

Microwave dielectric properties of glass-Bi₂Ti₂O₇ ceramic composites

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The microwave dielectric properties of glass-Bi₂Ti₂O₇ ceramic composites were investigated. Using bismuth-zinc borosilicate (BZBS) glass and TiO₂, glass-Bi₂Ti₂O₇ composites were prepared by liquid phase sintering. The linear shrinkage exhibited a two-stage sintering behavior; viscous flow of the liquid phase and then crystallization. The crystalline phases of Bi₂Ti₄O₁₁ and Bi₂Ti₂O₇ were observed at 700 and 900°C, respectively. The dielectric constant (ϵ_r) and the quality factor ($Q \times f_0$) were affected by the formation of crystalline phases as well as the density. For the specimen sintered at 900°C, the dielectric constant, the quality factor and the temperature coefficient of the resonant frequency (τ_f) was respectively 56.4, 518 GHz (105 at 4.898 GHz), and +119 ppm/K.

Key words: LTCC, Glass-ceramic, TiO₂, Bismuth-zinc borosilicate, Bi₂Ti₂O₇.

Introduction

A number of studies of low temperature co-fired ceramics (LTCC) have been intensively investigated. There are two basic methods to prepare LTCC [1, 2]. The first is to use crystallizable glasses as starting materials which undergo devitrification to crystalline phases during the firing process. Ideally no glass phases, hence, exist in the final microstructure. The properties of crystallizable glasses depend on the degree of crystallization, i.e., the thermal history. Cordierite-based glass, showing a low dielectric constant and good mechanical properties including strength and thermal expansion coefficient (TEC), is a material typical of crystallizable glasses [3]. The second method is to use a mixture of low melting temperature glasses working as a flux agent and ceramics. The final structure is composed of ceramic particles in a glass matrix, i.e. glass-ceramics. Generally, borosilicate glasses are used as flux materials due to their capability of glass formation at low temperature and good dielectric properties [4].

Bi₂Ti₂O₇ with a cubic pyrochlore structure is one of the compounds in the Bi₂O₃-TiO₂ system and a candidate material for LTCC due to a high dielectric constant ($\epsilon_r=118$) [5]. In this study, the glass-Bi₂Ti₂O₇ ceramic system was prepared using bismuth-zinc borosilicate glass and TiO₂ and its microwave dielectric properties were investigated.

Experimental Procedure

Powders of Bi₂O₃, ZnO, B₂O₃, SiO₂, and Na₂O of extra-pure reagent grade were weighed in the weight percentage of 65, 19, and 10, 5, 1 respectively, and well mixed in a dry condition. Bismuth-zinc borosilicate (BZBS) glass was prepared by a quenching method after a melting process above 1100°C using an alumina crucible. By disk milling and ball milling using zirconia balls in a wet condition with ethanol, a glass frit was obtained. The deformation temperature of the BZBS glass was measured by a dilatometer (DIL 402, Netzsch). 50 vol% BZBS glass frit and TiO₂ was ball milled for 24 h and then dried. The disk type samples a 15 mm in diameter were prepared by pressing the powder mixtures under ca. 14 MPa and a sintering at between 600~950°C for 2 h. The phase analysis of the sintered samples was carried out by an X-ray diffractometer (MO3XHF, Mac science) using a Cu-K α target and a Ni filter within the 2 θ range between 10~80. The microstructures were observed by a FE-SEM (S-4200, Hitachi). The dielectric constant (ϵ_r) and the temperature coefficient of the resonant frequency ($Q \times f_0$) were measured by the Hakki-Coleman method using a network analyzer (HP8720ES) and samples which were placed between two parallel metal plates; the resonant frequency f_0 , the half power bandwidth Δf_{3dB} , which was recorded at the 3dB level of the resonant peak, and the insertion loss were measured [6]. The temperature coefficient of the resonant frequency (τ_f) was measured using an Invar cavity in the temperature range 25~85°C.

Results and Discussion

The deformation temperature of the BZBS glass, i.e.,

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the temperature at the maximum value of the thermal expansion curve, was determined as 442°C which was lower than that of the quaternary glass with a composition of 25Bi₂O₃-45ZnO-10B₂O₃-20SiO₂ in mol% (494°C) [7] and higher than those of the Bi₂O₃·ZnO·10B₂O₃·R₂O (R=alkali) quaternary glasses (from 272 to 339°C) [8]. The dielectric constant (ϵ_r), the quality factor ($Q \times f_0$), and the temperature coefficient of the resonant frequency (τ_f) of the BZBS glass were 15.6, 1 526 GHz (149 at 10.239 GHz), and -40 ppm/K, respectively.

