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Effects of Al_2O_3 addition on physical properties of diopside based glass–ceramics for LED packages

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Abstract

One of the main problems of currently used Al_2O_3/glass composites for LED (light emitting diode) packaging materials is deterioration of the heat emission property due to the lower thermal conductivity of glass. In the present study, glass frit of a CaO–MgO–SiO_2 system of stoichiometric diopside composition with the addition of various amounts of Al_2O_3 was milled, pressed into pellets isostatically, and heat-treated to fabricate diopside-based glass–ceramics. Effects of microstructure and crystallinity of the diopside phase produced in the glass–ceramics on the thermal conductivity, thermal diffusivity, density, and specific heat capacity were analyzed as a function of Al_2O_3 addition to investigate the feasibility of utilizing diopside-based glass–ceramics in LED packaging applications.

Keywords: C. Thermal conductivity; C. Thermal properties; D. Al_2O_3; D. Glass ceramics

1. Introduction

The illumination market using LEDs (light emitting diodes) has grown explosively owing to significant advantages such as energy savings, long life time, and low power consumption [1]. The recent trend for LEDs is high power and luminance, and thus releasing the heat accumulated in the LED device in use is a serious problem that should be resolved. If the heat is not released from the LED device, the chips and PCB (printed circuit board) will be deteriorated, causing decreased life time of the LED. With current packaging technology, however, it is difficult to maintain optimum temperature of 25–30 °C for LEDs [2].

Pure alumina, Al_2O_3, is a ceramic that exhibits high thermal conductivity of about 40 W/mK at 20 °C. However, its sintering temperature of around 1700 °C in air is too high for LED packaging applications. Hence, a small amount of glass frit is normally added to Al_2O_3 in order to lower the sintering temperature. The thermal conductivity of Al_2O_3/glass composites, however, is reduced to approximately 1.1, which is not sufficient to ensure suitable operating conditions for high power LEDs.

The LTCC (low temperature co-fired ceramic) process can be used to make packages for LEDs. In the LTCC context, ‘co-fired ceramic’ means that the ceramic support structure and conductive, resistive, or dielectric materials are fired in a kiln at the same time, and ‘low temperature’ means that the sintering temperature is less than 1000 °C. Glass–ceramics are known to be favorable for the LTCC process, because there is typically no pressing or sintering. As a result, in contrast with sintered ceramics, no pores are fabricated at lower temperature [2,3].

Glass–ceramics fabricated via the LTCC concept have been applied to various modules and substrates, including radio and micro-wave application components in electronic packaging [4,5].

In this study, a diopside ($CaMgSi_2O_6$) with a melting point of 1391 °C [4], density of 3.27 g/cm^3, and thermal conductivity of 3.1 W/mK [6] was chosen as the main crystalline phase of the fabricated glass–ceramics.

The thermal properties, crystallization tendency, and microstructural change of the diopside-based glass–ceramics were evaluated as a function of Al_2O_3 addition [7]. Finally, the possibility of utilizing the diopside-based glass–ceramics

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fabricated in this study for application to LED packaging in conjunction with the LTCC concept was investigated.

2. Experimental procedures

Al_2O_3 of 0–6 wt% was added to the parent glass of a CaO–MgO–SiO_2 system. High-purity oxide powders of SiO_2 (High Purity Chemicals, Japan, 99.9%), CaO (High Purity Chemicals, Japan, 99.9%), MgO (High Purity Chemicals, Japan, 99.9%) and Al_2O_3 (Samchun Chemicals, Korea, 99%) were used as starting materials. A batch of stoichiometric diopside composition was milled using zirconia balls for 24 h. The uniformly mixed powder was melted in a alumina crucible at 1450 °C for 30 min and quenched in cold water to obtain a transparent glass sample.

The glass with diopside composition was crushed to less than 45 μm, mixed with Al_2O_3 of 0–6 wt% for 20 min in an alumina mortar, pressed into pellets under isostatic pressure of 1500 kg/cm^2, and sintered at 888 °C for 2 h in air with a heating rate of 10 °C/min.

