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Low temperature and microwave dielectric properties of TiO_2/ZBS glass composites

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Abstract

TiO_2 based ceramic/glass composites were prepared by a non-reactive liquid phase sintering (NLPS) using zinc borosilicate (ZBS) glass having the deformation temperature of 588 °C. The compounds of Zn_2SiO_4 and $Zn_4B_6O_{13}$ were formed after the sintering process, indicating that the ZBS glass was a non-reactive one in this system. For TiO_2/50 vol% ZBS glass composite, the two-stage sintering behavior was conducted as the sintering temperature increased. The former might be correlated to the NLPS process and the latter appeared to be related to the crystallization. The dielectric constant (ε_r) was mainly affected by the porosity and obeyed the logarithmic mixing rule. The quality factor ($Q \times f_0$) showed an increase and then a steep decrease after the maximum at 850 °C. TiO_2/50 vol% ZBS glass composite sintered at 900 °C demonstrated 36 in the dielectric constant (ε_r) and 7500 GHz in the quality factor ($Q \times f_0$) for an application to LTCC filters.

Keywords: C. Dielectric properties; D. TiO_2; LTCC; Ceramic/glass; ZBS glass

1. Introduction

A number of studies on low temperature co-fired ceramics (LTCC) have been intensively investigated. There are two basic methods to prepare LTCC [1–3]. 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 low dielectric constant and good mechanical properties including strength and thermal expansion coefficient (TEC), is a typical material of crystallizable glasses [4]. The second method is to use mixture of low melting temperature glasses working as a flux agent and ceramics as filler. 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 the glass formation at low temperature and good dielectric properties [5].

TiO_2 has been extensively studied in electronic application because it shows a high dielectric constant (ε_r = 105) and a high quality factor ($Q \times f_0$ = 46,000) [6]. The aim of this work is to investigate the low-temperature sintering and microwave dielectric properties of the ceramic/glass composites using TiO_2 powder as filler and zinc borosilicate glass as a flux agent for an application to LTCC filters.

2. Experimental procedure

The powders of ZnO, B_2O_3, and SiO_2 with the grade of extra-pure reagent were weighed in the weight percentage of 65, 25, and 10, respectively (in mol% of 60.3, 27.1, and 12.6, respectively) and well mixed in a dry condition. Zinc borosilicate glass (hereafter ZBS glass) was prepared by a quenching method after a melting process above 1300 °C using an alumina crucible. The deformation temperature of the ZBS glass was measured by a dilatometer (DIL 402, Netzsch). By a

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disk milling and a ball milling using zirconia balls in a wet condition with ethanol, glass powders were obtained. TiO_2/glass composites with 20–50 vol% ZBS glass were ball milled for 24 h and then dried. The disk type samples with 15 mm in diameter were prepared by a pressing of powder mixtures under ca. 50 MPa and sintering between 600 and 950 °C for 2 h.

The phase analysis of the sintered glasses was carried out by an X-ray diffractometer (MO3XHF, Mac science) using a Cu-Kα target and a Ni filter within range between 10° and 80°. The microstructures were observed by a FE-SEM (S-4200, Hitachi). The dielectric constant (ε_r) and the temperature coefficient of resonance frequency ($Q \times f_0$) were measured in the TE_{011} mode by Hakki and Coleman method using a network analyzer (HP8720ES, 500 MHz–20 GHz) 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 3 dB level of the resonant peak, and the insertion loss were measured [7].

3. Results and discussion

The deformation temperature of the ZBS glass, i.e., the temperature at the maximum value of thermal expansion curve, was determined as 588 °C, which was similar with the value in the literature; zinc borosilicate glass with the composition of $60ZnO–30B_2O_3–10SiO_2$ (in mol%, Zn60B30Si10) was reported at 582 °C by Wu and Huang [8]. They also determined the dielectric constant (ε_r), quality factor ($Q \times f_0$), and the temperature coefficient of resonant frequency (τ_f) of this glass as 7.56, 1439 GHz (93 at 15.5 Hz), and −21 ppm/°C, respectively. Density, deformation point and dielectric properties of the ZBS glasses were summarized in Table 1 and these glasses showed similar properties except $Q \times f_0$ and τ_f.

