

Microwave dielectric properties of ceramic/glass composites with bismuth-zinc borosilicate glass

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The microwave dielectric properties of ceramic/bismuth zinc borosilicate (BZBS) glass composites were investigated. The crystalline phases of ZnAl_2O_4 with a spinel structure in the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite and $\text{Bi}_2\text{Ti}_2\text{O}_7$ with a cubic pyrochlore structure in the TiO_2/BZBS glass composite were observed, indicating that BZBS glass was a reactive glass in these systems. A one-stage sintering occurred in the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite whereas a two-stage one might occur in the TiO_2/BZBS glass composite. The dielectric constant (ϵ_r) of the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite exhibited almost the same value of about 10 within the sintering temperature range between 600-950 °C, implying that the application of the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite to substrates may therefore be shown to be appropriate. For the TiO_2/BZBS glass composite, however, an improvement of the temperature coefficient of the resonant frequency ($\tau_f = +119$ ppm/K) is necessary for the application as LTCC materials although the dielectric constant of this system had a proper value (~ 56) for an application to filters.

Key words: LTCC, Ceramic/glass, Al_2O_3 , TiO_2 , Bismuth-zinc borosilicate glass.

Introduction

A number of studies of low temperature co-fired ceramics (LTCC) have been made intensively. 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 glasses, showing a low dielectric constant and good mechanical properties including strength and thermal expansion coefficient (TEC), is a typical example of crystallizable glasses [3]. The second method is to use a mixture of low melting temperature glasses working as a fluxing agent and ceramics as a filler. The final structure is composed of ceramic particles in a glass matrix, i.e. a glass-ceramic [4]. Generally, borosilicate glasses are used as flux materials due to their capability of glass formation at low temperature and good dielectric properties.

TiO_2 has been extensively studied in electronic applications because it shows a high dielectric constant ($\epsilon_r = 105$) and a high quality factor ($Q \times f_0 > 40,000$ GHz) [5]. On the other hand, to diminish the signal propagation delay, LTCC materials for substrates are required to have a low dielectric constant [6]. Al_2O_3 is known as one of the

typical materials having a low dielectric constant (9~10) [7]. The aim of this study is to investigate the microwave dielectric properties of ceramic/bismuth zinc borosilicate (BZBS) glass composites using Al_2O_3 and TiO_2 as fillers.

Experimental Procedure

Powders of Bi_2O_3 , ZnO , B_2O_3 , SiO_2 , and Na_2O of extra-pure reagent grade were respectively weighed in the weight percentages of 65, 19, 10, 5, and 1 (in mol%; 22.7, 37.9, 23.3, 13.5, and 2.6, respectively) and well mixed in a dry condition. Bismuth zinc borosilicate glass (hereafter 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 with zirconia balls in a wet condition, a glass frit was obtained. 50 vol% BZBS glass frit and ceramic powers of Al_2O_3 or TiO_2 (rutile structure with a small amount of anatase) were ball milled for 24 h and then dried. Disk-type samples 15 mm in diameter were prepared by pressing powder mixtures under ca. 50 MPa and sintering at between 600 and 950 °C for 2 h.

The softening temperature of BZBS glass was measured by a dilatometer (DIL 402, Netzsch), and the density based on Archimedes' method was measured. The phase analysis of the sintered glass-ceramics was carried out by an X-ray diffractometer (MO3XHF, Mac science) using a $\text{Cu-K}\alpha$ target and a Ni filter within a 2theta range of between 10 and 80 degrees. The microstructures were observed by a FE-SEM (S-4200, Hitachi). Using a network analyzer (HP 8720ES), the dielectric constant (ϵ_r) and

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the quality factor ($Q \times f_0$) were measured by the Hakki-Coleman method with disk-type samples which were placed between two parallel metal plates; the resonant frequency f_0 , the half power bandwidth $\Delta f_{3\text{dB}}$, which was recorded at the 3 dB level of the resonant peak, and the insertion loss were measured [8]. The temperature coefficient of the resonant frequency (τ_f) was measured using a Invar cavity in the temperature range of 25–85 °C.

