

Effects of borosilicate glass addition on the structure and dielectric properties of ZnTiO_3 ceramics

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Abstract

ZnTiO_3 powders and borosilicate glass were made by sol–gel method, and then mixed for co-firing at low temperatures. The results show that the borosilicate glass was liquefied to improve the density of the ceramic during sintering. However, $\text{Zn}_4\text{O}(\text{BO}_2)_6$ and TiO_2 were formed if too much borosilicate glass was added (over 10 wt.%). The microwave dielectric properties of the ZnTiO_3 co-fired with borosilicate glass were also improved dramatically. With 5 wt.% borosilicate glass addition, ZnTiO_3 ceramics can be sintered at 850 °C and shows excellent microwave properties: 22.2 for dielectric constant, and 52,460 for $Q \times f$ value at a frequency of 6 GHz.

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1. Introduction

Fundamental studies concerning the phase diagram and the characterization of the $\text{ZnO}-\text{TiO}_2$ system have been published by Dulin and Rase [1] and Bartram and Slepetyts [2] since 1960s. They reported that there are three compounds existing in the $\text{ZnO}-\text{TiO}_2$ binary system including $\alpha\text{-Zn}_2\text{TiO}_4$ (cubic), Zinc titanate (ZnTiO_3 , hexagonal), and $\text{Zn}_2\text{Ti}_3\text{O}_8$ (cubic). ZnTiO_3 is of a perovskite type oxide and could be a potential candidate as microwave resonator [3], gas sensor [4] (for ethanol, NO, CO, etc.), and paint pigment. Yamaguchi et al. [5] clarified that $\text{Zn}_2\text{Ti}_3\text{O}_8$ is a low-temperature form of ZnTiO_3 . Zn_2TiO_4 can be easily prepared by the conventional solid state reaction using 2ZnO and 1TiO₂. In addition, Wang et al. [6,7] also indicated that ZnTiO_3 doped with some transition metal ions could be applied in luminescent purpose. Nevertheless, the preparation of pure ZnTiO_3 from a mixture of 1ZnO and 1TiO₂ has not been successful because the compound decomposes into $\alpha\text{-Zn}_2\text{TiO}_4$ and rutiles at about 945 °C. There are several methods to prepare ZnTiO_3 powder including solid state reaction, sol–gel [8], etc. In this study, it is attempted to synthesize ZnTiO_3 and borosilicate glass powders by sol–gel process, and mixed them for co-firing at low temperatures. The microwave dielectric properties were used as a criterion to evaluate the compatibility of low-temperature co-fired ceramics. The co-firing compatibility of ZnTiO_3 and borosilicate glass was investigated.

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The effects of borosilicate glass on the phase, microstructure, and microwave dielectric properties were also discussed.

2. Experimental procedures

Precursor solutions used to synthesize ZnTiO_3 were prepared by the following procedures. First, $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were weighed according to the stoichiometric ratio of $\text{Zn}/\text{Ti}=1:1$, dissolved with ethanol, stirred, and refluxed for 3 h. Sufficient amount of citric acid then was added to the solution as a chelating agent. The molar ratio of citric acid to the total metal ions was 3:2. In addition, the borosilicate glass was prepared by adding $\text{C}_{12}\text{H}_{27}\text{BO}_3$ and $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ into a dilute HCl –ethanol solution. The precursor solution was dried in an oven at 120°C for 10 h and then calcined at 800°C for 10 h in air to obtain the mixed powders. The ZnTiO_3 powders were mixed with borosilicate glass (at 1, 5, 10, 30 wt.%) and pressed at 200 MPa into discs. The discs were sintered in ambient air at 800 – 900°C for 24 h and the microstructure was examined over the surface onto which gold was deposited. The phases of the samples were determined by X-ray powder diffraction (XRD, Rigaku D/max) with $\text{Cu K}\alpha$ radiation at room temperature. The grain morphology was characterized by scanning electron microscopy (HR-SEM, S4200, Hitachi). The relative densities of the sintered ZnTiO_3 ceramics with different amount of borosilicate glass were measured using Archimedes method in de-ionized water. The microwave dielectric properties were measured using Network analyzer (HP-8757) and Sweep Oscillator (HP-8350).