Table 1
Density, deformation point and dielectric properties of ZBS glasses.

	ZBS glass	Zn60B30Si10
Density (g/cm^3)	3.57	–
Deformation point (°C)	588	582
Dielectric constant, ε_r	6.53	7.56
Resonant frequency (GHz)	17.1	15.5
Q	261	93
$Q \times f_0$ (GHz)	4465	1439
τ_f (ppm/°C)	−10	−21
Remarks	This work	Ref. [8]

The microstructures of the TiO_2/ZBS glass composites containing 20–50 vol% ZBS glass sintered at 900 °C are shown in Fig. 1. A large amount of pore was observed at 20 vol% and the density appeared to increase as the amount of glass increased. The investigation of linear shrinkage, phase formation and microwave dielectric properties, therefore, was conducted for the composition of 50 vol% glass although some closed pores still existed. The powder X-ray diffraction patterns of TiO_2/50 vol% ZBS glass composite sintered between 700 and 900 °C are shown in Fig. 2. The crystalline phases of α- and β-zinc orthosilicate (Zn_2SiO_4) and zinc metaborate ($Zn_4B_6O_{13}$) were observed in addition to TiO_2 filler; β-Zn_2SiO_4 at 700 °C and α-Zn_2SiO_4 and $Zn_4B_6O_{13}$ above 800 °C.

Five polymorphs of Zn_2SiO_4 have been found at various temperatures and pressures [9]. Among them, α-form of the willemite structure with a hexagonal was reported as the only stable compound at temperatures between 800 °C and the liquidus according to the phase diagram of the SiO_2–ZnO system [10]. And β-form as a metastable phase could be obtained from the crystallization of glass phases whereas an

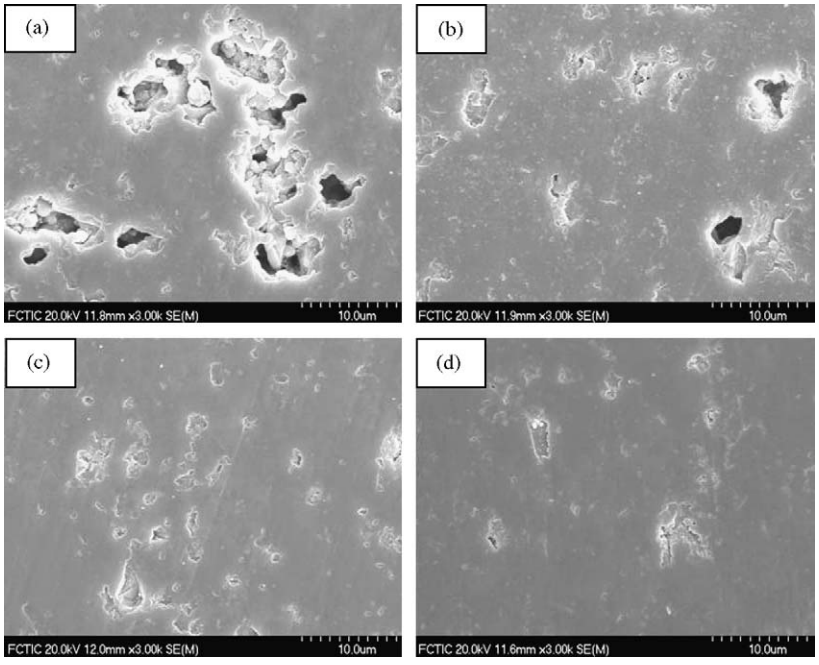

Fig. 1. Microstructures of TiO_2/ZBS glass system sintered at 900 °C for 2 h: (a) 20 vol% glass, (b) 30 vol%, (c) 40 vol% and (d) 50 vol%.

