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Short communication

Low-temperature preparation and microwave dielectric properties of ZBS glass–Al_2O_3 composites

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Abstract

The preparation and microwave dielectric properties of $ZnAl_2O_4$-based glass–ceramic composites were investigated. Using zinc borosilicate (ZBS) glass and Al_2O_3, glass–$ZnAl_2O_4$ composites with high quality factor was successfully prepared at temperatures below 950 °C. The linear shrinkage for 50 vol% ZBS glass–$ZnAl_2O_4$ composite showed a steep increase up to 650 °C and a plateau between 700 °C and 950 °C, implying that one-stage densification process occurred. The crystallization of $ZnAl_2O_4$ was observed above 700 °C and an insufficient densification occurred due to the consumption of the glass. As the sintering temperature increased, the quality factor ($Q \times f_0$) showed an increase with an S-type curve whereas the dielectric constant was almost constant. The formation of $ZnAl_2O_4$ might correspond to the increase of $Q \times f_0$; a high value of 17,757 GHz (1415 at 12.6 GHz) was obtained for the specimen sintered at 900 °C.

Keywords: Sintering; Porosity; Dielectric properties; Glass ceramics

1. Introduction

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 remain 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 crystallizable glass [4]. Ferro A6M tape, moreover, which is one of the commercial LTCC materials, forms crystalline phases of wollastonite ($CaSiO_3$) and CaB_2O_4 after a sintering process [3].

The second method is to use a 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., a glass–ceramic. Generally, borosilicate glasses are used as flux materials due to the glass formation at low temperature and good dielectric properties [5]. Also the anorthite ($AO{\cdot}Al_2O_3{\cdot}SiO_2$, A = alkali earth ion) based glass ceramic system has been intensively studied in this method [6–8]. T2000 dielectric of Motorola includes a specially formulated B_2O_3–K_2O–SiO_2–CaO–SrO–BaO glass (TG glass), Al_2O_3 as ceramic filler, and TiO_2 as a τ_f (temperature coefficient of resonant frequency) adjustment agent; the sintered T2000 dielectric shows a dielectric constant of ~9.1 and a dielectric Q in a range of 1000–1200 at 0.5 GHz. The glass promotes the densification of the glass–ceramics and reacts with Al_2O_3 filler to form anorthite-type crystalline phases.

To diminish signal propagation delay, LTCC materials for substrates are required to have a low dielectric constant [9]. Typical commercial LTCC materials such as those mentioned above have low dielectric constant in the range of 3.9–7.9, which is lower than that of alumina (~9) [1]. Recently, it was reported that $ZnAl_2O_4$ with the spinel structure exhibited interesting dielectric properties (dielectric constant of 8.5, unloaded quality factor of 4590 at 12.27 GHz, and τ_f of −79 ppm/°C), implying that it is a good candidate for substrate applications [10]. However, $ZnAl_2O_4$ could only be synthesized at the high temperature of 1200 °C or above through a solid-state reaction of ZnO and Al_2O_3, which is too high to be applied

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for a LTCC system [11]. However a few studies on the low-temperature sintering of $ZnAl_2O_4$ ceramics have been investigated. Thomas et al. have recently reported that $0.83ZnAl_2O_4$–$0.17TiO_2$ ceramics doped with 10 wt% B_2O_3–Bi_2O_3–SiO_2–ZnO (BBSZ) glass could be sintered at 950 °C [12]. The aim of this work is to prepare $ZnAl_2O_4$-based glass–ceramic composites using a reaction between zinc borosilicate (ZBS) glass and Al_2O_3 at low temperature.

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 the 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 disk milling and a ball milling using zirconia balls in a wet condition with ethanol, glass powders were obtained. ZBS glass–Al_2O_3 system composed of 20–50 vol% glass was ball milled for 24 h and then dried. The disk type samples with a 15 mm in diameter were prepared by a pressing of powder mixtures under ca. 14 MPa and a sintering at between 600 °C 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 2θ range of 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 by 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 $\Delta f_{3\ dB}$, which was recorded at 3 dB level of the resonant peak, and the insertion loss were measured [13]. The temperature coefficient of resonant frequency (τ_f) was measured using an Invar cavity in the temperature range of 25–85 °C.

3. Results and discussion

The deformation temperature of the ZBS glass, i.e., the temperature at the maximum value of the thermal expansion curve, was determined as 588 °C, which was similar to the value in the literature; the value for ZBS glass with the composition of $60ZnO$–$30B_2O_3$–$10SiO_2$ (in mol%, Zn60B30Si10) was reported as 582 °C by Wu and Huang [14]. 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. The density, deformation point and dielectric properties of ZBS glasses are summarized in Table 1 and these glasses showed similar properties except $Q \times f_0$ and τ_f.