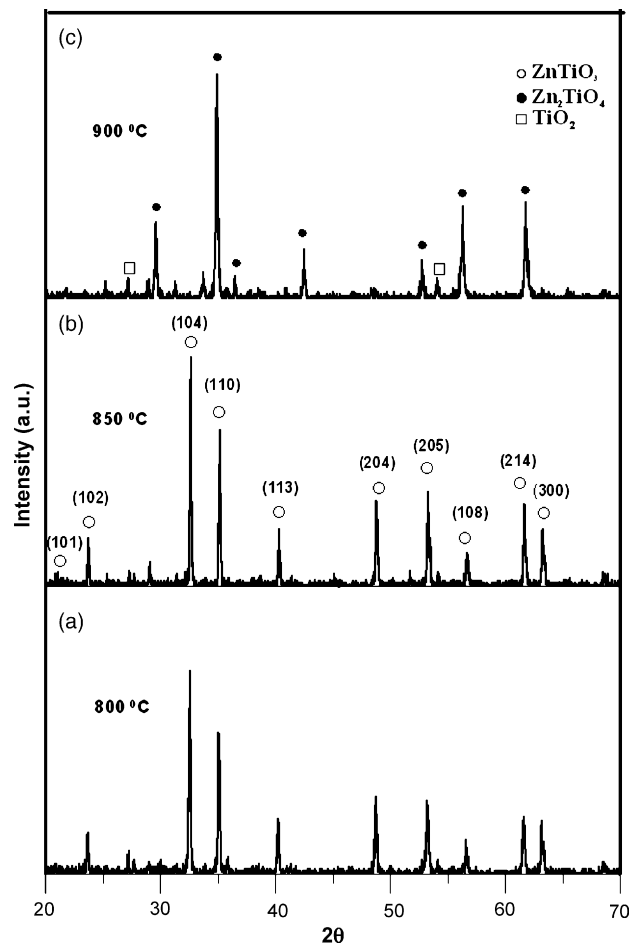


Fig. 1. XRD profiles of ZnTiO_3 with borosilicate glass 5 wt.% sintered at: (a) 800°C , (b) 850°C , and (c) 900°C for 24 h in air.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the XRD patterns of the ZnTiO_3 with 5 wt.% borosilicate glass sintered at 800, 850, and 900 °C for 24 h, respectively. It can be seen that the peaks of crystalline phase appeared at 800 °C. It was identified as hexagonal ZnTiO_3 phase, which is a low-temperature form in ZnO-TiO_2 binary system, as reported by Chang et al. [8]. It should be noted that when the temperature was further increased to 900 °C, besides the hexagonal form of ilmenite ZnTiO_3 , other compounds such as Zn_2TiO_4 and TiO_2 were also observed. This result indicated that the transformation of hexagonal ZnTiO_3 phase to cubic Zn_2TiO_4 and TiO_2 was possible. This may be caused by the reduction of zinc oxide to volatile element zinc creating a deficiency of zinc in ZnTiO_3 , which thus becomes sub-stoichiometric and decomposed.

Fig. 2 is the XRD patterns of ZnTiO_3 ceramics with different concentration of borosilicate glass addition. The main phase of ZnTiO_3 was maintained, as borosilicate glass content was less than 10 wt.%. However, the peak intensity of ZnTiO_3 decreased as the borosilicate glass was increased. Obviously, it is due to the substitution of amorphous glasses for crystalline phase. When the addition reached to 10 wt.%, traces of $\text{Zn}_4\text{O}(\text{BO}_2)_6$ and TiO_2 phases appeared.

