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Sintering behavior and dielectric properties of ceramic/glass composites using lead borosilicate glass

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TiO_2 and Al_2O_3 based ceramic/glass composites were prepared by a liquid phase sintering method using lead borosilicate (PBS) glass with a deformation temperature of about 627 °C. The non-reactive liquid phase sintering (NLPS) was conducted in both systems; there was no crystallization in the TiO_2/PBS glass composite and although the crystallization of the anorthite-type phase occurred in the Al_2O_3/PBS glass composite, this phase might be crystallized from the PBS glass. The linear shrinkage behavior could be interpreted as one stage sintering for both systems. The dielectric constant (ε_r) of the TiO_2/PBS glass composite was about 30, implying that an application to filters may therefore be shown to be appropriate. The temperature coefficient of the resonant frequency (τ_f), however, was +135 ppm/K and an improvement is necessary for the application to LTCC materials. The dielectric constant (ε_r) of the Al_2O_3/PBS glass composite was about 10 and an application to substrates may be proper.

Key words: LTCC, Ceramic/glass, TiO_2, Al_2O_3, Lead borosilicate.

Introduction

A number of low temperature co-fired ceramics (LTCC) have been intensively investigated. There are two basic methods to prepare an LTCC [1, 2]. The first is to use crystallizable glasses as starting materials which undergo devitrification to crystalline phases during the firing process. Hence, ideally no glass phases, exist in the final microstructure. The properties of crystallizable glasses depend on the degree of crystallization, i.e., the thermal history. A cordierite-based glass, showing a low dielectric constant and good mechanical properties including strength and thermal expansion coefficient (TEC), is a typical example of a crystallizable glass [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 ceramic-glass [4]. Generally, borosilicate glasses are used as flux materials due to their capability of glass formation at low temperature and good dielectric properties [5].

TiO_2 has been extensively studied in electronic applications because it shows a high dielectric constant (ε_r = 105) and a high quality factor ($Q \times f_0 > 40,000$ GHz) [6]. On the other hand, to diminish the signal propagation delay, LTCC materials for a substrate are required to have a low dielectric constant [7]. Al_2O_3 is known as one of the typical materials having a low dielectric constant (9~ 10) [8]. The aim of this study is to investigate the sintering behavior of TiO_2- and the Al_2O_3-lead borosilicate (PBS) glass composites and to prepare materials with moderate and low dielectric constants, respectively.

Experimental procedure

Powders of PbO, CaO, SiO_2, B_2O_3, and Al_2O_3 with the grade of extra-pure reagent were weighed in the weight percentage of 40, 5, 45, 5, and 5, respectively and well mixed in a dry condition. Lead borosilicate (PBS) glass was prepared by a quenching method after a melting process above 1400 °C using an alumina crucible. The deformation temperature of the PBS glass was measured by a dilatometer (DIL 402, Netzsch). With a disk milling and a ball milling using zirconia balls in a wet condition with ethanol, glass powders were obtained. To prepare TiO_2 and Al_2O_3 based ceramic/glass composites containing 20~50 vol% glass, TiO_2 (rutile structure with a small amount of anatase, purity 99.9%, and average particle size ca. 2 μm) and Al_2O_3 (99.9% and ca. 3 μm) powders of ceramic fillers and the PBS glass were ball milled for 24 h and then dried. Disk type samples with 15 mm in diameter were prepared by pressing the powder mixtures under ca. 50 MPa and sintering at between 600-950 °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 a 2 θ

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range of between 10-80°. The microstructures were observed by a FE-SEM (S-4200, Hitachi). The dielectric constant 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 3 dB level of the resonant peak, and the insertion loss were measured [9]. The temperature coefficient of resonant frequency was the measured using an Invar cavity in the temperature range of 25-85 °C.