The linear shrinkage behavior of ZBS glass–Al_2O_3 composite containing from 20 vol% to 50 vol% ZBS glass sintered between 600 °C and 950 °C for 2 h is shown in Fig. 1.

Table 1
Density, deformation temperature and dielectric properties of ZBS glasses

	ZBS glass	Zn60B30Si10
Density (g/cm^3)	3.57	3.60[a]
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)	4 465	1 439
τ_f (ppm/°C)	−10	−21
Remarks	This work	Ref. [13]

[a] Ref. [15].

For all specimens sintered at 600 °C the shrinkage was limited to 1–4% due to the low sintering temperature. When the sintering process was carried out above 650 °C, 50 vol% ZBS glass–Al_2O_3 composite showed a large shrinkage whereas the compositions up to 40 vol% glass exhibited a relatively low shrinkage below 6%. It is understandable that the glass content in this system needs 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% [16]. The microstructures of ZBS glass–Al_2O_3 composite containing from 20 vol% to 50 vol% ZBS glass sintered at 900 °C are shown in Fig. 2. The large amount of pore was observed for the compositions up to 40 vol% glass. The investigation of phase formation and microwave dielectric properties, therefore, was conducted for 50 vol% ZBS glass–Al_2O_3 composite although some closed pores still existed.

By and large, as the amount of glass increased, the shrinkage increased as shown in Fig. 1, implying that the sintering behavior of this work could be explained by the theory of the liquid phase sintering. It has been reported that the classical theory of liquid phase sintering assumed densification occurred in three stage; particle rearrangement, solution-precipitation, and solid-state sintering [17]. In the first stage of particle rearrangement, densification occurred rapidly as soon as the liquid phase was formed. Pores were filled through liquid phase

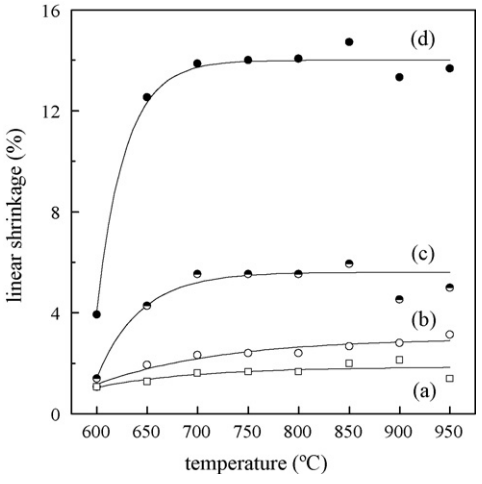

Fig. 1. Linear shrinkage of ZBS glass–Al_2O_3 system: (a) 20 vol% glass, (b) 30 vol%, (c) 40 vol%, and (d) 50 vol%.

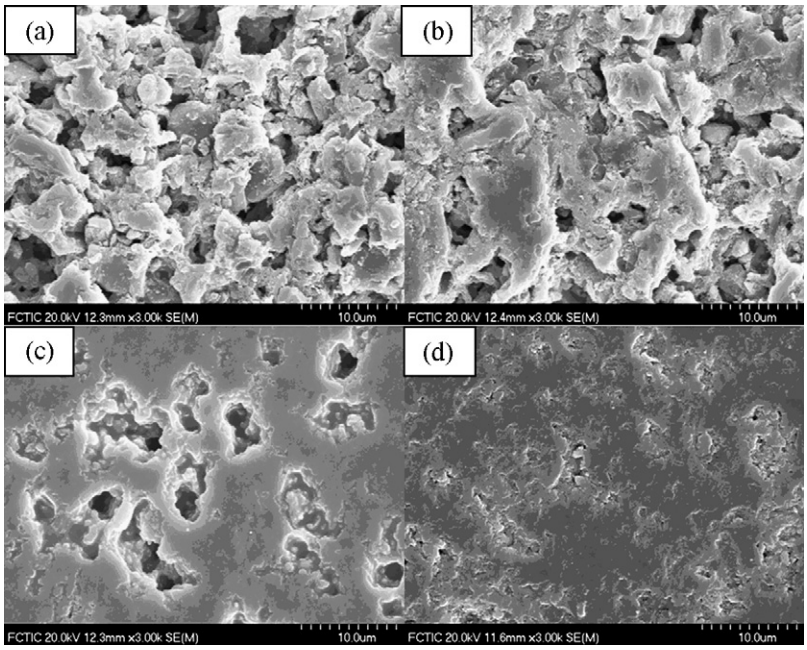

Fig. 2. Microstructures of ZBS glass–Al_2O_3 system sintered at 900 °C for 2 h: (a) 20 vol% glass, (b) 30 vol%, (c) 40 vol%, and (d) 50 vol%.

redistribution, and the particles were rearranged due to capillary pressure, resulting in closer packing. For 50 vol% ZBS glass–Al_2O_3 composite, a steep increase of the shrinkage was observed up to 700 °C. And the shrinkage behavior was almost flat above 700 °C after the steep increase, indicating that one-stage densification process occurred.