The SEM photographs of the as-fired ZnTiO_3 ceramics doped with 0–30 wt.% borosilicate glass sintered at 850 °C for 24 h are shown in Fig. 3. In Fig. 3a, it is shown that the particles seem to coalesce together, and the surface porosity decreases when borosilicate glass ($x = 1, 5, 10$ wt.%) was added. The sphere-like particles seem to be able to distribute in the matrix homogeneously. It is believed that the lower melting point of the borosilicate glass promotes liquid phase sintering and results in higher density. The abnormal grain growth occurred as the dopant, borosilicate glass, increasing to $x = 30$ wt.%. It is quite possible that large amount of $\text{Zn}_4\text{O}(\text{BO}_2)_6$ phase was precipitated in the ZnTiO_3 matrix. This created large polygonal particles and decreased the bulk density as shown in Fig. 3e.

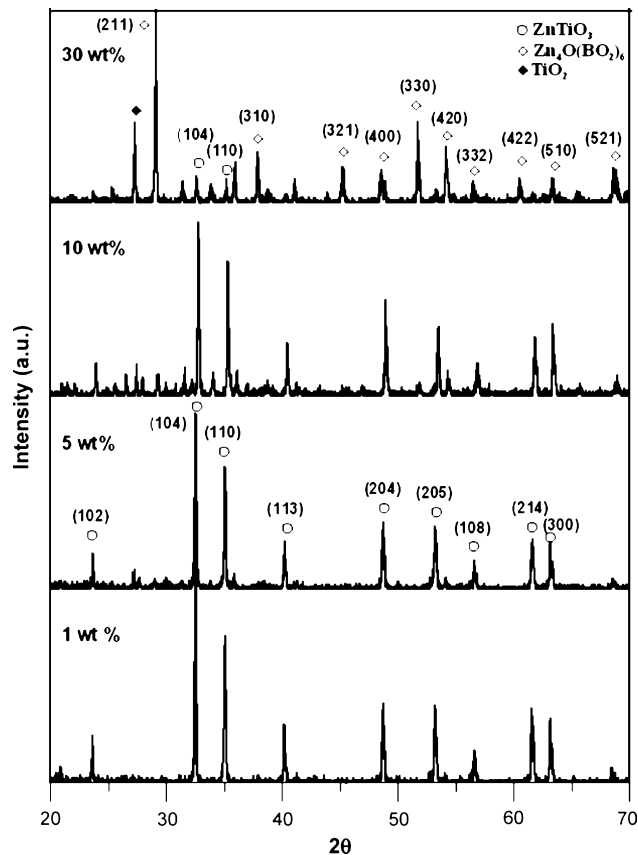


Fig. 2. XRD profiles of ZnTiO_3 with different borosilicate glass content sintered at 850 °C for 24 h in air.