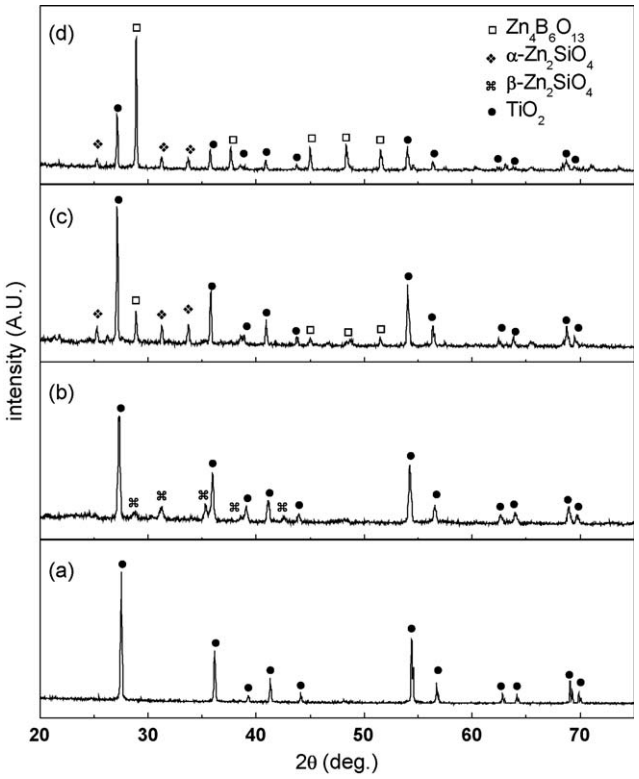

Fig. 2. Powder XRD patterns of (a) TiO_2 filler and TiO_2/50 vol% ZBS glass composite sintered at (b) 700 °C, (c) 800 °C and (d) 900 °C.

attempt to prepare this phase by direct solid-state reaction was unsuccessful [11]. When the sintering was conducted at 700 °C, β-form was formed and maintained at room temperature. According to the study for the formation of Zn_2SiO_4 with 3.2 mol% TiO_2 additive and without TiO_2 addition in the temperature range of 650–1515 °C, Lee et al. reported that TiO_2 was found to stabilize the metastable β-form to room temperature after cooling from melts and they suggested that the substitution of a Si^{4+} site by a Ti^{4+} ion on contribution to the stabilization of the β-form from the result of the larger *d*-spacings for β-form obtained in the TiO_2-added samples compared with those without TiO_2 [12]; the ionic radius of Ti^{4+} ion is larger than that of Si^{4+} ion. On the other hand, Lin and Shen reported that amorphous Zn_2SiO_4 crystallized into β-form at about 722 °C and subsequently transformed into α-form at 919 °C [13]. In this work as shown in Fig. 1, however, the phase transition from β- to α-form occurred between 700 and 800 °C. Lee et al., also suggested that the addition of TiO_2 to Zn_2SiO_4 reduced the activation energy for the formation of α-form [12]. It is, therefore, understandable that some of TiO_2 filler in this work was dissolved into the ZBS glass and then contributed to the stabilization of β-form and to the formation of α-form.

$Zn_4B_6O_{13}$ with a cubic structure is one of the compounds such as ZnB_4O_7 and $Zn_3B_2O_6$ in the ZnO–B_2O_3 system [14]. It was suggested that $Zn_4B_6O_{13}$ was obtained from the decomposition of ZnB_4O_7 above 710 °C and ZnB_4O_7 existed at temperatures as high as 900 °C due to the sluggish decomposition [14]. In this study, however, ZnB_4O_7 was not observed and $Zn_4B_6O_{13}$ appeared to be crystallized from the ZBS glass above 800 °C.

