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Short communication

Phase formation in the Al_2O_3-, quartz-, and cordierite-zinc borosilicate glass composites

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Abstract

Phase formation in the Al_2O_3-, quartz-, and cordierite-zinc borosilicate (ZBS) glass composites was investigated. Zinc in the ZBS glass reacted with ceramics with formation of zinc compounds such as zinc silicate and zinc aluminate. In the Al_2O_3-ZBS glass composite, $ZnAl_2O_4$ with a spinel structure was observed at relatively low temperature of 700 °C. β-$Zn_3B_2O_6$ of the high-temperature polymorph and α-Zn_2SiO_4 of willemite structure were formed at 800 °C in the quartz-ZBS glass composite and β-$Zn_3B_2O_6$ disappeared above 850 °C whereas α-Zn_2SiO_4 was observed up to 900 °C. In the cordierite-ZBS glass composite, the cordierite phase was decomposed by the reaction with the ZBS glass with formation of α-Zn_2SiO_4 and $ZnAl_2O_4$.

Keywords: A. Sintering; B. Composites; X-ray methods; D. Glass ceramics

1. Introduction

Studies on low-temperature co-fired ceramics (LTCC) have been intensively carried out due to their applications to multichip modules (MCM) and surface mounting devices (SMD). The sintering temperature of LTCC with Ag electrode should be less than 900 °C due to a relatively low-melting temperature of Ag [1]. The ceramic-glass composite which is one of LTCC-types is obtained by a liquid phase sintering using low-melting point glasses working as a flux agent and ceramics as filler [2]. Al_2O_3 has been widely used as ceramic filler and some candidates such as spinels, forsterite, and willemite have lately attracted considerable attention because of their excellent dielectric properties [3,4].

On the other hand, Borosilicate glasses are generally used as flux agent due to their capability of the glass formation at low temperature, superior chemical resistance, and good dielectric properties [5]; borosilicate glasses have high-electrical resistance and low-dielectric losses according to their continuous atomic structures with SiO_4 and BO_3 configurations joined to form (–Si–O–B–O–) linkage whereas alkali containing glasses show relatively high-dielectric losses due to weak bonding in glass network [6]. Zinc borosilicate glass exhibited superior dielectric properties with the dielectric constant, $\varepsilon_r = 6.88 \sim 7.56$, the $Q \times f$ value $= 1412 \sim 1733$ GHz, and the temperature coefficient of resonant frequency, $\tau_f = -84 \sim -3$ ppm/°C [7]. In this work, phase formation in the Al_2O_3-, quartz-, and cordierite-zinc borosilicate (ZBS) glass composites was investigated.

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. The commercial powders of Al_2O_3 (purity 99.9%) and quartz (99.9%) and the synthesized cordierite powder which was fabricated through a solid-state reaction with MgO (99.99%), Al_2O_3 (99.9%), and quartz (99.9%) powders were used as

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ceramic filler and the ceramic-ZBS glass mixtures containing 40 or 50 vol.% glass were prepared by a ball milling for 24 h. The disk type specimens were obtained by a pressing of powder mixtures under ca. 14 MPa and then the sintering process was conducted between 700 and 900 °C for 2 h. The phase analysis of the sintered ceramic-glass composites 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.

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; it of zinc borosilicate glass with the composition of 60ZnO–30B_2O_3–10SiO_2 (in mol%, Zn60B30Si10) was reported as 582 °C by Wu and Huang [7].

The powder X-ray diffraction patterns of the Al_2O_3-50 vol.% ZBS glass composite sintered at 700 and 900 °C are shown in Fig. 1. The crystalline phase of $ZnAl_2O_4$ was already formed at 700 °C and it showed the strong intensity in the diffraction pattern at 800 °C whereas the peak intensity of Al_2O_3 decreased, indicating that the reaction between zinc in the ZBS glass and Al_2O_3 was accelerated by the sintering temperature. However, the diffracted pattern of 900 °C was very similar with that of 800 °C due to the consumption of zinc in the ZBS glass. The adjustment of ratio between the ZBS glass and Al_2O_3 is, therefore, necessary to prepare complete $ZnAl_2O_4$-glass composites. It has been reported that $ZnAl_2O_4$ could be synthesized at high temperature of 1200 °C or above through a solid-state reaction of ZnO and Al_2O_3 [8]. It is understandable that $ZnAl_2O_4$ was easily prepared at least 700 °C through the solid–liquid reaction between the Al_2O_3 powder and the ZBS glass, i.e., the liquid phase sintering. It has been reported that the classical theory of the liquid phase sintering assumed densification occurred in three stage; particle rearrangement, solution-precipitation, and solid-state sintering [9]. On the other hand, $ZnAl_2O_4$ with a spinel structure is one of the candidate materials for substrate application in low-temperature co-fired ceramics (LTCCs) due to its excellent dielectric properties with $\varepsilon_r = 8.5$, $Q \times f = 56{,}320$ GHz, and $\tau_f = -79$ ppm/°C [10].