The powder X-ray diffraction patterns of Al_2O_3 and 50 vol% ZBS glass–Al_2O_3 composite sintered between 700 °C and 900 °C are shown in Fig. 3. The crystalline phase of $ZnAl_2O_4$ was already formed at 700 °C, indicating that the solution-precipitation stage of the liquid phase sintering might occur below 700 °C; it is considered that $ZnAl_2O_4$ was precipitated as a crystalline phase after the dissolution of Al_2O_3 particles in the liquid ZBS glass. The steep increase of the shrinkage, therefore, might be simultaneously corresponded to the first stage of particle rearrangement and the second of solution-precipitation in the liquid phase sintering. The formation of crystalline $ZnAl_2O_4$ with the consumption of liquid phase below 700 °C caused a diminution of liquid phase and a hindrance of further shrinkage.

On the other hand, Jantunen et al. reported that nearly full density of 97% was achieved in the ZBS glass/$MgTiO_3$–$CaTiO_3$ system using 70 wt% of ZBS glass [18]. Two-stage sintering behavior in this system may be correlated to the high density; the first stage shrinkage correlated with the onset of liquid phase and the second corresponded to the formation of crystalline phases such as $ZnSiO_4$, TiO_2, $ZnTiO_3$, and $Mg_2ZnTi(BO_3)_2O_2$ with the extinction of all amorphous phases. According to the consumption of zinc in the ZBS glass by the formation of $ZnAl_2O_4$, the composition of the glass was shifted to the B_2O_3 and SiO_2 rich side and it might be 71.4 wt%B_2O_3–28.6 wt%SiO_2 on the assumption of the complete consumption of zinc. It was reported that there was a large range of liquid phase in the B_2O_3–SiO_2 binary system at 950 °C [19]; the range from B_2O_3 to a composite 33 wt%B_2O_3–67 wt%SiO_2 approximately was an amorphous phase. To get further shrinkage in this work, therefore, the crystallization of the amorphous phase composed of B_2O_3 and SiO_2 is necessary. Because unreacted Al_2O_3 and SiO_2 in amorphous phase existed after the sintering, the supplementary addition of alkali earth oxide to the ZBS glass might be one of the methods to achieve the formation of crystalline phases such as

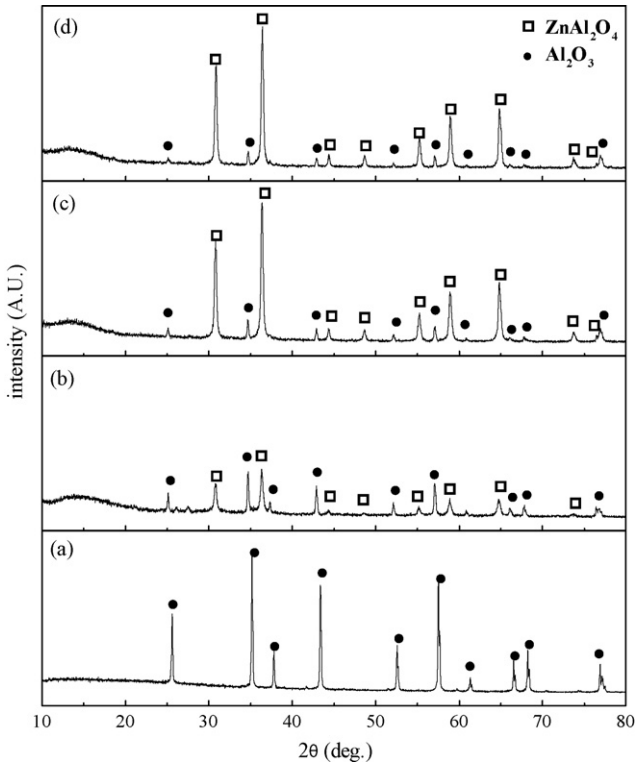

Fig. 3. Powder XRD patterns of (a) Al_2O_3 and 50 vol% ZBS glass–Al_2O_3 composite sintered at (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Table 2
Physical and dielectric properties of 50 vol% ZBS glass–Al_2O_3 composite sintered between 700 °C and 950 °C