Besides TiO_2, on the other hand, crystalline phases were only composed of $Zn_4B_6O_{13}$ and Zn_2SiO_4 at 900 °C, which is in accord with the result of the phase equilibrium in the ZnO–B_2O_3–SiO_2 system at 950 °C [15]; a tie line exists between the $Zn_4B_6O_{13}$–Zn_2SiO_4 quasi-binary system and the composition of the ZBS glass in this work lies exactly on the tie line. It is, therefore, understandable that there is no reaction between TiO_2 and the ZBS glass except the substitution of Ti^{4+} ion on Si^{4+} site as mentioned above, i.e., the ZBS glass is a non-reactive one in the system including TiO_2 and then a non-reactive liquid phase sintering (NLPS) is expected to occur. The NLPS is one of the liquid-assisted sintering (LAS) [16]; LAS distinguishes between the NLPS, where a glass phase content of at least 20–40 vol% is necessary for the densification and a reactive liquid phase sintering, where a glass content <20 vol% is sufficient. The densification in the NLPS was proposed in three stages; the first stage is glass redistribution and local grain rearrangement where only slight densification occurs, the second is the main densification process including global rearrangement, glass redistribution, and closure of pores where the density from 65 to 90% of the theoretical density is accomplished, and the third is viscous flow where the residual porosity of about 10% is closed.

The linear shrinkage of TiO_2/50 vol% ZBS glass composite as a function of the sintering temperature is shown in Fig. 3. The two-stage sintering behavior was observed; the first stage with a small shrinkage of about 5% occurred up to 750 °C and the second with a large one about 15% took place above 800 °C. The former might be correlated to the NLPS as mentioned above. And the latter appeared to be mainly correlated to the crystallization of $Zn_4B_6O_{13}$ as shown in Fig. 2. Moreover, the relatively large shrinkage above 800 °C might be correlated to the consumption of Si^{4+} ion in the ZBS glass by the formation of α-Zn_2SiO_4, which may cause a decrease of viscosity of remained glass and then promote the densification. The

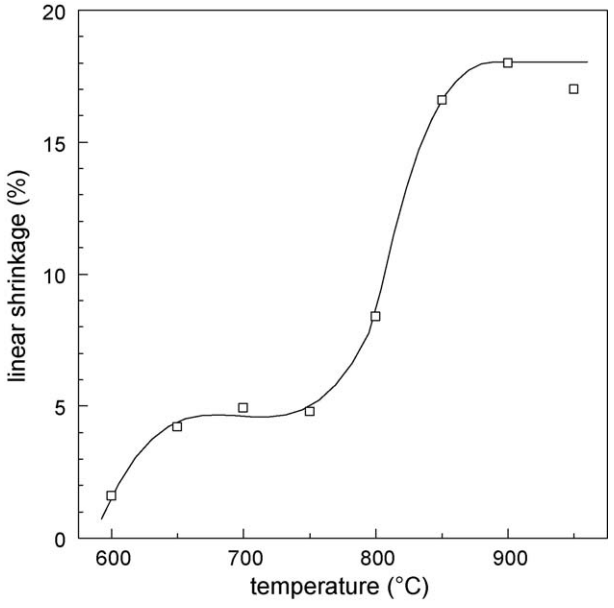

Fig. 3. Linear shrinkage of TiO_2/50 vol% ZBS glass composite as a function of sintering temperature.