Results and Discussion

The deformation temperature of lead borosilicate (PBS) glass, i.e., the temperature at the maximum peak of the thermal expansion curve, was determined as 627, and the dielectric constant (ε_r), the quality factor ($Q \times f_0$), and the temperature coefficient of the resonant frequency (τ_f) were 6.9, 1,123 GHz, and –23.9 ppm/K, respectively. The microstructures of the TiO_2– and the Al_2O_3-PBS glass composites sintered at 900 °C are shown in Fig. 1 and 2, respectively. The compositions with 50 vol% PBS glass showed dense microstructures in both systems. It is understandable that the glass content in this system is necessary to be at least 50 vol% for the densification. The glass content of nearly all commercial LTCC composites is, indeed, greater than 50 vol%, mostly between 63% and 85% [10]. The study following in this investigation was, hence, focused on in this composition.

The powder X-ray diffraction patterns of the TiO_2–50 vol% PBS glass composite sintered at between 700 and 900 °C are shown in Fig. 3. Within the sintering temperature range, only the rutile structure of TiO_2 was observed as the crystalline phase, indicating that a non-reactive liquid phase sintering (NLPS) occurred in this system. The NLPS is one of the liquid-assisted sintering (LAS) method [10]; LAS distinguishes between 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 as occurring 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 a density changes 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.

Fig. 4 shows powder X-ray diffraction patterns of Al_2O_3–50 vol% PBS glass composite. Al_2O_3 was the only crystalline