Powder X-ray diffraction patterns of 50 vol% BZBS glass-TiO₂ composite sintered between 700 and 900°C are shown in Fig. 1. Besides TiO₂, the crystalline phases of Bi₂Ti₄O₁₁ with a monoclinic structure and Bi₂Ti₂O₇ with a cubic were formed, implying that BZBS is a reactive glass in this system. As the sintering temperature increased, the crystalline phase changed from Bi₂Ti₄O₁₁ to Bi₂Ti₂O₇; Bi₂Ti₄O₁₁ completely disappeared and only Bi₂Ti₂O₇ was formed at 900°C. For the formation of Bi₂Ti₂O₇ with a pyrochlore structure, i.e., A₂B₂O₇, there have been contradictory results. It was reported that Bi₂Ti₂O₇ did not exist in the phase diagram of the Bi₂O₃-TiO₂ system [9], and this result has been supported by other studies that only three compounds of Bi₄Ti₃O₁₂, Bi₂Ti₄O₁₁, and Bi₁₂TiO₂₀ existed in the system [10, 11]. The large difference of the ionic radius between Bi³⁺ and Ti⁴⁺ was suggested as the reason for the instability of Bi₂Ti₂O₇ [12]. It has been suggested that the structural stability of pyrochlores was generally

governed by the radius ratio of A and B cations.

On the other hand, there have been some research concerning the existence of Bi₂Ti₂O₇ [13-15]. By an investigation of the heat-treatment of Bi₂O₃·2TiO₂ above 1100, the formation of a pyrochlore structure as a minor phase having the lattice parameter of 1.0354 nm besides the compounds of Bi₂Ti₄O₁₁ and Bi₄Ti₃O₁₂ was reported [13]. It was also reported that Bi₂Ti₂O₇ could be synthesized by wet chemical methods at low temperatures or crystal growing methods using a flux [14, 15]. Shimada et al. stated that Bi₂Ti₂O₇ was prepared using bismuth titanates with Bi₂O₃-V₂O₅ fluxes [14]; this compound could only be crystallized when small amounts of ZnO were added to melts and it was later shown to be Bi_{1.61}Zn_{0.18}Ti_{1.94}V_{0.06}O_{6.62} with a cubic lattice parameter of 1.0327(1) nm by a reinvestigation [15]. The decrease of the radius ratio of A and B cations by the substitution of Zn with a small ionic radius ($r_{Zn} = 0.09$ nm, C.N = 8) on A-site i.e., Bi-one ($r_{Bi} = 0.117$ nm), caused the increase of the structural stability. It was, therefore, understandable that zinc in BZBS glass might also contribute to the crystallization of Bi₂Ti₂O₇ above 800°C. This suggestion was supported by the result that the lattice parameter of Bi₂Ti₂O₇ in this study was calculated as 1.0334(2) nm using an extrapolation method, which is similar with that of the zinc-substituted compound as mentioned above (1.0327 nm) and smaller than those of the compound without zinc (1.0354-1.0379 nm) [12, 13].

The linear shrinkage of 50 vol% BZBS glass-TiO₂ composite sintered between 700 and 900°C are shown in Fig. 2. A shrinkage of about 10% already appeared at 600°C. A plateau subsequently emerged up to 750°C and then a further shrinkage occurred above 800°C, indicating that the shrinkage behavior exhibited a two-stage sintering. The low deformation point for BZBS

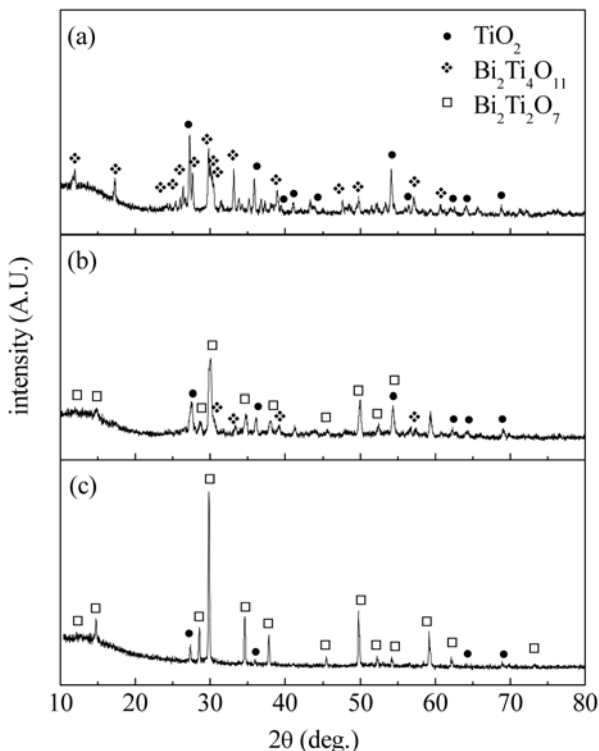


Fig. 1. Powder XRD patterns of 50 vol% BZBS glass-TiO₂ composite sintered at (a) 700°C, (b) 800°C, and (c) 900°C.