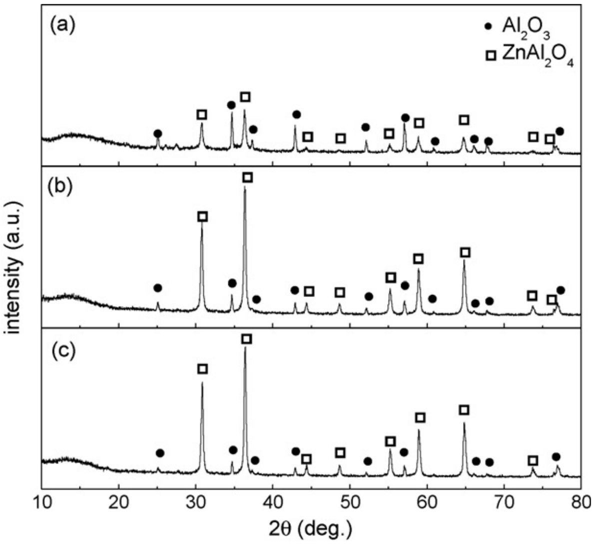

Fig. 1. Powder X-ray diffraction patterns of the Al_2O_3-50 vol.% ZBS glass composite sintered at (a) 700 °C, (b) 800 °C, and (c) 900 °C.

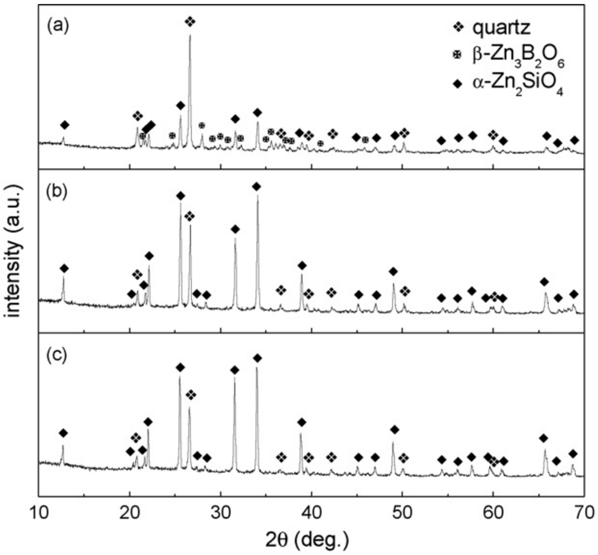

Fig. 2. Powder X-ray diffraction patterns of the quartz-50 vol.% ZBS glass composite sintered at (a) 800 °C, (b) 850 °C, and (c) 900 °C.

Fig. 2 shows the powder X-ray diffraction patterns of the quartz-50 vol.% ZBS glass composite sintered between 800 and 900 °C. At 800 °C, β-$Zn_3B_2O_6$ was crystallized but it disappeared above 850 °C. $Zn_3B_2O_6$ (zinc orthoborate, ZnO·B_2O_3) is one of the compounds such as $Zn_4B_6O_{13}$ (zinc metaborate, 4ZnO·3B_2O_3) and ZnB_4O (zinc diborate, ZnO·2B_2O_3) in the ZnO–B_2O_3 binary system [11]. It was reported that this compound was crystallized from the ZBS glass having the same composition with this work in the temperature range of 690–730 °C [12]. It has two polymorphs of the low-temperature α-form with a triclinic structure and the high-temperature β-form with a monoclinic. The transition and the melting point of this compound were, however, respectively, reported as 964 and 1080 °C in the ZnO–B_2O_3 binary system [11,13]. The presence of silica in the ZBS might affect on the phase transition and the melting point and further study is necessary.