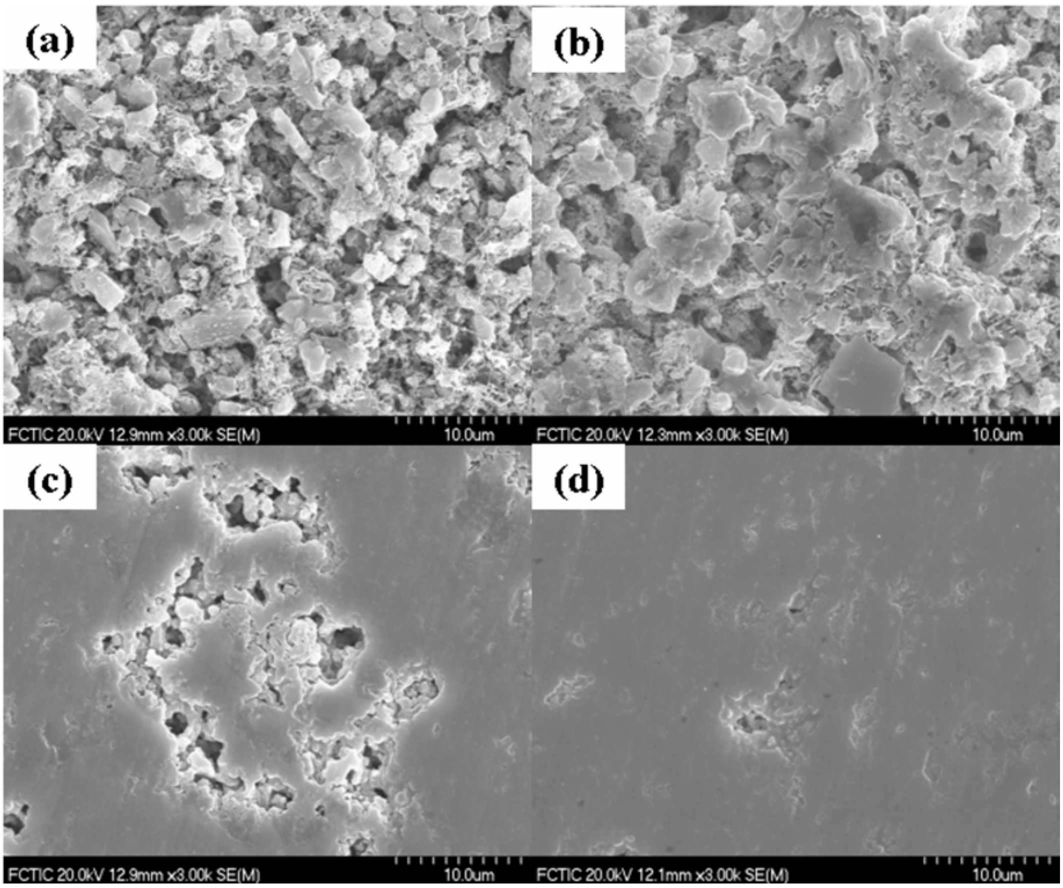

Fig. 1. Microstructures of the TiO_2/PBS glass composites sintered at 900 °C; (a) 20 vol%, (b) 30 vol%, (c) 40 vol%, and (d) 50 vol% glass.

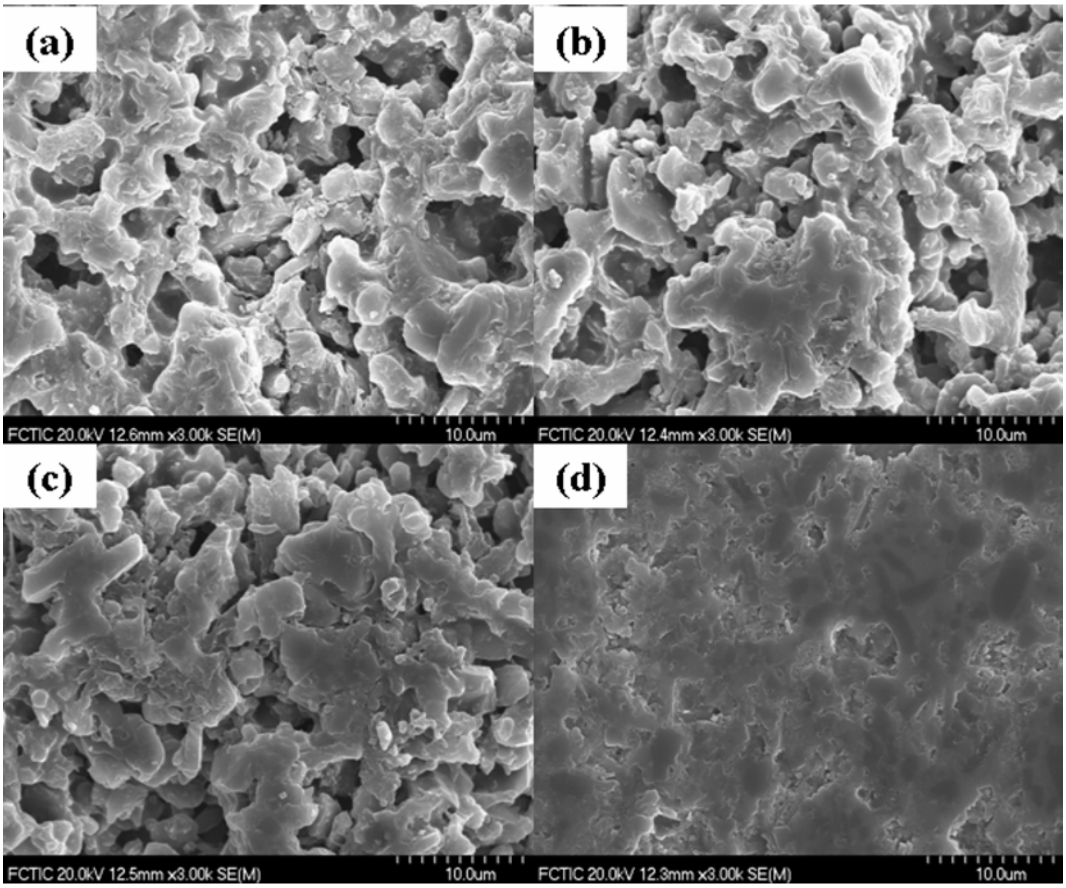

Fig. 2. Microstructures of the Al_2O_3/PBS glass composites sintered at 900 °C; (a) 20 vol%, (b) 30 vol%, (c) 40 vol%, and (d) 50 vol% glass.

