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Effect of frit size on microwave properties of glass–ceramic in low temperature co-fired ceramics

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Abstract

For low temperature co-fired ceramics (LTCC) materials, glass–ceramic composites consisting of a $BaNd_2Ti_5O_{14}$ ceramic and the lead-free rare earth derived boron glasses (L glass) were tested with different frit size. The glass–ceramic composites were evaluated for thermal properties and microwave dielectric properties (ε_r, Qf_0: quality factor). At low temperature, the sintered body demonstrated applicable properties such as high relative density of over 80% and various dielectric properties, namely, 17–20 for ε_r and 3376–10,000 GHz for Qf_0. The results suggest that the microwave properties are controlled by frit size for low temperature co-fired ceramic compositions at high-frequency application.

Keywords: LTCC; Glass–ceramic; Microwave dielectric properties; Surface crystallization

1. Introduction

Owing to the limited sintering temperature capability of metal electrodes such as Ag or Cu, low temperature co-fired ceramics (LTCCs) with a sintering temperature below 900 °C have been in great demand. LTCCs are also of great importance to the electronic industry for building smaller RF modules and for fulfilling the need to miniaturize the devices in the wireless communication industry [1]. However, the microwave dielectric materials that possess large dielectric constant and high quality factor usually need a very high sintering temperature and long soaking time to achieve high enough density.

There are three approaches to reducing the sintering temperature of the dielectric ceramics: low melting glass addition [2], chemical processing [3], and smaller particle sizes for the starting materials [4]. Liquid-phase sintering with glass additives is the least expensive among them. However, if the amount of frits is large, the network formers contained in the remaining glass materials such as B_2O_3 and SiO_2 can profoundly absorb the microwave power at high frequencies, degrading the quality factor of the final materials [5].

Compared to the liquid phase sintering with low-melting glass frits in which the glass phase remains, another approach using a ‘glass–ceramic’ produces a different result since the glass frits crystallize during the sintering stage. The advantages offered by this glass–ceramic approach include shape stability after sintering, improved dielectric properties, mechanical strength, and controlled thermal expansivity. Yet there have been few studies concerning the use of glass–ceramic materials with a mid-range dielectric constant (>15) [6,7].

In this study, the glass/ceramic matrix composites consisting of the rare earth derived L (La_2O_3–B_2O_3–TiO_2) glass and a commercial ceramic (BaO–Nd_2O_3–TiO_2 system) were investigated for their microwave properties according to the frit size. We discuss the sintering characteristics of this composite, the mechanism of interaction between the glass and ceramic materials under different frit sizes, and finally the effect of microstructure of the sintered composites on the dielectric properties.

2. Experimental procedure

The raw materials for the glass frit were La_2O_3, H_3BO_3, and TiO_2, which have high purity (Aldrich, USA). The batch L glass ($20La_2O_3$–$60B_2O_3$–$20TiO_2$ (in mol%)) was melted in a platinum crucible at 1300 °C for 1 h. The glass melt was quickly poured and quenched on a copper plate and pulverized in a planetary mono mill for 10 h (d_{50}: 1.5 μm) and vibration mill (d_{50}: 6 μm). The ceramic material used was a commercial BNT (BaO–Nd_2O_3–TiO_2) ceramic powder (MBRT90, Fuji Titanium Ind., Japan, d_{50}: 2.9 μm), which was determined via XRD (X-ray diffractometer, APD system, PANalytical, Almero, The Nether-

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lands) to be thermally stable in the single $BaNd_2Ti_5O_{14}$ phase. The glass powder and ceramic materials (60:40, wt.%) were mixed using a ball mill for 24 h and then dried. The dried powder was formed into pellets using a metal mould (1.5 cm in diameter and 0.8 cm in height).

To improve the densification, cold isostatic pressing (under 200 MPa) was applied to the pellets, which were sintered at 850 °C for 1 h with a heating rate of 10 °C/min.

The bulk density of the sintered samples was determined by the Archimedes method. The glass transition temperature (T_g), the onset point of crystallization (T_c), and the crystallization peak (T_p) were determined using a differential thermal analyzer (DTA-TA 1600, TA instruments, New Castle, DE) at a heating rate of 10 °C/min. The shrinkage of the samples was measured by a dilatometer (Model DIL402 PC, Netzsch Instruments, Selb, Germany). The microstructure of the samples was examined using a scanning electron microscopy (SEM, HITACHI, Tokyo, Japan). The crystal phase of the samples was detected using XRD (X-ray diffractometer, APD system, PANalytical, Almero, The Netherlands). Microwave dielectric properties were measured on a network analyzer (8720Es, Agilent, Palo Alto, CA) at a range of 7 GHz using a resonant cavity and a split-post test fixture [8,9].