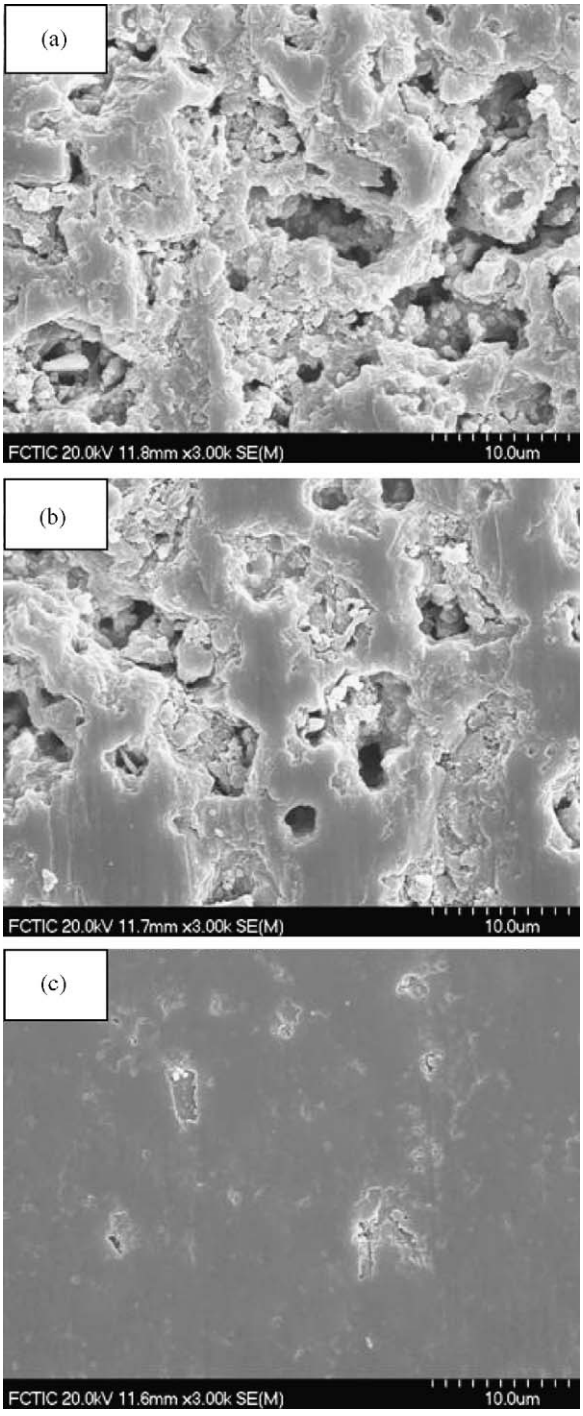

Fig. 4. Microstructures of TiO_2/50 vol% ZBS glass composite sintered at (a) 700 °C, (b) 800 °C and (c) 900 °C for 2 h.

viscosity of glass is dependent on the composition, which generally decreases with lower SiO_2 content due to the formation of non-bridging oxygens in SiO_4 tetrahedra [17]. It is considered that the global rearrangement in the NLPS might be accelerated by the crystallization of $Zn_4B_6O_{13}$ and the consumption of Si^{4+} ion above 800 °C. Fig. 4 shows the microstructures of TiO_2/50 vol% ZBS glass composite sintered between 700 and 900 °C; the densification was promoted as an increase of the sintering temperature.

