

Dependence of thermal properties on the CaO/MgO ratio of CaO-MgO-SiO₂-(Li₂O) glass-ceramics

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The crystallization behavior and thermal properties of diopside-based glass ceramics fabricated from a CaO-MgO-SiO₂-(Li₂O) glass system were studied as functions of the CaO/MgO ratio. Crystalline diopside was identified as the main phase in all specimens with CaO/MgO ratios of 0.4 ~ 2.3. Small amounts of β -wollastonite and forsterite were generated in specimens of higher and lower ratios of CaO/MgO compared to the specimen of CaO/MgO = 1, respectively. The thermal conductivity increased with increasing major peak intensity of diopside. The thermal conductivities of the glass ceramics of CaO/MgO = 2.3 and 0.4 were 34% and 14% lower, respectively, in comparison with the value for the CaO/MgO = 1. The chemical resistance of the glass-ceramics to HF acid solution increased with decreasing CaO/MgO ratio due to the formation of forsterite phase. The diopside-based glass-ceramics of CaO/MgO ratio = 0.7 sintered at 823°C/2 hrs in the CaO-MgO-SiO₂-(Li₂O) system had a thermal conductivity of 3.3 W/mK, as high as in pure diopside, and much higher chemical durability than the pure diopside glass-ceramics. Thus, the diopside-based glass-ceramics containing a small amount of forsterite showed high feasibility for application to LED packaging materials through LTCC processing.

Key words: Thermal properties, Glass ceramics, Dopside, Forsterite, Chemical durability, CaO/MgO ratio.

Introduction

A light-emitting diode (LED) package is a device in which an LED chip is built and attached to a printed circuit board (PCB) [1]. Many efforts have been made to improve the output of LEDs in order to replace all other illuminators with LEDs. The main problem, however, is to release the heat that is generated and accumulated in LEDs, because the increased temperature due to heat accumulation reduces the efficiency and lifetime of the LED chips [2-4]. LED package technology using ceramics for this solution has been intensively studied, and alumina has been widely used for its high thermal conductivity and stability. Alumina, however, is difficult to sinter, thus requiring high heating temperature. Many ceramic compounds, such as diopside, wollastonite, and cordierite, have been studied over the last two decades to find possible substrates for electronic devices using the glass-ceramic process. These materials could be sintered at relatively low temperature by the glass-ceramic route, which is sufficient for them to be applied to LTCC (low temperature co-fired ceramics) processing [5].

Among these ceramic compounds, crystalline diopside fabricated using glass-ceramic processing has been applied to many fields due to its high physicochemical

stability [6-7]. However, the thermal properties of diopside-based glass-ceramics are not well known, including the thermal conductivity and diffusivity, and chemical durability as a function of crystal phase formed, which is crucial for application as LED package materials.

In this study, diopside-based compositions were selected in the CaO-MgO-SiO₂ system. A small amount of Li₂O was added as a fluxing agent for homogeneous melting and promoting crystallization upon heat-treating. The thermal properties, crystallization behavior, and chemical durability of the diopside-based glass-ceramics were studied as functions of the CaO/MgO ratio. The possibility of applying the diopside-based glass-ceramics as LED packaging materials was investigated.

Experimental

The compositions of the specimens chosen from the CaO-MgO-SiO₂ ternary system with Li₂O fluxing agent are shown in Table 1. In the specimen I.D., 'C' and 'M' refer to the CaO and MgO, respectively, and the latter number indicates the CaO/MgO ratio. The reagents used were all oxides of high purity of over 99.9%. For homogeneous mixing of the batch, ball milling was performed for 24 hrs using zirconia balls. The milled batch was melted in an alumina crucible at 1450°C for 30 min in an electric furnace, and the melt was quenched by pouring it into water to obtain glass frit. The glass frit obtained was crushed to a particle size of less than 45 μ m. Green pellets were formed by

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Table 1. The composition of parent glasses.