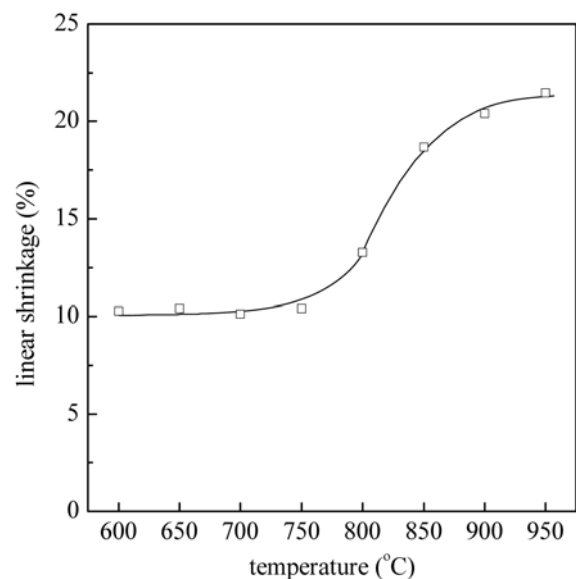


Fig. 2. Linear shrinkage of 50 vol% BZBS glass-TiO₂ composite as a function of sintering temperature.

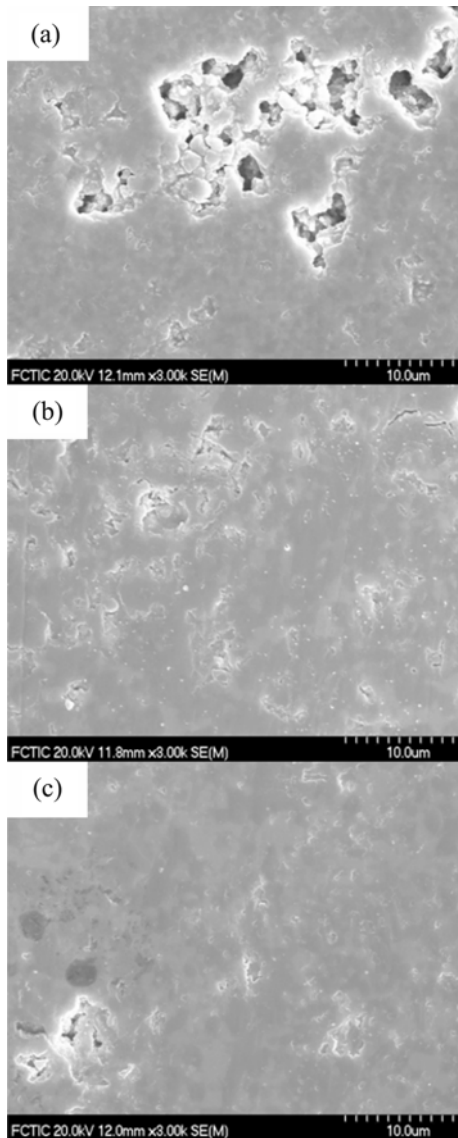


Fig. 3. Microstructures of 50 vol% BZBS glass-TiO₂ composite sintered at (a) 700°C, (b) 800°C, and (c) 900°C.

(442°C) may cause the large shrinkage below 600°C, i.e., the first-stage sintering to which the particle rearrangement caused by the viscous flow of the liquid phase might mainly contribute. It has been reported that the classical theory of liquid phase sintering assumed densification occurred; particle rearrangement, solution-precipitation, and solid state sintering [16]. In the process of particle rearrangement, densification occurred rapidly as soon as the liquid phase was formed. Pores were filled through liquid phase redistribution, and the particles were rearranged due to capillary pressure, resulting in a closer packing. Above 800°C, the crystallization of Bi₂Ti₂O₇ may contribute to the second-stage shrinkage. Figure 3 shows the microstructures of 50 vol% BZBS glass-TiO₂ system sintered between 700 and 900°C; the densification was promoted with an increase of the sintering temperature.