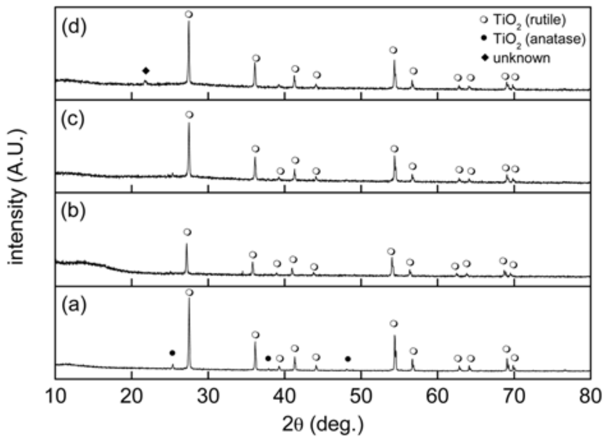

Fig. 3. Powder XRD patterns of (a) TiO_2 and TiO_2-50 vol% PBS glass composite sintered at (b) 700 °C, (c) 800 °C, and (d) 900 °C.

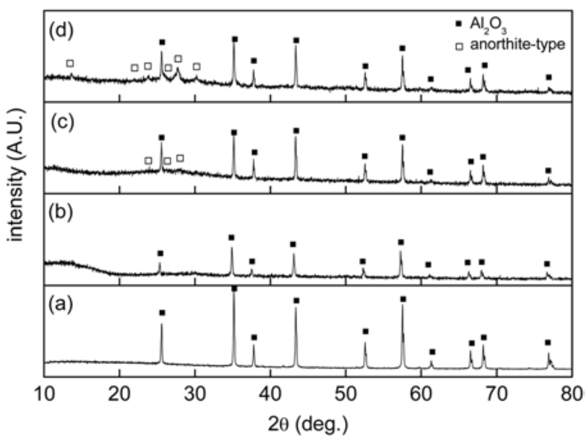

Fig. 4. Powder XRD patterns of (a) Al_2O_3 and Al_2O_3-50 vol% PBS glass composite sintered at (b) 700 °C, (c) 800 °C, and (d) 900 °C.

phase at 700 °C and the anorthite-type phase was formed above 800 °C. The formation temperature of the anorthite-type phase is in accord with the work of Jean *et al.*, that it was detected at temperatures higher than 800 °C [11]. The anorthite ($M^{2+}O{\cdot}Al_2O_3{\cdot}2SiO_2$) based glass-ceramic system has been intensively studied because it shows a relatively low dielectric constant (~9.1) and a high quality factor in the range of 1 000~1200 at 0.5 GHz [12]. T2000 tape dielectric from Motorola is well known as a specific commercial material for anorthite and it includes a specially formulated B_2O_3-K_2O-SiO_2-CaO-SrO-BaO glass (TG glass), Al_2O_3 as the ceramic filler, and TiO_2 as τ_f an adjustment agent. On the other hand, it is suggested that anorthite was crystallized from the PBS glass because the PBS glass originally contained the constituents of anorthite such as Pb^{2+}, Ca^{2+}, Al^{3+}, and Si^{4+}. The densification, therefore, might also occur through NLPS.