Results and Discussion

The deformation point of BZBS glass, i.e., the temperature at the maximum peak of the thermal expansion curve, was determined as 442 °C which was lower than that of a quaternary glass with the composition (in mol%) of 25Bi₂O₃–45ZnO–10B₂O₃–20SiO₂ (494 °C) [9] and higher than those of the Bi₂O₃·ZnO·10B₂O₃·R₂O (R = alkali) quaternary glasses (from 272 to 339 °C) [10]. The dielectric constant, the quality factor, and the temperature coefficient of the resonant frequency of the BZBS glass were 15.63, 149 at 10.239 GHz, and –40 ppm/K, respectively.

X-ray powder diffraction patterns of a Al₂O₃/50 vol% BZBS glass composite sintered between 700 and 900 °C are shown in Fig. 1. ZnAl₂O₄ with a spinel structure and unreacted Al₂O₃ were observed as crystalline phases. From the result that the diffracted patterns showed similar peak-intensities within the sintering temperature range, it is suggested that ZnAl₂O₄ crystallized below 700 °C. The formation of ZnAl₂O₄ was also observed by other authors in Al₂O₃/zinc borosilicate glass composites [11], suggesting that ZnAl₂O₄ was easily formed when glasses containing zinc were reacted with Al₂O₃.

Fig. 2 shows X-ray powder diffraction patterns of a TiO₂/50 vol% BZBS glass composite. Besides unreacted TiO₂, the crystalline phases of Bi₂Ti₄O₁₁ with a monoclinic structure and Bi₂Ti₂O₇ with a cubic pyrochlore structure were found, implying that BZBS glass is a reactive glass in this composite. As the sintering temperature increased, the crystalline phase changed from Bi₂Ti₄O₁₁ to Bi₂Ti₂O₇,

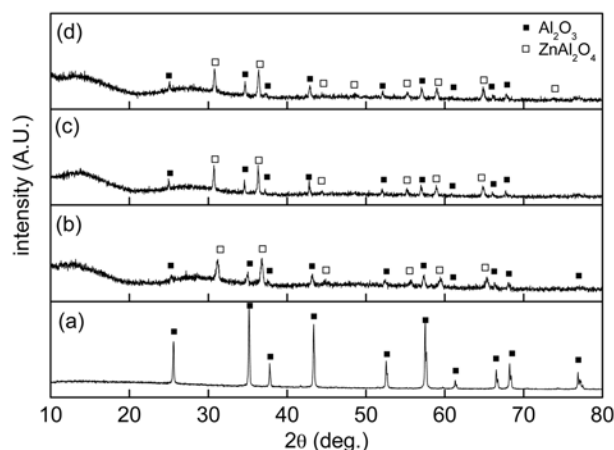


Fig. 1. XRD patterns powder of (a) Al₂O₃ and Al₂O₃/50 vol% BZBS glass composite sintered at (b) 700 °C, (c) 800 °C, and (d) 900 °C.

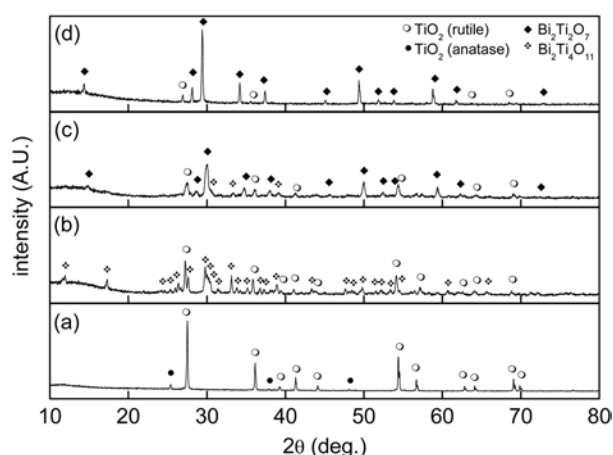


Fig. 2. XRD patterns powder of (a) TiO₂ and TiO₂/50 vol% BZBS glass composite sintered at (b) 700 °C, (c) 800 °C, and (d) 900 °C.