A DTA (differential thermal analysis, STA 409C/CD, Netzsch Co., Germany) experiment for glass frit of under 45 μm was performed from room temperature to 1350 °C in air to determine the glass transition temperature and crystallization temperature. The identification of crystal phases of the sintered body was carried out using XRD (X-ray diffraction analysis, Pan'alytical, X'pert pro, Netherlands). The microstructure of the cross-section of the glass–ceramic was analyzed using a SEM (field emission scanning electron microscope, JSM-6500F, JEOL, Japan) after etching in 2 vol% HF solution for 30 s [8,9].

The thermal conductivity, thermal diffusion coefficient, and specific heat capacity were measured using a LFA (laser flash apparatus, NETZSCH, Germany).

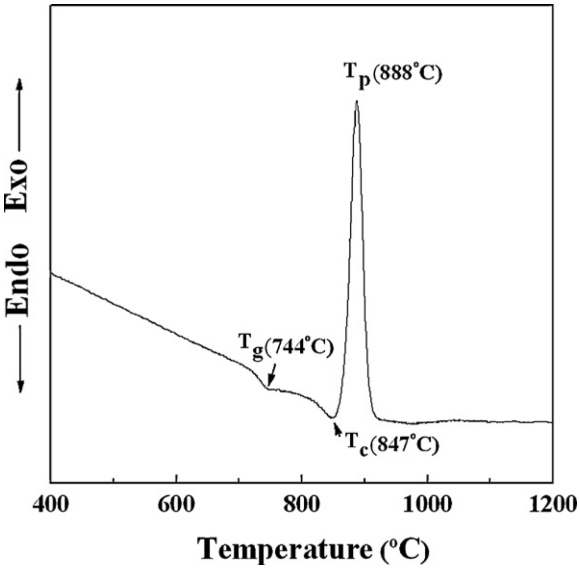


Fig. 1. DTA curve of CaO–MgO–SiO_2 glass frit system measured at a heating rate of 10 °C/min.

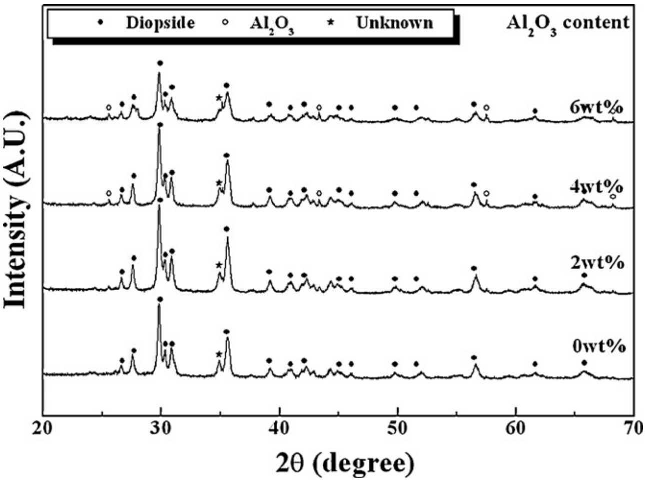


Fig. 2. XRD patterns of glass–ceramics of CaO–MgO–SiO_2 system containing various amounts of Al_2O_3.

3. Results and discussion

The glass transition temperature (T_g) and crystallization temperature (T_c) of the glass frit of stoichiometric diopside ($CaMgSi_2O_6$) composition were measured to be 744 °C and 888 °C, respectively, from the DTA curve obtained with a heating rate of 10 °C/min, as presented in Fig. 1. The crystallization temperature is sufficient for application to the LTCC process, and thus the glass–ceramics with added alumina were sintered at 888 °C for 2 h.