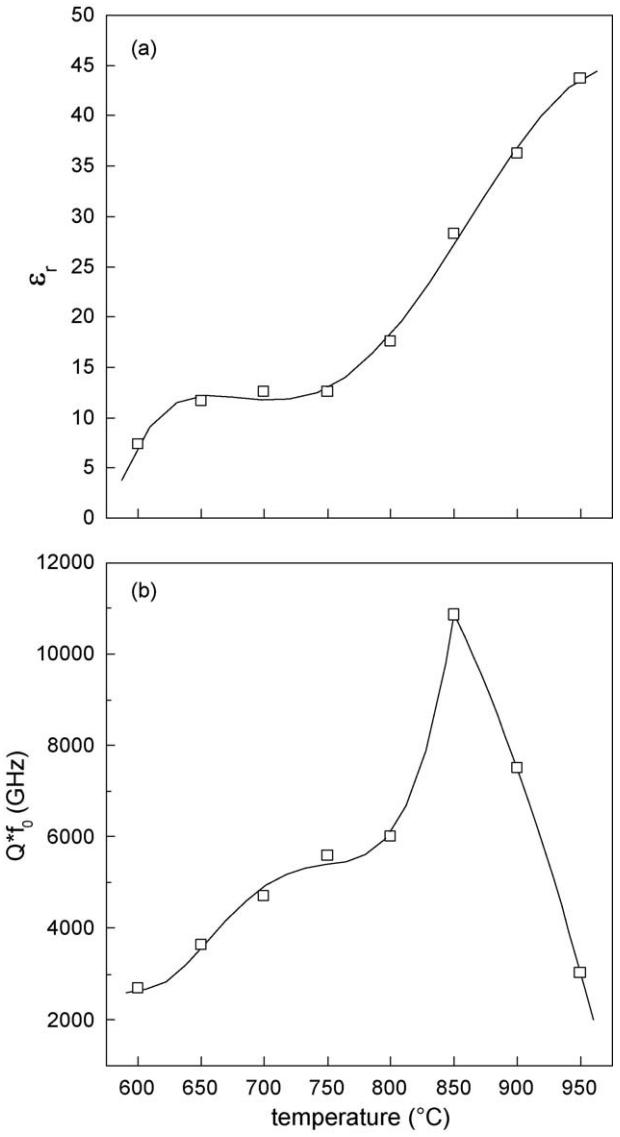

Fig. 5. (a) Dielectric constant and (b) quality factor of TiO_2/50 vol% ZBS glass composite as a function of sintering temperature.

Fig. 5 shows the dielectric constant (ε_r) and the quality factor ($Q \times f_0$) of TiO_2/50 vol% ZBS glass composite as a function of the sintering temperature. The plot of the dielectric constant was very similar with that of the linear shrinkage as shown in Fig. 3, implying that ε_r of TiO_2/50 vol% ZBS glass composite was mainly affected by the porosity, i.e., the relative density. Although the ε_r of $Zn_4B_6O_{13}$ is lower than that of the general ceramics, it is much higher than that of pore ($\varepsilon_r = 1$). Therefore, an increase of the densification with sintering temperature demonstrated an increase of the dielectric constant. The dielectric constant was 43.7 when the sintering was conducted at 950 °C which was similar with the calculated value of about 45 using the logarithmic mixing rule [18] of Eq. (1) with the data of TiO_2 ($\varepsilon_r = 105$) [6], $Zn_4B_6O_{13}$ (7.24) [19] and α-Zn_2SiO_4 (6.6) [20]:

$$\log \varepsilon_r = {}_1 \log \varepsilon_1 + {}_2 \log \varepsilon_2 + {}_3 \log \varepsilon_3, \quad (1)$$

where $_1$, $_2$, and $_3$ represent the volume fraction of phase 1, 2, and 3 in the mixture, respectively. The volume fraction of $Zn_4B_6O_{13}$ and α-Zn_2SiO_4 was determined by the lever rule in the tie line of the $Zn_4B_6O_{13}$–Zn_2SiO_4 quasi-binary system. As the increase of the sintering temperature, the quality factor showed an increase up to 850 °C and then decrease after the maximum. The increase of the quality factor in low temperatures might be related to the formation of α-Zn_2SiO_4 having the high value of 219,000 GHz [20] as well as the density as likes the dielectric constant. In particular, the crystallization of ZnB_2O_4 [8] have a low $Q \times f_0$ (1733 GHz) which may be similar to that of the crystalline phase of $Zn_4B_6O_{13}$. Because the value of $Q \times f_0$ was independent of the density or the porosity for theoretical density >90%, the crystallization of $Zn_4B_6O_{13}$ might be one of the reasons of the decrease [21]. Generally, the extrinsic losses of dielectric were dominated by second phases, impurities, grain boundary, lattice defects such as oxygen vacancies, residual stresses, and density/porosity [21,22].

4. Summary

Low-temperature sintering and microwave dielectric properties of the TiO_2/ZBS glass composites with 20–50 vol% ZBS glass 600–950 °C for 2 h were investigated. For TiO_2/50 vol% ZBS glass composite, the two-stage sintering behavior was conducted as the sintering temperature increased. The former might be correlated to the NLPS process and the latter appeared to be related to the crystallization. TiO_2/50 vol% ZBS glass composite sintered at 900 °C demonstrated 36 in the dielectric constant (ε_r) and 7500 GHz in the quality factor ($Q \times f_0$) for an application to LTCC filters.