Specimen I.D.	3 Major oxides (mol ratio)			Additives (mol)	CaO/MgO ratio
	SiO ₂	CaO	MgO	Li ₂ O	
CM0.4	2	0.6	1.4	0.07	0.4
CM0.7	2	0.8	1.2	0.07	0.7
CM1.0	2	1.0	1.0	0.07	1.0
CM1.5	2	1.2	0.8	0.07	1.5
CM2.3	2	1.4	0.6	0.07	2.3

cold isostatic pressing of the glass frit. The glass-ceramic material was fabricated by sintering the green pellets at 823°C for 2 hrs with a heating rate of 10°C/min. Then, the specimen was cooled in the furnace.

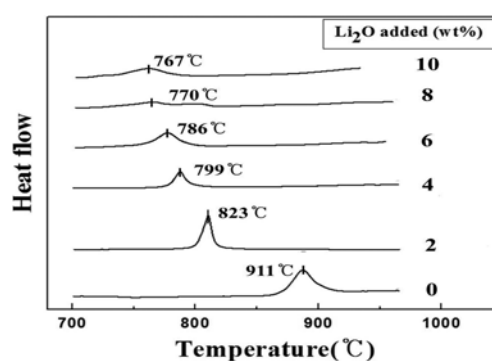
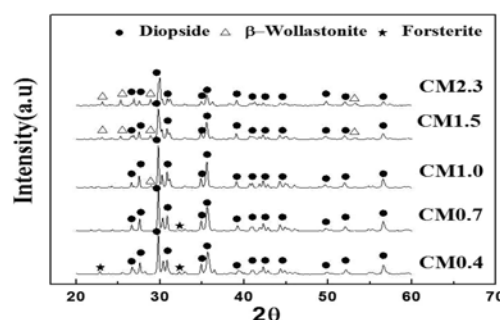
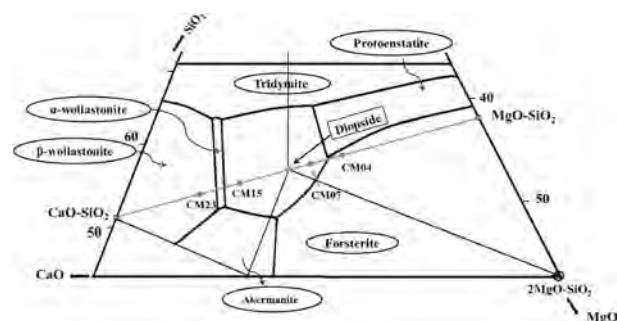
The bulk density of the sintered specimen was measured using Archimedes's method, and the analysis of the crystalline phase was performed using XRD (X-ray diffraction analysis, Pan'alytical, X'pert Pro, Netherlands). The microstructure was observed with FE-SEM (Field Emission Scanning Electron Microscope, JSM-6500F, JEOL, Japan) after etching in 5 vol% HF solution for 20 sec. An LFA (laser flash apparatus, Netzsch, Germany) was used for the thermal conductivity and thermal diffusion coefficient analysis.

Results and Discussion

The temperature for generation of diopside crystal is very high, around 1330 ~ 1390°C, as confirmed in the CaO-MgO-SiO₂ phase diagram [8]. The CaO-MgO-SiO₂ batch system is difficult to melt homogeneously due to its high viscosity. Thus, Li₂O was added in this study as a modifier for promoting crystal formation and homogeneous melting. In order to analyze the optimum amount of Li₂O added, DTA graphs of diopside glasses containing 0 ~ 10 wt% Li₂O with a heating rate of 10°C/min are shown in Fig. 1. Increasing the amount of Li₂O added to the diopside glass decreased the crystallization temperature (*T_p*), showing that Li₂O can act as a flux to promote the crystallization.

Even though the crystallization temperature for the diopside glass without Li₂O added was 911°C, which is sufficient for LTCC processing, the diopside glass containing 2 wt% Li₂O had the highest intensity and the narrowest width of the exothermic peak. The glass with 2 wt% Li₂O can be crystallized at 823°C, which is 10% lower compared to the pure diopside glass. Thus, the amount of Li₂O added and the crystallization temperature were determined in this study as 2 wt% and 823°C, respectively.