The XRD patterns of glass–ceramics containing 0–6 wt% alumina sintered at 888 °C for 2 h are shown in Fig. 2. The crystal phases in the fabricated glass–ceramics were identified as diopside (●) and Al_2O_3 (○), as shown in Fig. 2. The relative intensities of the main peak for the diopside of all specimens are shown in Fig. 3. The peak intensity of glass–ceramics containing 2 wt% Al_2O_3 was the highest among all specimens. The above results can be interpreted on the basis of microstructural observations.

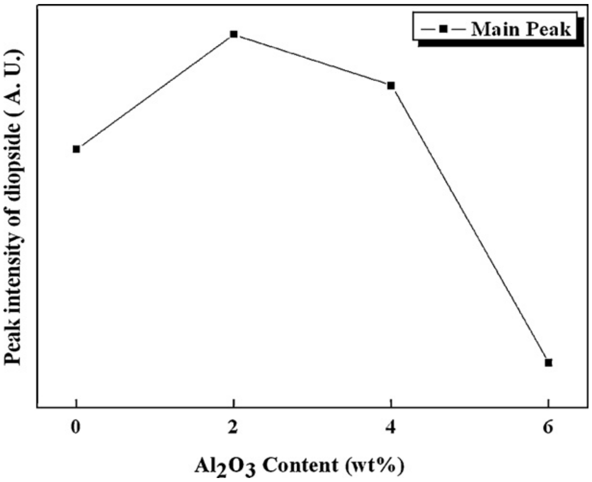
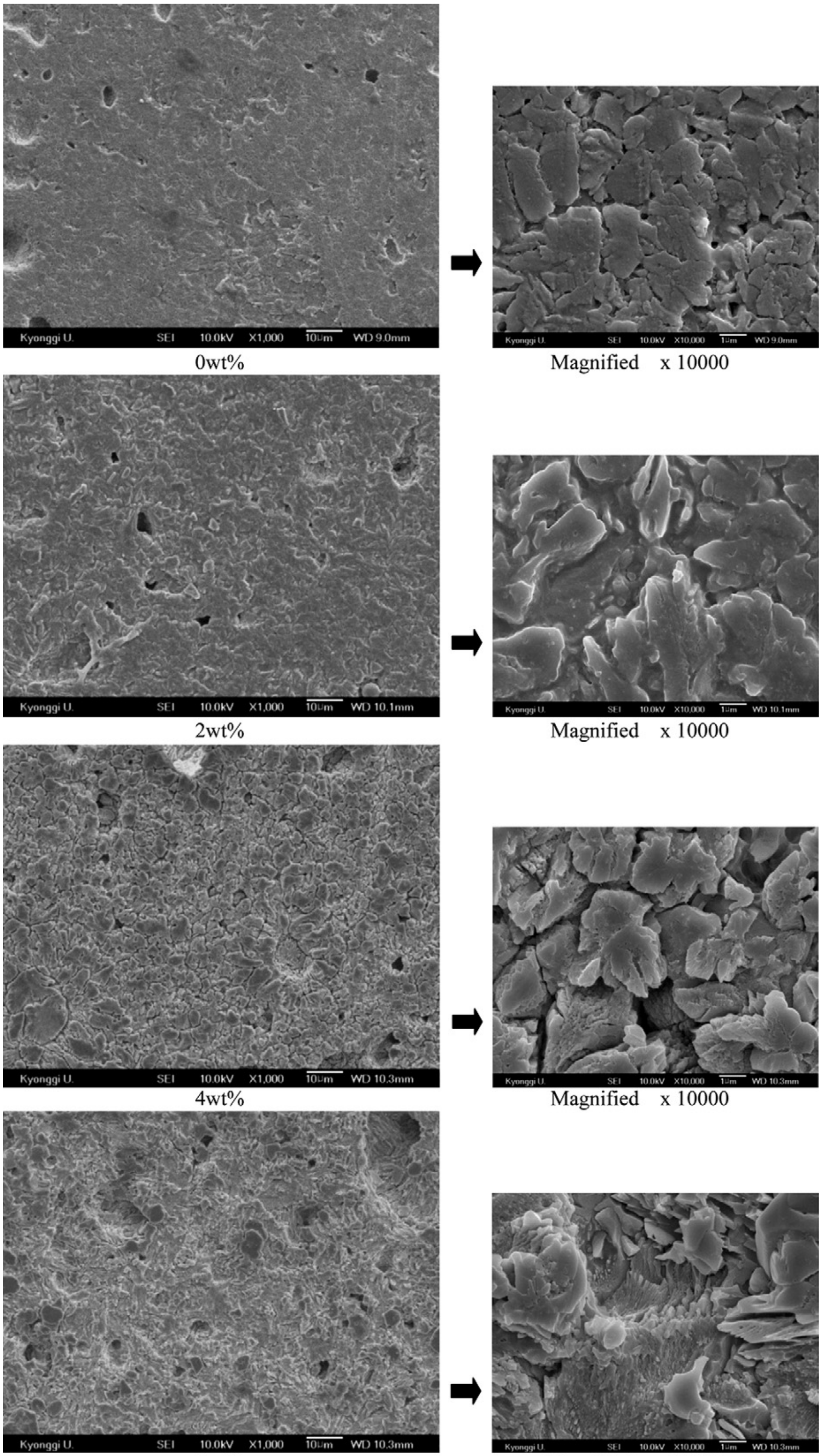