References

[1] Y. Imanaka, Multilayered Low Temperature Cofired Ceramics (LTCC) Technology, Springer, New York, 2005, pp. 1–17.

[2] R.R. Tummala, Ceramic and glass–ceramics packaging in the 1990s, J. Am. Ceram. Soc. 74 (1991) 895–908.

[3] C.R. Chang, J.H. Jean, Crystallization kinetics and mechanism of low-dielectric, low-temperature, cofirable $CaO–B_2O_3–SiO_2$ glass–ceramics, J. Am. Ceram. Soc. 82 (1999) 1725–1732.

[4] S.H. Knickerbocker, A.H. Kumar, L.W. Herron, Cordierite glass–ceramics for multilayer ceramic packaging, Am. Ceram. Soc. Bull. 72 (1993) 90–95.

[5] Y.J. Choi, J.H. Park, J.H. Park, S. Nahm, J.G. Park, Middle- and high-permittivity dielectric compositions for low-temperature co-fired ceramics, J. Eur. Ceram. Soc. 27 (2007) 2017–2024.

[6] K. Fukuda, R. Kitoh, I. Awai, Microwave characteristics of $TiO_2–Bi_2O_3$ dielectric resonator, Jpn. J. Appl. Phys. 32 (1993) 4584–4588.

[7] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IRE Trans. Microwave Theory Tech. 8 (1960) 402–410.

[8] J.M. Wu, H.L. Huang, Microwave properties of zinc, barium and lead borosilicate glasses, J. Non-Cryst. Solids 260 (1999) 116–124.

[9] Y. Syono, S.I. Akimoto, High pressure transformation in zinc silicate, J. Solid State Chem. 3 (1971) 369–380.

[10] E.N. Bunting, Phase equilibria in the system SiO_2–ZnO, J. Am. Ceram. Soc. 13 (1930) 5–10.

[11] J. Williamson, F.P. Glasser, Crystallisation of zinc silicate liquids and glasses, Phys. Chem. Glasses 5 (1964) 52–59.

[12] C.C. Lee, P. Shen, H.Y. Lu, Formation of willemite from powder mixture with TiO_2 addition, J. Mater. Sci. 24 (1989) 3300–3304.

[13] C.C. Lin, P. Shen, Nonisothermal site saturation during transformations of Zn_2SiO_4, J. Solid State Chem. 112 (1994) 387–391.

[14] A. Whitaker, Temperature dependence of the stability of zinc borates, J. Mater. Sci. 7 (1972) 189–193.

[15] M.A. Eidem, B.R. Orton, A. Whitaker, Phase equilibria in the system $ZnO–B_2O_3–SiO_2$ at 950 °C, J. Mater. Sci. 22 (1987) 4139–4143.

[16] S. Kemethmuller, M. Hagymasi, A. Stiegelschmitt, A. Roosen, Viscous flow as the driving force for the densification of low-temperature co-fired ceramics, J. Am. Ceram. Soc. 90 (2007) 64–70.

[17] M.K. Karapet'yants, The viscosity–temperature relationship for silicate glasses, Glass Ceram. 15 (1960) 26–32.

[18] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, 2nd edition, John Wiley and Sons, New York, 1976, pp. 947–960.

[19] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1993) 348–366.

[20] Y. Guo, H. Ohsato, K.I. Kamimoto, Characterization and dielectric behavior of willemite and TiO_2-doped willemite ceramics at millimeter-wave frequency, J. Eur. Ceram. Soc. 26 (2006) 1827–1830.

[21] C.L. Huang, M.H. Weng, H.L. Chen, Effects of additives on microstructures and microwave dielectric properties of $(Zr,Sn)TiO_4$ ceramics, Mater. Chem. Phys. 71 (2001) 17–22.

[22] S. Kume, M. Yasuoka, K. Watari, Annealing effect on dielectric property of AlN ceramics, J. Eur. Ceram. Soc. 26 (2006) 1831–1834.