The variation of the linear shrinkage and the relative

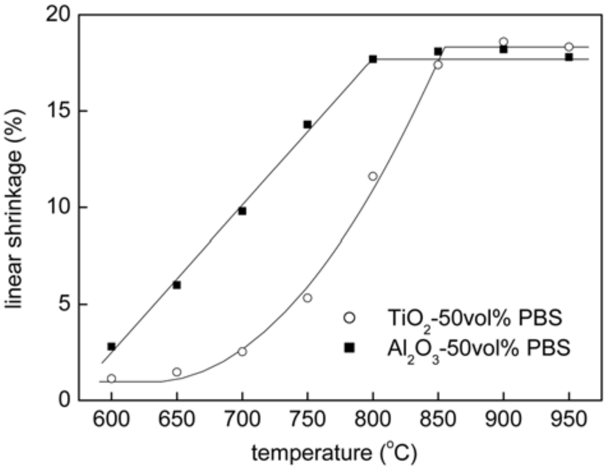

Fig. 5. Linear shrinkage of (TiO_2, Al_2O_3)-50 vol% PBS glass composites as a function of sintering temperature.

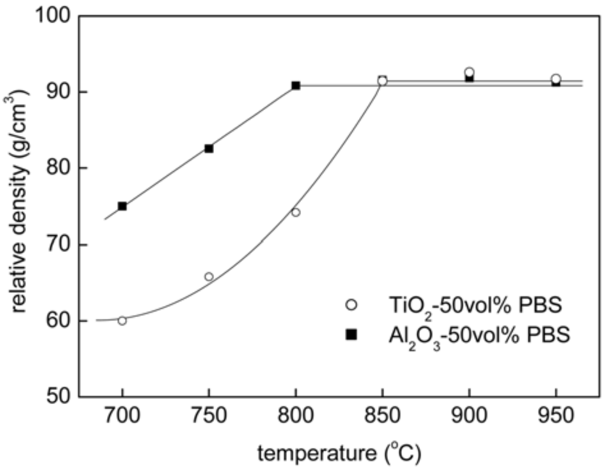

Fig. 6. Relative density of (TiO_2, Al_2O_3)-50 vol% PBS glass composites as a function of sintering temperature.

density as a function of the sintering temperature are shown in Fig. 5 and 6, respectively. For both systems, the shrinkage and the density showed an increase as the sintering temperature was increased and then a plateau above 800 ºC for the Al_2O_3/PBS glass composite and 850 ºC for the TiO_2/PBS glass composite. It is considered that the shrinkage behavior in these systems was governed by the deformation point of the glasses; a one-stage densification process was conducted. It is considered that the formation of the anorthite-type phase in the Al_2O_3/PBS glass composite did not affect the shrinkage because this phase was formed above 800 ºC as shown in Fig. 4 at which the shrinkage already reached the maximum value. The reason for the relatively low shrinkage for the TiO_2 system at the temperature range of between 650 and 800 ºC because there was a one-stage densification process the by the PBS glass and the average particle size of the filler was similar about 2 μm for TiO_2 powder and ca. 3 μm for Al_2O_3; as the particle size of filler decreased, the sintering temperature generally increased. By a study on the particle size effect of filler on sintering,

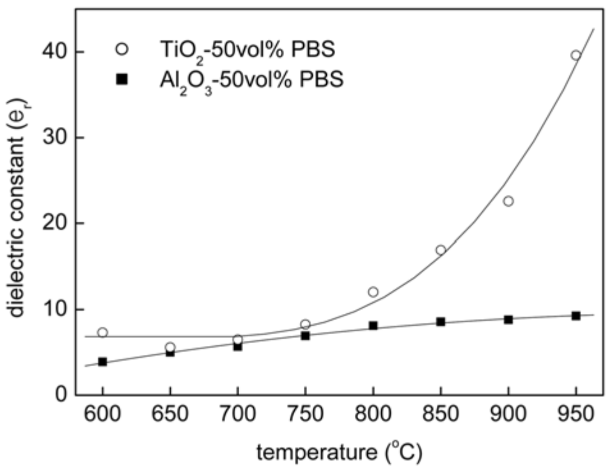

Fig. 7. Dielectric constant of (TiO_2, Al_2O_3)-50 vol% PBS glass composites as a function of sintering temperature.

Miyauchi and Arashi concluded that the viscosity of a ceramic-glass was affected by the particle size of TiO_2 and this effect was explained by the ability of the smaller particles to more effectively obstruct glass liquidity [13]. A further study concerning the reason for the difference of the shrinkage between here two systems in the middle temperature range is necessary.