Fig. 3. The relative intensity of main peak of diopside phase in XRD patterns shown in Fig. 2.



0wt% Magnified x 10000

2wt% Magnified x 10000

4wt% Magnified x 10000

6wt% Magnified x 10000

Fig. 4. Microstructures for glass–ceramics of CaO–MgO–SiO_2 system containing various amounts of Al_2O_3.

The microstructures observed by SEM for the glass–ceramics containing 0–6 wt% alumina sintered at 888 °C for 2 h are shown in Fig. 4. The specimens with Al_2O_3 content above 4 wt% showed many pores and cracks in the microstructure. Meanwhile, for the glass–ceramics with 2 wt% alumina, a significant amount of liquid formed, covering most of the crystal particles. Furthermore, the edges and corners of these particles were blunt, and voids and cracks were filled.

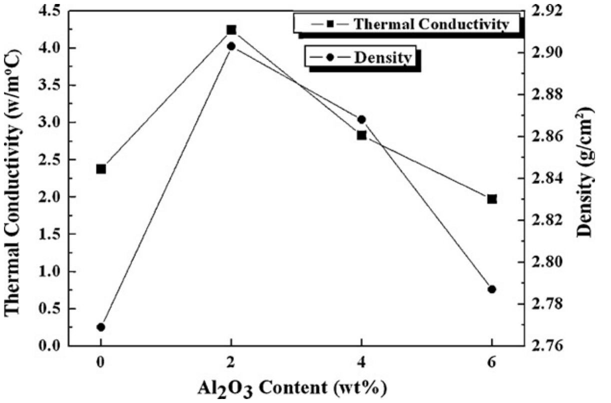


Fig. 5. Thermal conductivity and density of glass–ceramics of CaO–MgO–SiO_2 system containing various amounts of Al_2O_3.

Hence, the higher crystal peak intensity of the specimen with 2 wt% is attributed to the liquid, which accelerates the diffusion of ions, leading to crystallization.

The observation that the liquid was not formed in the glass–ceramics containing 4–6 wt% Al_2O_3 is ascribed to the higher refractoriness of ceramics with high Al_2O_3 content, which results in increased liquid formation temperature. The glass–ceramics with 4–6 wt% Al_2O_3 therefore have excessively high refractoriness to form a liquid at 888 °C. The exact amount of liquid and its effect on the degree of crystallinity, however, should be quantitatively analyzed by additional study.