3. Results and discussion

The thermal and dielectric properties of the L glass have been investigated in our previous studies [10]. Using with the dielectric constant of the L glass, the dielectric constant was predicted by various equations (Fig. 1) [11]. The equations for the prediction of permittivity are limited with porosity, grain size, crystal phases, and grain boundary. As shown in Fig. 1, the composites have an optimal dielectric constant for LTCC dielectric materials. In this study, the composite mixed with L glass and BNT ceramic (60:40, wt.%) was chosen with different frit sizes.

The starting temperature of shrinkage was remarkably different for the BNT ceramic and for the composites, as shown in Fig. 2. The shrinkage of the BNT ceramic started at 1210 °C, while the composites mixed with BNT ceramic and L glass frit shrank at 710 °C. Above the Littleton softening point of the glass ($T_s = 722\,°C$), the shrinkage of composites dramatically increased, and a different maximum shrinkage was reached depending upon the frit size. The finishing (complete) temperature for shrinkage in Fig. 2 shifted slightly to higher temperature with increasing ceramic content in the composites. The shrinkage of the (a) composite (6 μm L glass frit and BNT ceramic (60:40, wt.%)) was higher than that of the (b) composite (1.5 μm L glass frit and BNT ceramic (60:40, wt.%)).

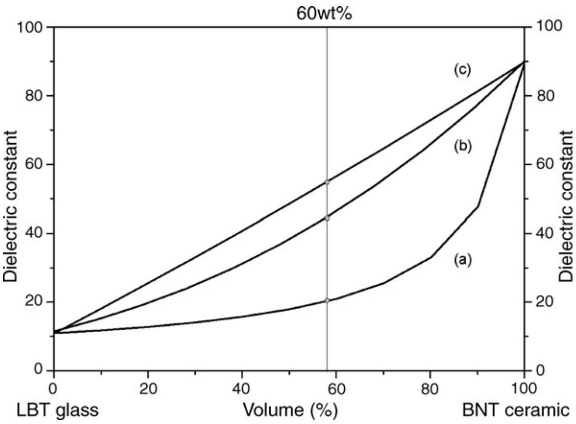

Fig. 1. Prediction for dielectric constant of composites (L glass and BNT ceramic) calculated by (a) Peon–Iglesias equation, (b) Looyenga equation, and (c) a mixture rule [11].

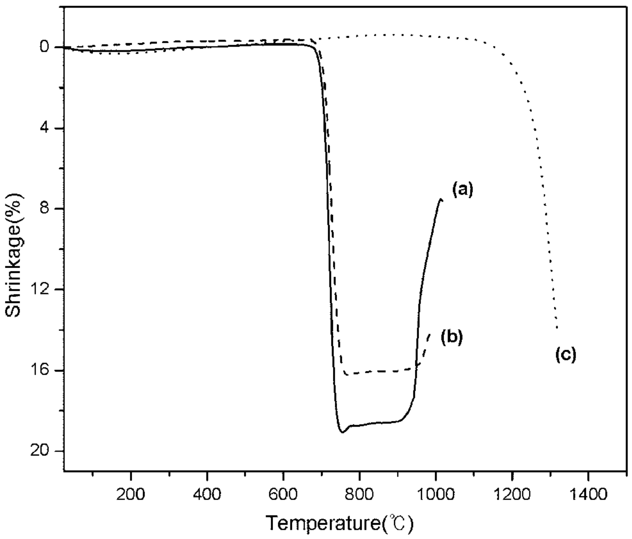

Fig. 2. Shrinkage of different materials (a) 6 μm L glass frit and BNT ceramic (60:40, wt.%), (b) 1.5 μm L glass frit and BNT ceramic (60:40, wt.%), and (c) only BNT ceramic.

The degree of densification was calculated by the relative density according to the frit size. The relative density for composite (6 μm L glass frit and BNT ceramic (60:40, wt.%)) sintered at 850 °C for 1 h was approximately 95%. However, that of another composite (1.5 μm L glass frit and BNT ceramic (60:40, wt.%)) was 80%. The high shrinkage induced a high relative density.