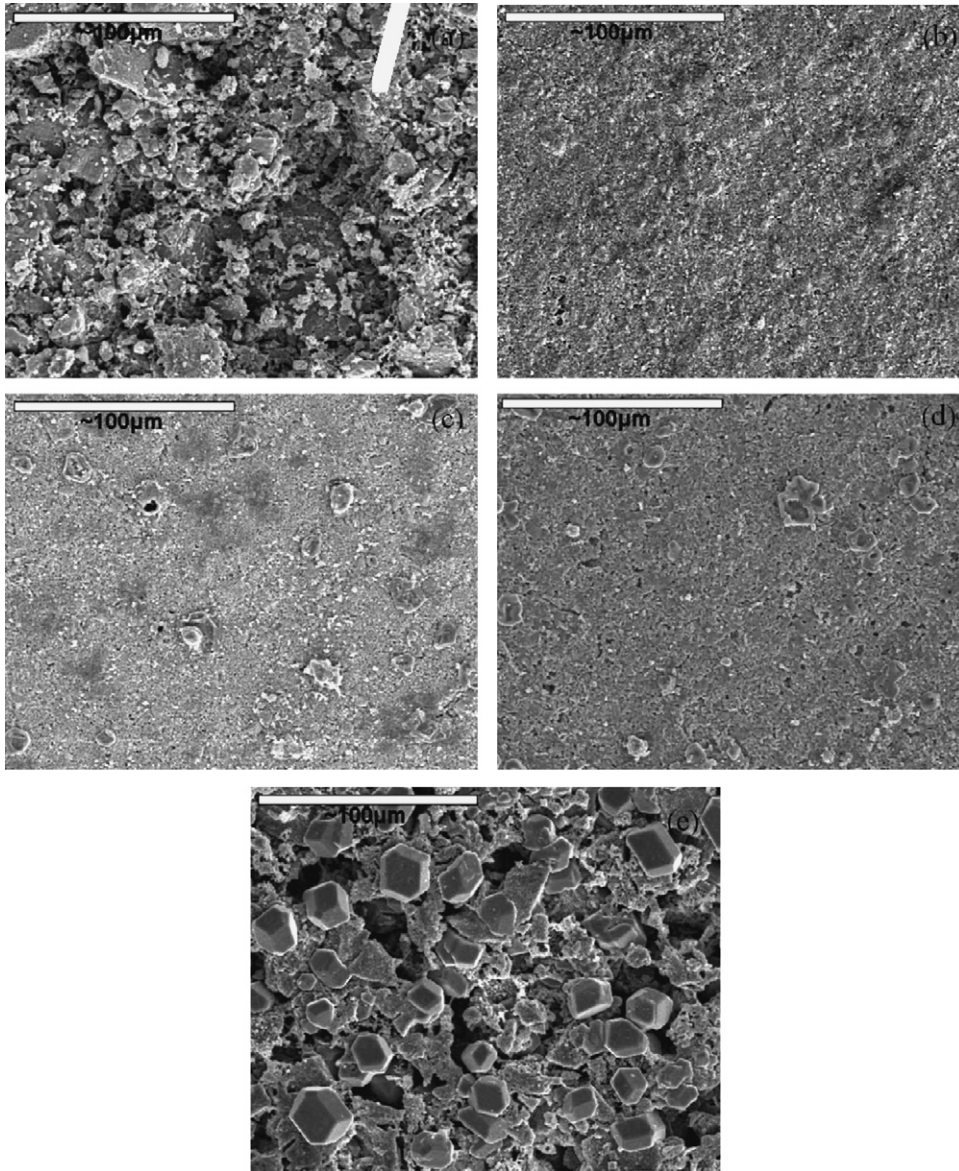


Fig. 3. SEM photographs of the as-fired ZnTiO_3 ceramics with different borosilicate glass contents: (a) 0, (b) 1, (c) 5, (d) 10 and (e) 30 wt.% sintered at 850°C for 24 h.

It is well known that the existence of pores will affect the microstructure and dielectric properties of materials. The porosity and density of ZnTiO_3 doped with various amount of borosilicate glass and sintered at 850°C are shown in Fig. 4a and the effects of sintering temperature on the porosity and density of samples with 1 wt.% borosilicate glass is shown in Fig. 4b. The results show that the liquid phase sintering for doping borosilicate glass could be the reason of improving the densification during sintering. As the content of the borosilicate glass increased to 10 wt.%, a maximum density of about 4.1 g/cm^3 was obtained, and the porosity was 1.2%. However, $\text{Zn}_4\text{O}(\text{BO}_2)_6$ could be formed if too much borosilicate glass was added, and the formation of large $\text{Zn}_4\text{O}(\text{BO}_2)_6$ grains may weaken the mechanical strength.