The relation between thermal conductivity and density is clearly shown in Fig. 5, where it is seen that these two factors are proportional to each other. The thermal conductivity and density of the glass–ceramics with no added Al_2O_3 are 2.37 W/mK and 2.77 g/cm^3, respectively. These values are low compared to the results of Jeon et al. [6], where diopside glass–ceramics sintered at 900 °C/5 h in air had a thermal conductivity of 3.1 W/mK and density of 3.27 g/cm^3.

It is thought that the discrepancies between the measured values in this study and previously reported values could be narrowed if proper nucleation agents were used such that the degree of crystallinity was greatly enhanced [7].

In contrast, the glass–ceramics of 2 wt% alumina displayed thermal conductivity of 4.24 W/mK, which is 75% higher than that of glass–ceramics with no added Al_2O_3. On the contrary, for the glass–ceramics with more than 4 wt% Al_2O_3, the thermal conductivity and density decreased. These trends are consistent with the XRD results shown in Figs. 2 and 3.

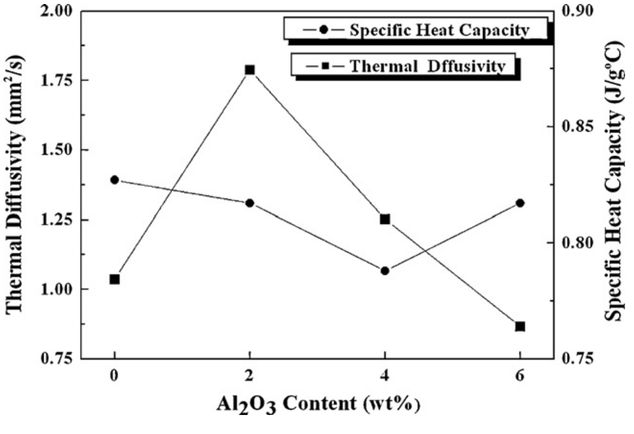


Fig. 6. Thermal diffusivity and specific heat capacity of glass–ceramic of CaO–MgO–SiO_2 system containing various amounts of Al_2O_3.

The thermal diffusivity and specific heat capacity are plotted as a function of the amount of added alumina in Fig. 6. The thermal diffusivity of the glass–ceramics with various amounts of Al_2O_3 showed the same trend as the thermal conductivity vs. Al_2O_3 addition in Fig. 5. The thermal diffusivity of 2 wt% alumina was the highest of 1.79 mm^2/s, which is 73% higher than that of the glass–ceramics with no added Al_2O_3.

The thermal conductivity (K) is given by Eq. (1),

$$K = k \times \rho \times C_p \tag{1}$$

where k is the thermal diffusivity [mm^2/s], ρ is density [g/cm^2], and C_p is the specific heat capacity [J/gk]. From several preliminary experiments, the thermal diffusivity was identified as the dominant factor among these three parameters in terms of expressing the thermal conductivity of the glass–ceramics fabricated in this study. The trend of specific heat capacity with the amount of Al_2O_3 added shown in Fig. 6 does not agree well with the trend of the thermal conductivity.

4. Conclusions

Al_2O_3 in a range of 0–6 wt% was added to a CaO–MgO–SiO_2 glass frit system in order to investigate the influence of alumina content on the thermal properties of diopside-based glass–ceramics. Low temperature sintering at 888 °C was possible to crystallize the diopside phase in the CaO–MgO–SiO_2 glass, thus making it suitable for application in a LTCC process. In addition, thermal conductivity of 4.24 W/mK and thermal diffusivity of 1.79 mm^2/s, the highest among all specimens, were obtained for glass–ceramics containing 2 wt% alumina. The addition of 2 wt% alumina also increased the degree of crystallization and induced densification of the glass–ceramics owing to the formation of a large quantity of liquid, which increased the diffusion rate of ions. The diopside-based glass–ceramics prepared in this study have better thermal conductivity than that of previously reported glass–ceramics and thus hold promise for LED packaging applications as they are expected to afford enhanced heat-releasing ability for high power LEDs.

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