	Sintering temperature (°C)					
	700	750	800	850	900	950
Density (g/cm^3)	–	2.81	3.00	3.00	2.98	2.86
Linear shrinkage (%)	13.9	14.0	14.1	14.7	13.3	13.7
Dielectric constant, ε_r	6.61	6.01	5.96	6.00	5.72	5.77
Resonant frequency (GHz)	11.8	12.4	12.5	12.5	12.6	12.6
Q	223	746	1,156	1,357	1,415	1,458
$Q \times f_0$ (GHz)	2632	9239	14,412	16,951	17,757	18,346

the anorthite phase ($AO{\cdot}Al_2O_3{\cdot}2SiO_2$, A = alkali earth) which is now applied to LTCC substrates as mentioned at the part of introduction. It was reported that the anorthite phase was crystallized at temperatures above 900 °C [6]. Although glass–$ZnAl_2O_4$ composites could be successfully prepared using the ZBS glass and Al_2O_3 at relatively low temperatures, a study for the development of the appropriate densification process is necessary to improve the microstructure for the application to LTCC substrates.

Physical and dielectric properties of 50 vol% ZBS glass–Al_2O_3 composite sintered between 700 °C and 950 °C are summarized in Table 2. The dielectric constant (ε_r) was between 5.7 and 6.6; low density might be one of the reasons for the low dielectric constant. As sintering temperature increased, the quality factor ($Q \times f_0$) showed an increase of an S-type curve (Fig. 4); a high value of 17,757 GHz (1415 at 12.6 GHz) was obtained for the specimen sintered at 900 °C. It is understandable that an increase of the quality factor may be closely correlated with the amount of formed $ZnAl_2O_4$ as shown in Fig. 3. Although the quality factor of glass–$ZnAl_2O_4$ composite is lower than that of $ZnAl_2O_4$ (4590 at 12.27 GHz [10]) due to the low density and the presence of glass phase which did not crystallize at the sintering process, it is much higher than that of LTCC substrates; 200–600 at 2 GHz for alumina–borosilicate glass composite [1]. The temperature coefficient of resonant frequency (τ_f) was −21 ppm/°C, which may be mainly affected by $ZnAl_2O_4$ phase with −79 ppm/°C. In terms of dielectric properties, therefore, the application of glass–$ZnAl_2O_4$ ceramic composites to substrates for may be shown to be appropriate after an improvement of the density.

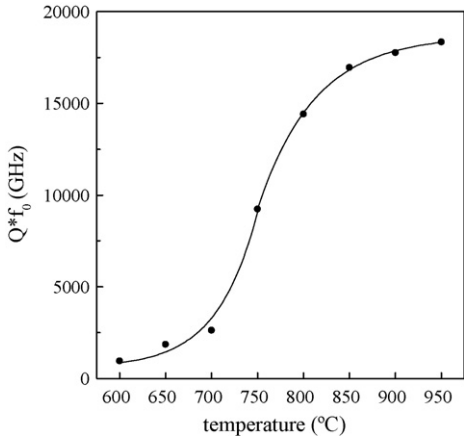

Fig. 4. Quality factor of 50 vol% ZBS glass–Al_2O_3 composite as a function of sintering temperature.

4. Summary

Glass–$ZnAl_2O_4$ composites were successfully prepared by a liquid phase sintering using Al_2O_3 powder and ZBS glass showing the deformation temperature of 588 °C. For the sufficient densification, the glass content was necessary at least 50 vol%. The linear shrinkage of 50 vol% ZBS glass–Al_2O_3 composite showed a steep increase up to 650 °C and a plateau behavior between 700 °C and 950 °C, indicating one-stage densification occurred. The powder X-ray diffraction results showed that $ZnAl_2O_4$ was formed even at low temperature of 700 °C. Consequently, the formation of the crystalline $ZnAl_2O_4$ caused the consumption of zinc in the ZBS glass, resulting in the hindrance of the shrinkage. The dielectric constant (ε_r) showed low value between 5.72 and 6.61 due to the relatively low density as well as the formation of $ZnAl_2O_4$ having a low ε_r. As the sintering temperature increased, the quality factor showed an S-type curve. It is considered that the amount of formed $ZnAl_2O_4$ might be corresponded to the increase of the quality factor; the quality factor ($Q \times f_0$) of the specimen sintered at 900 °C was 17,757 GHz (1415 at 12.6 GHz). The temperature coefficient of resonant frequency (τ_f) was −21 ppm/°C, which may be mainly affected by $ZnAl_2O_4$ phase with −79 ppm/°C.

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