + v_2\tau_2 + v_3\tau_3$, where τ_1, τ_2, and τ_3 represent the temperature coefficients of the resonant frequencies of phases 1, 2, and 3, and v_1, v_2, and v_3 are the volume fractions of phases 1, 2, and 3, respectively. However, there is no second major phase except the $ZnTiO_3$ phase, which is consistent with the scenario in Fig. 1. Therefore, the dependences of τ_f on the addition of H_3BO_3 for ZMT ceramics are almost the same. Because $ZnTiO_3$ ($\tau_f = -55$ ppm/ °C) and Zn_2TiO_3 ($\tau_f = -50$ ppm/ °C) have values of τ_f close to each other, the values of τ_f for ZMT ceramics must be negative and around −60 ppm/ °C.

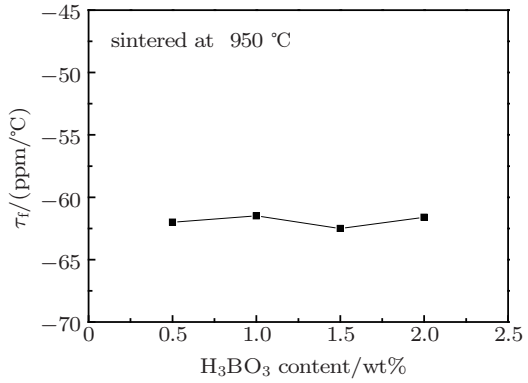


Fig. 6. The temperature coefficients of the resonant frequency of ZMT ceramics with different values of H_3BO_3 content, sintered at 950 °C.

4. Conclusions

In this work, the effects of the addition of H_3BO_3 on the sintering temperature, density, microstructure, and microwave dielectric are investigated. The addition of H_3BO_3 effectively reduces the sintering temperature of ZMT to 950 °C without remarkable deterioration in microwave dielectric properties, which is due to the liquid phase of H_3BO_3. The ZMT ceramic with an addition of 1 wt% H_3BO_3, sintered at 950 °C for 3 h, exhibits excellent dielectric properties: $\varepsilon_r = 19.8$, $Q \times f = 43800$ GHz (8.94 GHz), and $\tau_f = -60$ ppm/°C. The dielectric also shows good compatibility with the Ag electrode, which is a promising candidate material for LTCC application.

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