As shown in Fig. 3, the mixture of DTA and dilatometer curves assumes that the composites with different frit sizes crystallize at lower temperature and interrupt the shrinkage. Comparison of the thermal properties of the glass and those of the composites reveals a slight decrease in the T_c and T_p. From the DTA results of L glass and composites, the second T_p of the composites should be formed from L glass. Beside, the second T_p is moved by frit size in the DTA curve. Movement of the second T_p is attributed to the formation of a crystal phase with the mixed powder of L glass-1.5 μm and BNT ceramic (60:40, wt.%), which is faster than the mixed powder of L glass-6 μm and BNT ceramic (60:40, wt.%). Moreover, the faster formation of a crystal phase provides a lower shrinkage. Thus, the T_p of the L glass and the second T_p of the mixed powder of L glass frit and BNT ceramic is influenced by the frit size. In other words, the shrinkage of the composite is caused by the second T_p.

As shown in Fig. 4, the sintered composites include irregular pores generated by sintering and crystallization. The pores of the composite (L glass-6 μm and BNT ceramic (60:40, wt.%)) are positioned in homogenously. However, those of the composite (L glass-1.5 μm and BNT ceramic (60:40, wt.%)) are

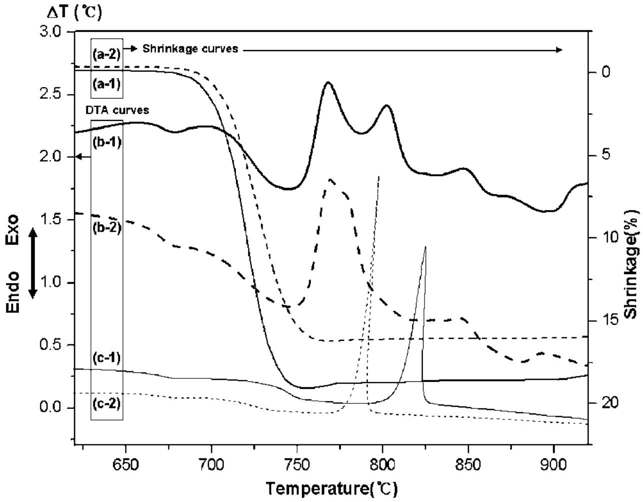

Fig. 3. DTA and shrinkage curves for L glass and composites with different frit sizes: (a-1), (b-1) 6 μm L glass frit and BNT ceramic (60:40, wt.%), (a-2), (b-2) 1.5 μm L glass frit and BNT ceramic (60:40, wt.%), (c-1) 6 μm L glass frit, and (c-2) 1.5 μm L glass frit.

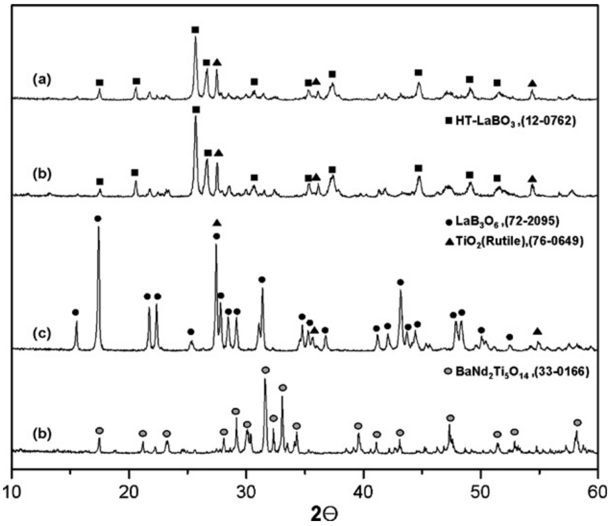

Fig. 5. X-ray diffraction patterns showing different phases according to the materials: (a) 1.5 μm L glass–BNT ceramic (60:40, wt.%), (b) 6 μm L glass–BNT ceramic (60:40, wt.%), (c) L glass sintered at 850 °C for 1 h, and (d) BNT ceramic as raw material.