On the other hand, α-Zn_2SiO_4 was observed above 800 °C. Five polymorphs of Zn_2SiO_4 have been found at various temperatures and pressures [14]. 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 [15]. From the result that the peak intensity of quartz decreased as the sintering temperature increased, it is considered that α-Zn_2SiO_4 was formed through the reaction between zinc in the ZBS glass and quartz powder. It was reported that β-form as a metastable phase could be crystallized from glass phases whereas an attempt to prepare this phase by direct solid-state reaction was unsuccessful [16]. This form

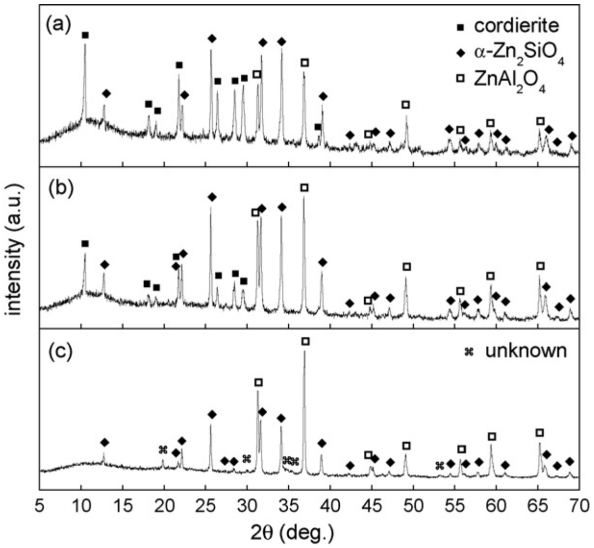

Fig. 3. Powder X-ray diffraction patterns of the cordierite-40 vol.% ZBS glass composite sintered at (a) 750 °C, (b) 800 °C, and (c) 850 °C.

could, however, not be obtained in this work. Because α-Zn_2SiO_4 also shows excellent dielectric properties with $\varepsilon_r = 6.6$, $Q \times f = 219{,}000$ GHz, and $\tau_f = -61$ ppm/°C, an application on substrates is expected [17].

The powder X-ray diffraction patterns of the cordierite ($Mg_2Al_4Si_5O_{18}$)-40 vol.% ZBS glass composite sintered between 750 and 850 °C are shown in Fig. 3. The crystalline phases of the cordierite, α-Zn_2SiO_4 and $ZnAl_2O_4$ were observed at 750 and 800 °C and the cordierite phase disappeared at 850 °C. It is understandable that the cordierite phase was decomposed by the reaction with the ZBS glass and the formation of α-Zn_2SiO_4 and $ZnAl_2O_4$ resulted in. It is interesting that the compounds containing magnesium were not formed in this system; magnesium might dissolve into the ZBS glass instead of zinc which was crystallized as the silicate and the aluminate. On the other hand, unknown phase(s) observed at 850 °C might contain magnesium. It could, therefore, be concluded that the ZBS glass reacted with Al_2O_3, quartz, and cordierite ceramics and α-Zn_2SiO_4 and $ZnAl_2O_4$ which are potential candidates of microwave dielectric ceramics were successfully formed at relatively low temperature. The investigation on dielectric properties of these composites will be reported.

4. Conclusions

Phase formation in the Al_2O_3-, quartz-, and cordierite-zinc borosilicate (ZBS) glass composites was investigated. In the Al_2O_3-50 vol.% ZBS glass composite, $ZnAl_2O_4$ with a spinel structure was observed at relatively low temperature of 700 °C. α-Zn_2SiO_4 of willemite structure was formed above 800 °C in the quartz-50 vol.% ZBS glass composite. In the cordierite-40 vol.% ZBS glass composite, α-Zn_2SiO_4 and $ZnAl_2O_4$ were formed above 750 °C and the cordierite phase disappeared at 850 °C. It could be concluded that zinc in the ZBS glass reacted with ceramics and zinc compounds such as zinc silicate and zinc aluminate were formed.

Acknowledgements

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