i.e., Bi₂Ti₄O₁₁ disappeared and Bi₂Ti₂O₇ was only observed at 900 °C. For the formation of Bi₂Ti₂O₇ with a pyrochlore structure, i.e., A₂B₂O₇, there have been contradictory results. It has been reported that Bi₂Ti₂O₇ did not exist in the phase diagram of the Bi₂O₃–TiO₂ system [12]. And this result has supported by other studies that only three compounds of Bi₄Ti₃O₁₂, Bi₂Ti₄O₁₁, and Bi₁₂Ti₂₀O₂₀ existed in the system [13, 14]. The large difference of the ionic radius between Bi³⁺ and Ti⁴⁺ was suggested as the reason for the instability of Bi₂Ti₂O₇ [15]. 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 researches concerning the existence of Bi₂Ti₂O₇. By an investigation of the heat-treatment of Bi₂O₃·2TiO₂ above 1100 °C, the formation of a pyrochlore structure as a minor phase having a lattice parameter of 1.0354 nm besides the compounds of Bi₂Ti₄O₁₁ and Bi₄Ti₃O₁₂ was reported [16]. Also it was reported that Bi₂Ti₂O₇ could be synthesized by wet chemical methods at low temperatures or crystal growing methods using a flux [17, 18]. The preparation of Bi₂Ti₂O₇ was reported by Shimada *et al.* using bismuth titanates with Bi₂O₃–V₂O₅ fluxes [17]; 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 nm by a reinvestigation [18]. The decrease of the radius ratio of A and B cations by the substitution of Zn with a small ionic radius ($r_{\text{Zn}} = 0.09$ nm, C.N = 8) on Bi-sites ($r_{\text{Bi}} = 0.117$ nm) might result in the increase of the structural stability. It is suggested that zinc in BZBS glass might also contribute to the crystallization of Bi₂Ti₂O₇ above 800 °C. This suggestion is supported by the result that the lattice parameter of Bi₂Ti₂O₇ in this study was calculated as 1.0334 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 which did not contain zinc (1.0354–1.0379 nm) [15, 16].

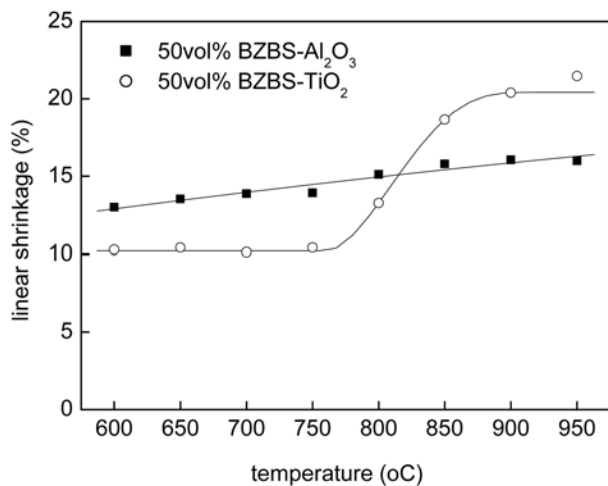


Fig. 3. Linear shrinkage of (Al₂O₃, TiO₂)/50 vol% BZBS glass composites as a function of the sintering temperature.

The linear shrinkage of glass-ceramics against the sintering temperature is shown in Fig. 3. For the Al₂O₃/BZBS glass composite, only a plateau behavior was observed above 600 °C, suggesting that there was a one-stage sintering and the densification might be finished below 600 °C. For the TiO₂ system, a shrinkage of about 10% appeared between 600 and 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 glass (442 °C) may cause the large shrinkage at low temperatures, i.e., the first-stage sintering to which the particle rearrangement caused by the viscous flow of the liquid phase might mainly contribute. Above 800 °C, the crystallization of Bi₂Ti₂O₇ may contribute to the second-stage shrinkage. It has been reported that the classical theory of liquid phase sintering assumed densification occurred; particle rearrangement, solution-precipitation, and solid state sintering [19]. 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. Fig. 4 and 5 respectively shows the microstructures of the (Al₂O₃, TiO₂)/BZBS glass composites as a function of the sintering temperature. For the Al₂O₃/BZBS glass composite, the densification was completed already at 700 °C, which is in accord with the result of the linear shrinkage as mentioned above. For the TiO₂/BZBS glass composite, the densification was promoted with an increase of the sintering temperature.