The microwave dielectric properties of ceramics with glass are related to the sintered density and the presence of secondary phase [9,10]. Generally, excess addition of glass to a ceramic lowers the sintering temperature and significantly deteriorates the microwave dielectric properties [10,11]. This is due to the decomposed glass remaining

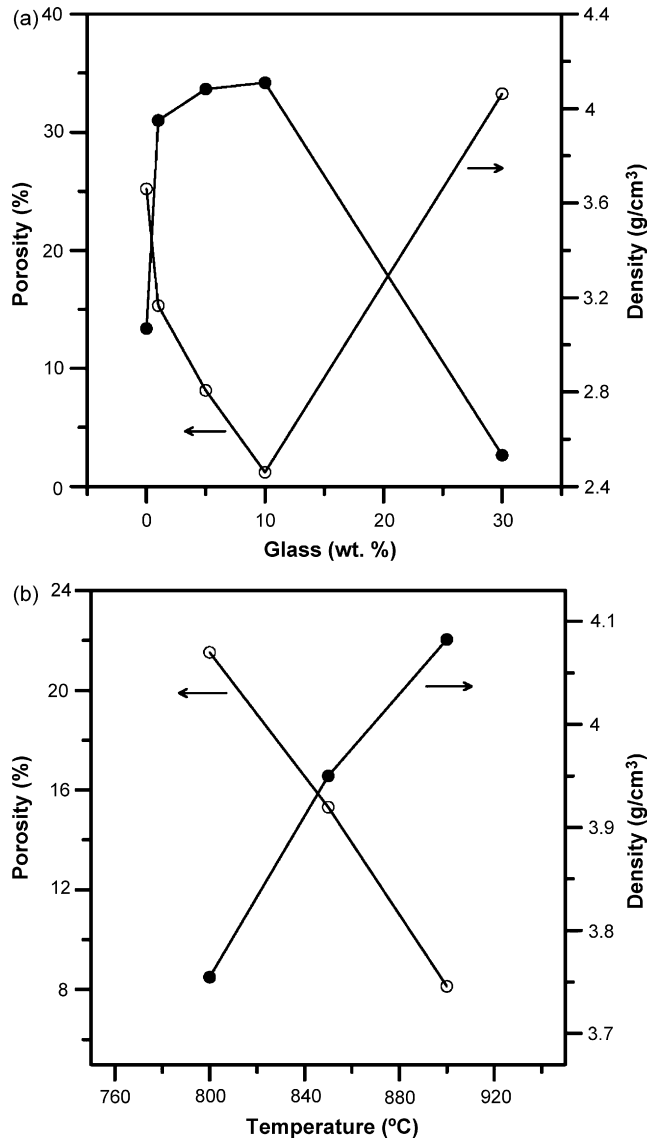


Fig. 4. Porosity and density of: (a) ZnTiO₃ ceramics with different borosilicate glass content sintered at 850 °C for 24 h; (b) ZnTiO₃ ceramics with borosilicate glass 1 wt.% sintered at different temperature for 24 h.

in the host material, or the formation of glass based secondary phases from chemical reactions between glass and matrix. However, it is noted that proper amount of glass addition increases the density and microwave dielectric properties of the host material [12], because the liquid phase enables better pore elimination by enhancing the material transport.

3.2. Dielectric properties

The dielectric constants of the borosilicate glass-added ZnTiO₃ ceramics are plotted as a function of weight percentages and sintering temperatures, as shown in Fig. 5. The relationship between the dielectric constants and sintering temperature shows similar trend as that between the density and sintering temperature since higher density represents lower porosity. The decrease in the dielectric constant of specimens with increasing borosilicate glass probably is due to the lower density as well as excess liquid phase. However, the dielectric constant increased from