Fig. 7 shows the variation of the dielectric constant as a function of the sintering temperature. The dielectric constant of the TiO_2 system sintered at 900 ºC increased with an increase of the sintering temperature, indicating that it was mainly affected by the porosity. The dielectric constants of the TiO_2/PBS glass composites sintered at 900 and 950 ºC were 22.6 and 39.6, respectively, implying that the application to filters may be shown to be appropriate. Also these values are similar to a calculated value of 26.8 using a logarithmic mixing rule (Eq. 1) with the data of TiO_2 (ε_r = 105) [6] and the PBS glass (6.9):

$$\ln \varepsilon_r = v_1 \ln\varepsilon_1 + v_2 \ln\varepsilon_2 + v_3 \ln\varepsilon_3 \quad (1)$$

where, v_1, v_2 and v_3 represent the volume fraction of phases 1, 2, and 3 in the mixture, respectively [14]. For the Al_2O_3/PBS glass composite, the dielectric constant was about 9 within the sintering temperature range. This result was reasonable because the dielectric constants of Al_2O_3, anorthite, and PBS glass are between 6.9 and 9 and an application to substrates may, therefore, be proper. For both systems, it is considered that the quality factor ($Q \times f_0$) was also governed by the porosity as shown in Fig. 8; it increased with an increase of the sintering temperature. The quality factor of the TiO_2/PBS glass composite showed low values about 3,000 GHz and it is suggested that the formation of defects such as the substitution of an Al ion on a Ti site might have occurred during the sintering. The temperature coefficient of resonant frequency (τ_f) of the TiO_2/PBS glass composite was +135 ppm/K; this value is too high to be applicable for LTCC materials and an improvement in τ_f is necessary.

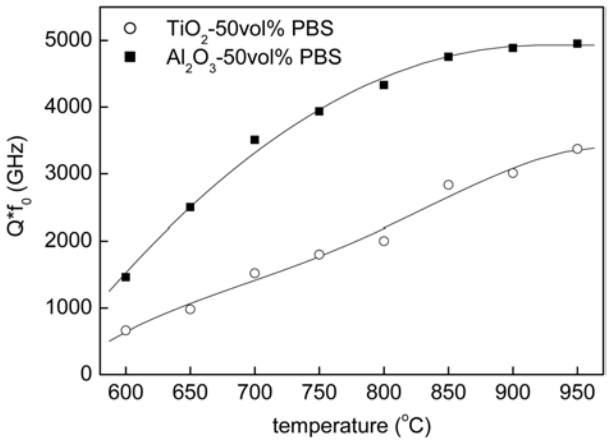

Fig. 8. Quality factor of (TiO_2, Al_2O_3)-50 vol% PBS glass composites as a function of sintering temperature.

Summary

TiO_2 and Al_2O_3 based ceramic/glass composites were prepared by a liquid phase sintering method using lead borosilicate (PBS) glass with a deformation temperature of 627 °C. There was no crystallization in the TiO_2/PBS glass composite indicating that a non-reactive liquid phase sintering (NLPS) was conducted. For the Al_2O_3/PBS glass composite, on the other hand, the NLPS might also occur although the anorthite-type phase was crystallized. Because the PBS glass originally contained the constituents of anorthite, it is considered that the anorthite phase might be crystallized from the PBS glass. The linear shrinkage behavior could be interpreted as one stage sintering for both systems. The dielectric constant (ε_r) and the temperature coefficient of the resonant frequency (τ_f) of the TiO_2/PBS glass composite were about 30 and +135 ppm/K, respectively. These results indicated that the TiO_2/PBS glass composite could be applied to filters after the adjustment of τ_f. The dielectric constant (ε_r) of the Al_2O_3/PBS glass composite was about 10 and an application to substrates may be proper.

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