The variation of the dielectric constant for the both systems is shown in Fig. 6. The dielectric constant of the Al₂O₃/BZBS glass composite exhibited values of about 10. This result is reasonable because the dielectric constants of the crystalline phases composed such as ZnAl₂O₄ and Al₂O₃ are about 9. It could be, therefore, concluded that the application of the Al₂O₃/BZBS glass composite to substrates may be shown to be appropriate.

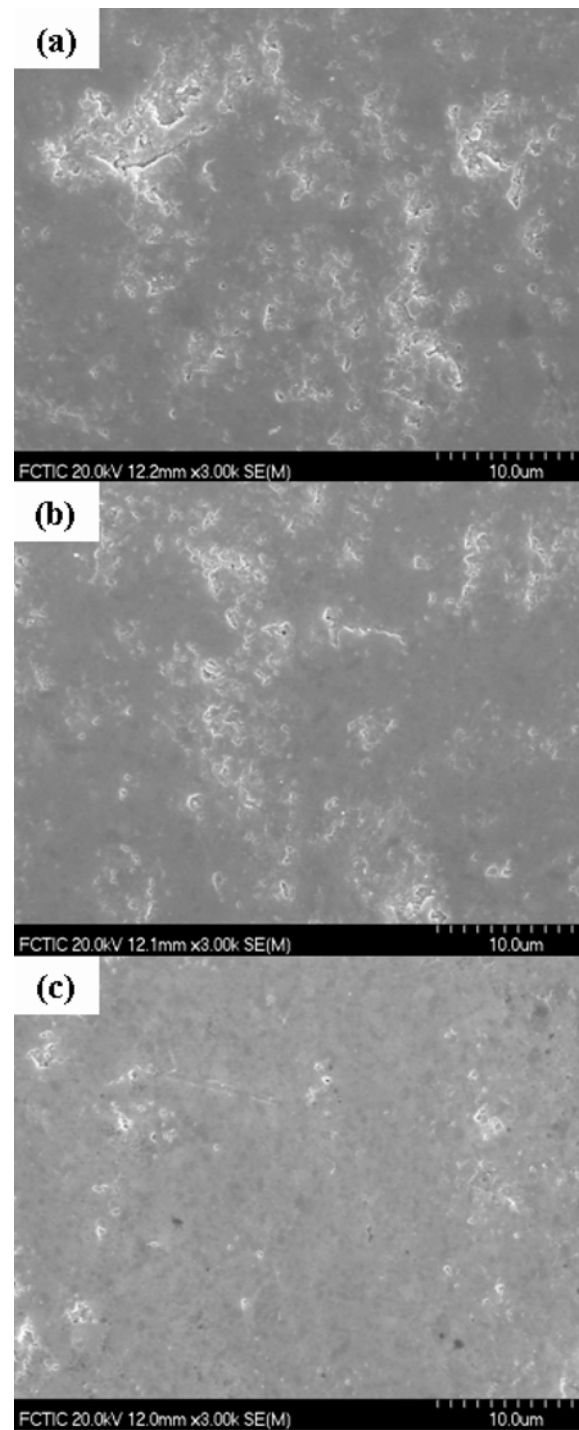


Fig. 4. Microstructures of Al₂O₃/50 vol% BZBS glass composite sintered at (a) 700 °C, (b) 800 °C, and (c) 900 °C.