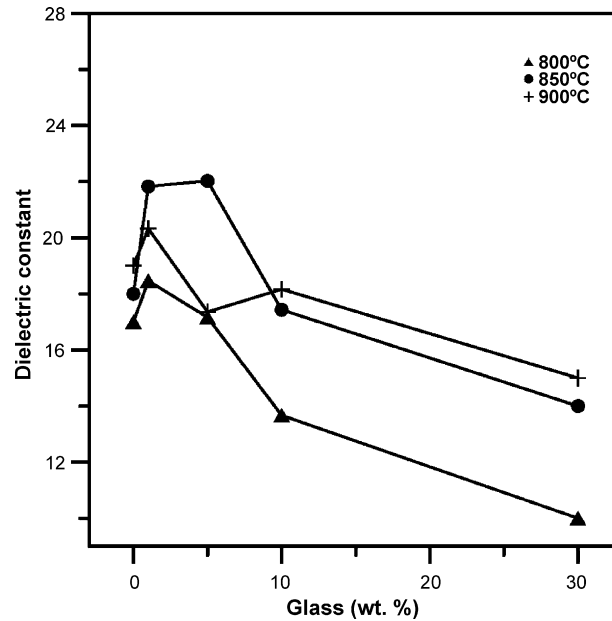


Fig. 5. The dielectric constant (measured at 6 GHz) of specimens with different contents of borosilicate glass in ZnTiO₃ ceramics sintered at different temperatures for 24 h.

18.1 to 22.2 at 6 GHz as the sintering temperature increased from 800 to 850 °C since appropriate amount of liquid phase would benefit the densification of the ceramics.

A plot of the $Q \times f$ values of the borosilicate glass-added ZnTiO₃ ceramics versus glass weight percentage and sintering temperature are illustrated in Fig. 6. The microwave dielectric loss was caused not only by the lattice vibration but also by the densification and the porosity. Relative density is also an important control factor for the

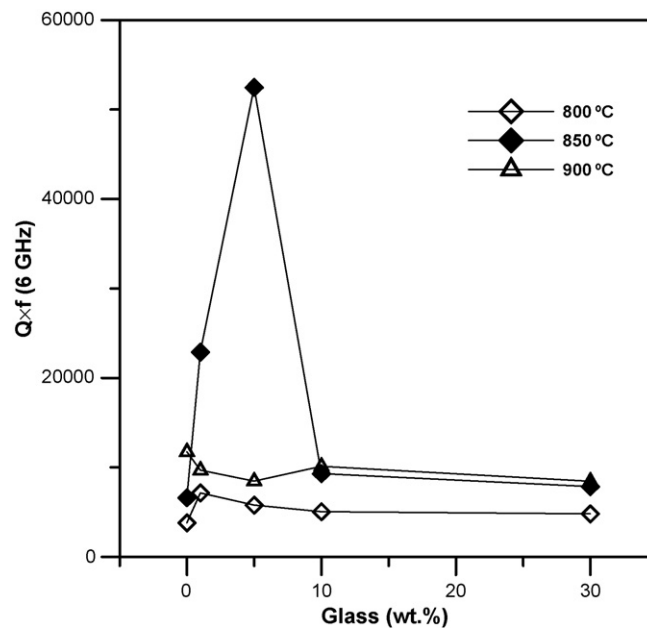


Fig. 6. $Q \times f$ constants (at 6 GHz) were showed with different content of borosilicate glass in ZnTiO₃ ceramics sintered at different temperatures for 24 h.

dielectric loss and has been found in other microwave dielectric materials. Variation of the $Q \times f$ values of the borosilicate glass-added ZnTiO₃ ceramics was similar to that of the apparent density. It is suggested that the density may dominate the dielectric loss of the samples. However, there is one exception, the specimen with 5 wt.% borosilicate glass addition, sintered at 850 °C possessed a maximum $Q \times f$ value of 52,460 at a frequency of 6 GHz. As observed in Figs. 3 and 5, for high borosilicate glass content, rapid grain growth might cause the increased dielectric loss resulting in a degradation of its $Q \times f$ value.

4. Conclusions

The microwave dielectric properties and the microstructures of the borosilicate glass-added ZnTiO₃ ceramics were investigated. The liquid phase was found to be the major factor in controlling the densification and the dielectric loss of the specimen. Appropriate amount of liquid phase not only can lower the sintering temperature but also possess compatible microwave dielectric properties of the ZnTiO₃ ceramics. With 5 wt.% borosilicate glass addition, ZnTiO₃ ceramics can be lowered the sintering temperature to 850 °C and shows excellent microwave dielectric properties: 22.2 for dielectric constant, and 52,460 for $Q \times f$ value at a frequency of 6 GHz.

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