The dielectric constant (ϵ_r) and the quality factor

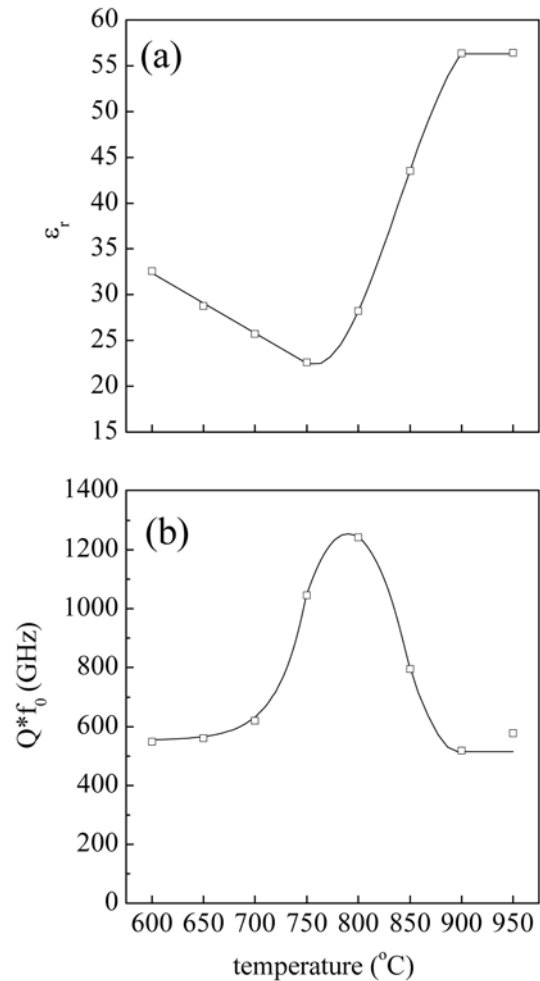


Fig. 4. (a) Dielectric constant (ϵ_r) and (b) quality factor ($Q \times f_0$) of 50 vol% BZBS glass-TiO₂ composite as a function of sintering temperature.

($Q \times f_0$) of 50 vol% BZBS glass-TiO₂ composite as a function of the sintering temperature are shown in Fig. 4. With an increase of the sintering temperature, ϵ_r decreased up to a minimum point at 750°C although the density increased. This result could be interpreted by the formation of the crystalline phases as mentioned above. The decrease of ϵ_r in the low temperature region might be related to the consumption of TiO₂ with a high value of 105 by the formation of Bi₂Ti₄O₁₁ having a relatively low ϵ_r (~53) [17]. Above 800°C, ϵ_r increased after the minimum point with an increase of the sintering temperature and the formation of Bi₂Ti₂O₇ with the extinction of Bi₂Ti₄O₁₁ might contribute to the increase because Bi₂Ti₂O₇ had a relatively high value of ~118 [5]. The quality factor ($Q \times f_0$) was about 500 ~1000 GHz and it exhibited an increase up to a maximum point at 800°C and then a decrease with an increase of the sintering temperature. The increase of the quality factor above 700°C might be related to the increase of the density as shown in Fig. 2. However, the reason for the decrease after the maximum point at 800°C was uncertain but the formation of Bi₂Ti₂O₇

might be correlated to the cause of the decrease because the value of $Q \times f_0$ was independent of the density or the porosity for a theoretical density >90% [18]. For a material having a high quality factor and a low dielectric loss, it is necessary to reduce the attenuation constant. It is known that the anharmonicity in the lattice vibration affects the attenuation constant for perfect crystals whereas dislocations, pores, defects, grain boundaries, and secondary phases have an influence on the attenuation constant for polycrystals [18]. When the specimen was sintered at 900°C, ϵ_r , $Q \times f_0$ and the temperature coefficient of resonant frequency (τ_f) was 56.4, 518 GHz (105 at 4.898 GHz), and +119 ppm/K, respectively; an improvement of $Q \times f_0$ and τ_f in this system is necessary for the application to the LTCC materials.

Summary

Glass-Bi₂Ti₂O₇ ceramic composites were prepared by liquid phase sintering using TiO₂ and bismuth-zinc borosilicate (BZBS) glass having a deformation temperature of 442°C. The crystalline phases of Bi₂Ti₄O₁₁ with a monoclinic structure and Bi₂Ti₂O₇ with a cubic pyrochlore structure were observed at 700 and 900°C, respectively. A linear shrinkage of about 10% existed even at low temperatures between 600 and 750°C and then a further shrinkage occurred above 800°C, indicating that the shrinkage behavior could be interpreted by a two-stage sintering process. The dielectric constant and the quality factor were affected by the formation of crystalline phases such as Bi₂Ti₄O₁₁ and Bi₂Ti₂O₇ as well as the density. For the specimen sintered at 900°C, ϵ_r , $Q \times f_0$ and the temperature coefficient of the resonant frequency (τ_f) were respectively 56.4, 518 GHz (105 at 4.898 GHz), and +119 ppm/K.

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