For the TiO₂/BZBS glass composite, a decrease up to a minimum point at 750 °C and then an increase of the dielectric constant were observed with an increase of the sintering temperature. This result was correlated with the formation of the crystalline phases as detected in Fig. 1. The decrease of the dielectric constant at low temperatures might be related to the consumption of TiO₂ ($\epsilon_r = 105$) and the formation of Bi₂Ti₄O₁₁ having a relatively low

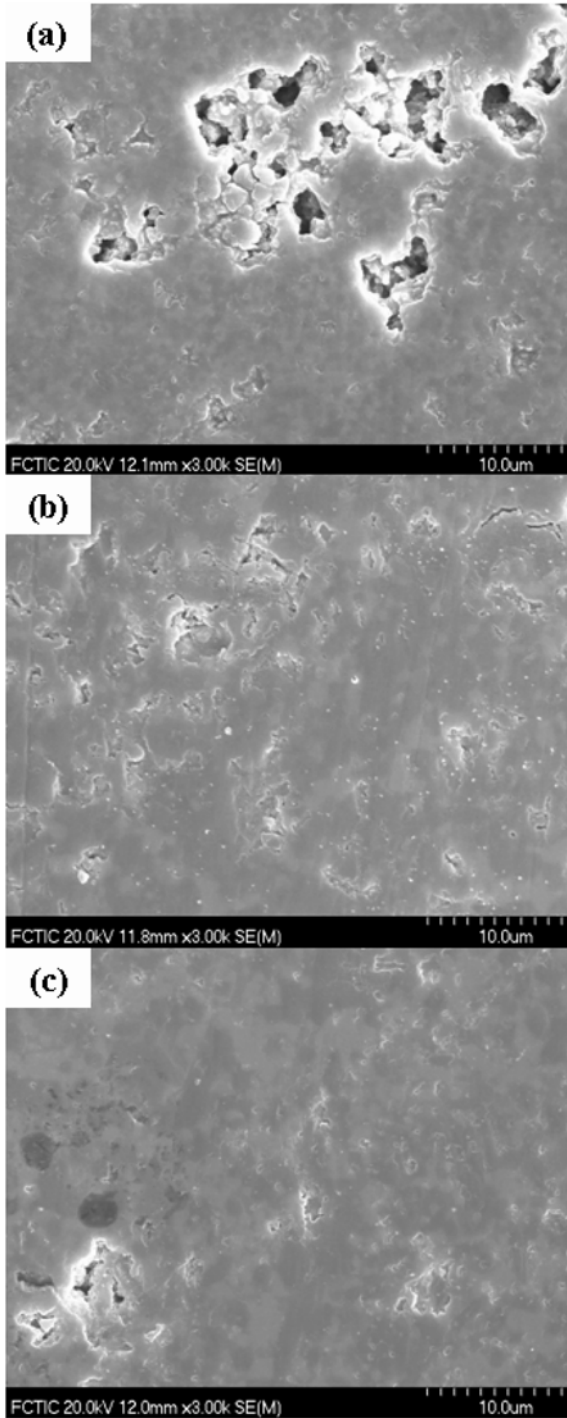


Fig. 5. Microstructures of TiO_2 and $\text{TiO}_2/50 \text{ vol}\%$ BZBS glass composite sintered at (a) 700°C , (b) 800°C , and (c) 900°C .

dielectric constant (~ 53) [5]. Above 800°C , the extinction of the $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and the formation of $\text{Bi}_2\text{Ti}_2\text{O}_7$ might contribute to the increase after the minimum point because $\text{Bi}_2\text{Ti}_2\text{O}_7$ has a relatively high dielectric constant of ~ 118 [20]. Also the increase of the shrinkage above 800°C might contribute to the enhancement of the dielectric constant.