Table 1
Microwave properties of the composites with different frit sizes

LBT glass and BNT ceramic (60:40, wt.%), glass frit size (μm)	Sintering at 850 °C for 1 h	
	ε_r	Qf_0 (GHz)
d_{50}: 1.5	17.7	3376
d_{50}: 6	19.9	8218

f_0: resonance frequency; Qf_0: quality factor at the resonace frequency.

distributed irregularly. In addition, the pore sizes of the composite (L glass-1.5 μm and BNT ceramic (60:40, wt.%)) sintered at 850 °C are bigger than the composite (L glass-6 μm and BNT ceramic (60:40, wt.%)). This variation in the pore size of the composites appears to be caused by a difference in the starting temperature for densification and crystallization (Fig. 3). Thus, the ceramic fillers (BNT ceramic) that are added to the glass matrix play the role of nuclei in crystallization of the glass matrix. Furthermore, the dissolution of the ceramic filler into the glass matrix changes the composition of the glass and the starting temperature of crystallization.

The crystal phases of the composites and only the L glass sintered at 850 °C for 1 h are shown in Fig. 5, and BNT ceramic powders were identified from JCPDS cards. Although the BNT ceramic has a stable crystal phase under 900 °C and crystal phases of L glass sintered at 850 °C for 1 h are LaB_3O_6 and TiO_2, the crystal phases of the composites sintered at 850 °C for 1 h are determined with the crystal phases of HT-$LaBO_3$ and TiO_2. The BNT ceramic that reacted to the L glass can dissolve into the L glass matrix. Furthermore, the crystal phase of LaB_3O_6 from the L glass may dissociate the crystal phase of $LaBO_3$ and B_2O_3 so that the B_2O_3 may play the role of a sintering agent. When the composite of L glass-6 μm and BNT ceramic (60:40, wt.%) is compared with the composite of L glass-1.5 μm and BNT ceramic (60:40, wt.%)) sintered at 850 °C in Fig. 5, the difference means the intensity of X-ray. It can also be the difference of crystallinity in each of the composite.

As shown in Table 1, although the composites consist of the same amount of glass and ceramic, the microwave properties are different when frit sizes are different. As mentioned earlier, the different frit sizes have led to different morphologies, relative

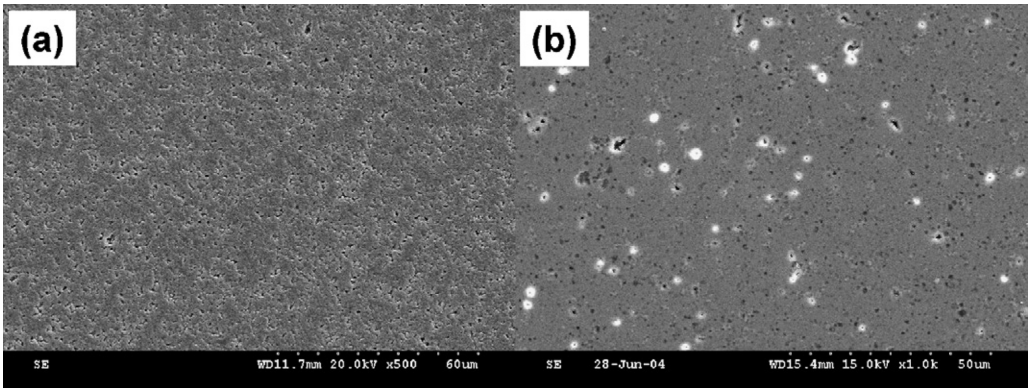

Fig. 4. Morphology of the composite sintered at 850 °C for 1 h: (a) L glass-6 μm and BNT ceramic (60:40, wt.%) and (b) L glass-1.5 μm and BNT ceramic (60:40, wt.%).

density and T_p. It means that the different frit sizes significantly affect in the microwave properties.

4. Conclusion

The glass–ceramic composites were evaluated for thermal properties and microwave dielectric properties (ε_r, Qf_0) according to the frit sizes used. At 850 °C, the sintered body demonstrated a relation between thermal and microwave properties. Thus, the composites consisting of different frit sizes affect the morphology, density of crystal phases, shrinkage, and relative density. These results make the composites consisting of different frit sizes to have different microwave properties, namely, 17–20 for ε_r, 3376–10,000 GHz for Qf_0. These findings lead us to conclude that frit size is capable of controlling the morphology, shrinkage, relative density, and microwave dielectric properties.

Acknowledgements

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