The $Q \times f_0$ value of the $(\text{Al}_2\text{O}_3, \text{TiO}_2)/\text{BZBS}$ glass composites are shown in Fig. 7 as a function of the sintering temperature. High $Q \times f_0$ values were expected

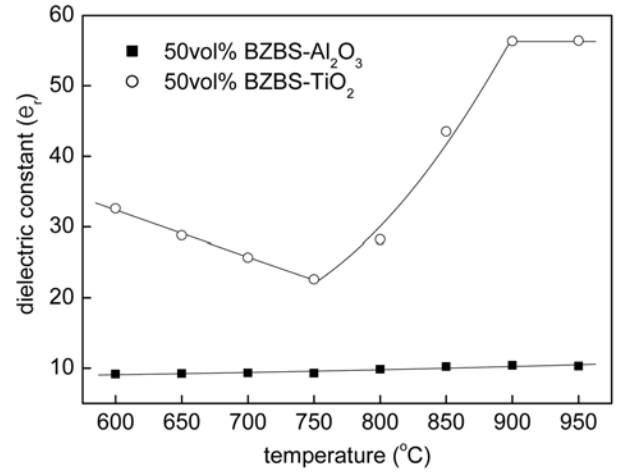


Fig. 6. Dielectric constant of $(\text{Al}_2\text{O}_3, \text{TiO}_2)/50 \text{ vol}\%$ BZBS glass composites as a function of the sintering temperature.

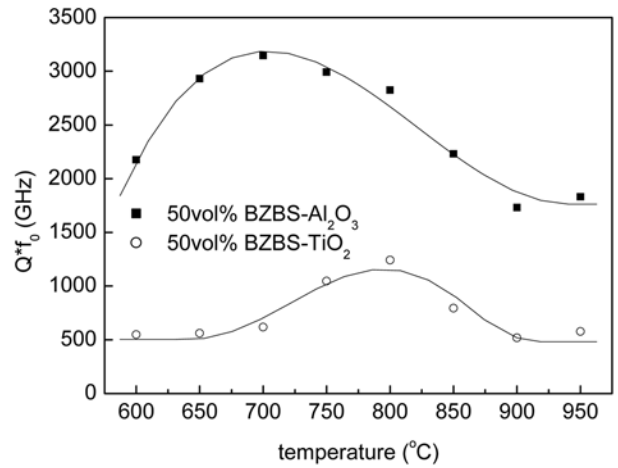


Fig. 7. Quality factor of $(\text{Al}_2\text{O}_3, \text{TiO}_2)/50 \text{ vol}\%$ BZBS glass composites as a function of the sintering temperature.

in the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite because the ZnAl_2O_4 formed showed very high $Q \times f_0 > 55,000 \text{ GHz}$ but the $Q \times f_0$ values in this system were measured as about 2,000–3,000 GHz. The reason for the low value of the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite including ZnAl_2O_4 with a high $Q \times f_0$ is uncertain but a large amount of the remaining glass showing a low $Q \times f_0$ value with a bismuth-rich composition according to the crystallization and/or formation of lattice defects such as the substitution of Bi^{3+} ions on the lattice sites of ZnAl_2O_4 could be suggested. It has been proposed that dielectric loss included an intrinsic loss and an extrinsic one; the intrinsic losses were mainly caused by the lattice vibration modes while the extrinsic losses were dominated by second phases, oxygen vacancies, the grain size, and densification/porosity [21].

On the other hand, the value of $Q \times f_0$ for the TiO_2/BZBS glass composite was about 500–1,000 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 densification, i.e., removal of porosity. The reason for the decrease after the maximum point at 800 °C is uncertain. The formation of $\text{Bi}_2\text{Ti}_2\text{O}_7$ might be correlated to the cause of the decrease and further study is necessary. The temperature coefficient of the resonant frequency (τ_f) of was -48 ppm/K for the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite and +119 ppm/K for the TiO_2/BZBS glass composite; an improvement of τ_f in the TiO_2/BZBS glass composite is necessary for its application as an LTCC material.

Summary

The microwave dielectric properties of ceramic/50 vol% bismuth zinc borosilicate (BZBS) glass composites were investigated. The deformation temperature of BZBS glass was about 442 °C and a liquid phase sintering occurred in both systems. The crystalline phases of ZnAl_2O_4 with a spinel structure in the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite and $\text{Bi}_2\text{Ti}_2\text{O}_7$ with a cubic pyrochlore structure in the TiO_2/BZBS glass composite were observed, indicating that BZBS glass was a reactive glass in these systems. The shrinkage behavior showed that there was a one-stage sintering for the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite whereas a two-stage sintering for the TiO_2/BZBS glass composite. The dielectric constant (ϵ_r) of the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite exhibited almost the same value of about 10 within the sintering temperature range between 600-950 °C, implying that the application of the $\text{Al}_2\text{O}_3/\text{BZBS}$ glass composite to substrates may therefore be shown to be appropriate. For the TiO_2/BZBS glass composite, however, an improvement of the temperature coefficient of the resonant frequency (τ_f = +119 ppm/K) is necessary for its application as an LTCC material although ϵ_r of this system had a proper value (~56) for an application to filters.

References

1. Y. Imanaka, in "Multilayered Low Temperature Cofired Ceramics (LTCC) Technology" (Springer, New York, 2005) p. 1.
2. S.-J. Hwang, Y.-J. Lim and H.-S. Kim, *J. Electroceram.* 18 (2007) 121-128.
3. S.H. Knickerbocker, A.H. Kumar and L.W. Herron, *Am. Ceram. Soc. Bull.* 72 (1993) 90-95.
4. D. Belavic, M. Hrovat, J. Holc, M.S. Zarnik, M. Kosec and M. Pavlin, *J. Electroceram.* 19[4] (2007) 363-368.
5. K. Fukuda, R. Kitoh and I. Awai, *Jpn. J. Appl. Phys.* 32 (1993) 4584-4588.
6. H. Ohsato, T. Tsunooka, T. Sugiyama, K. Kakimoto and H. Ogawa, *J. Electroceram.* 17 (2006) 445-450.
7. Q.-L. Zhang, H. Yang, J.-L. Zou and H.-P. Sun, *J. Electroceram.* 18[3-4] (2007) 225-229.
8. B.W. Hakki and P.D. Coleman, *IEEE Trans. Microwave Theor. Tech.* MMT-8 (1960) 402- 410.
9. I. Dyament, D. Itzhak and J. Hormadaly, *J. Non-Cryst. Solids*, 351 (2005) 3503-3507.
10. A. Nitta, M. Koide and K. Matsusita, *Phys. Chem. Glass.* 42 (2001) 275-278.
11. S.O. Yoon, S.H. Shim, K.S. Kim, J.G. Park and S. Kim, *Ceram. Inter.* 35[3] (2009) 1271-1275.
12. E.I. Speranskaya, I.S. Rez, L.V. Kozlova, V.M. S.Korikov and V.I. Slavov, *Russ. J. Inorg. Mater.* 1 (1965) 232-235.
13. M.L. Barsukova, V.A. Kuznetsov, A.N. Lobachev and Y.V. Shaldin, *J. Cryst. Growth*, 13/14 (1972) 530-534.
14. M. Udovic, M. Valant, B. Jancar, D. Suvorov, A. Meden and A. Kocevar, *J. Am. Ceram. Soc.* 89 (2006) 3462-3469.
15. A.L. Hector and S.B. Wiggan, *J. Solid State Chem.* 177 (2004) 139-145.
16. V. Kahlenberg and H. Bohm, *Cryst. Res. Technol.* 30 (1995) 237-241.
17. S. Shimada, K. Kodaira and T. Mashushita, *J. Cryst. Growth*, 41 (1977) 317-320.
18. V. Kahlenberg and H. Bohm, *J. Alloys Comp.* 223 (1995) 142-146.
19. R.M. German, S. Farooq and C.M. Kippur, *Mater. Sci. Eng.* A105/106 (1988) 215-224.
20. X. Wu, S.W. Wang, H. Wang, Z. Wang, S.X. Shang and M. Wang, *Thin Solid Films*, 370 (2000) 30-32.
21. C.-L. Huang, M.-H. Weng and H.-L. Chen, *Mater. Chem. Phys.* 71(2001) 17-22.

1. Y. Imanaka, in "Multilayered Low Temperature Cofired