The XRD patterns of glass-ceramics of various CaO/MgO ratios sintered at 823°C for 2 hrs are shown in Fig. 2. The main crystal phase for all specimens was confirmed to be that of diopside crystal, but the peak

**Fig. 1.** DTA curves for the diopside glass containing various Li₂O contents. The heating rate was 10 °C/min.**Fig. 2.** XRD patterns of diopside-based glass-ceramics sintered at 823 °C for 2 hrs with various CaO/MgO ratios.**Fig. 3.** Phase diagram of CaO-MgO-SiO₂ ternary system. A closed circle indicates the compositions of the specimens fabricated in this study.

intensity varied according to the CaO/MgO ratio. The CM1.0 specimen had the diopside phase only, and no other compounds relating to the CaO-MgO-SiO₂ system or Li₂O additives. The major peak intensity was decreased when the CaO/MgO ratio was smaller or larger than 1.0. A very small amount of forsterite was generated in the specimen with CaO/MgO ratio < 1.0, while a small amount of β-wollastonite was formed for the specimen with CaO/MgO ratio > 1.0.

The XRD results in Fig. 2 can be interpreted using the phase diagram for the CaO-MgO-SiO₂ ternary system (Fig. 3). The compositions of CM2.3 and CM1.5 exist on the line connecting the wollastonite (CaO·SiO₂) and diopside (CaO·MgO·2SiO₂) compositions, while the compositions of CM0.7 and CM0.4 are on the line

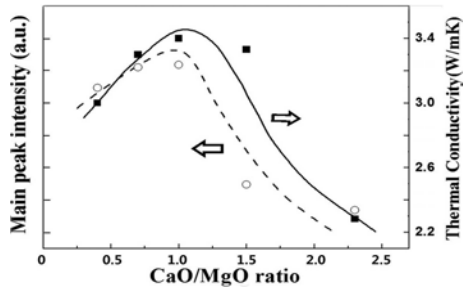


Fig. 4. Thermal conductivity vs. main peak intensity by XRD (Fig. 2) for the diopside based glass-ceramics of various CaO/MgO ratios.

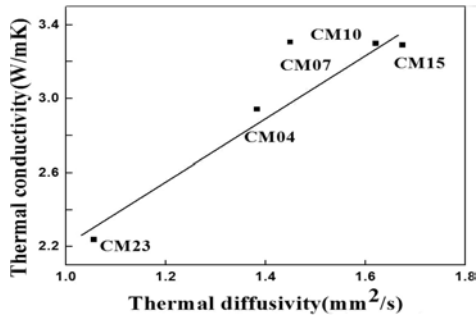


Fig. 5. The linear relationship between thermal conductivity vs. thermal diffusivity for the diopside based glass-ceramics of the various CaO/MgO ratios fabricated in this study.

connecting the diopside and the protoenstatite ($\text{MgO} \cdot \text{SiO}_2$) compositions. The primary crystal for the CM1.5 is diopside phase, while it is wollastonite for the CM2.3. The compound β -wollastonite will be generated in the late stage of the crystallization process for the CM1.5 and CM2. β -wollastonite was formed as a minor phase for the CM1.5 and CM2.3, as shown in Fig. 2. The small amount of forsterite was formed in the CM0.7, which is in good agreement with the interpretation that the forsterite would be generated in the late stage of the crystallization process. The predicted crystallization path for the CM0.4 begins with the forsterite as a primary phase, followed by the crystallization of protoenstatite and diopside. However, only diopside and a small amount of forsterite were found in CM0.4, as shown in Fig. 2. The disagreement between the estimation and the experiment may be due to some type of non-equilibrium situation.

The value of thermal conductivity vs. major peak intensity for the glass-ceramics of various CaO/MgO ratios is shown in Fig. 4. The thermal conductivity of the specimen showed a proportional relation with the major peak intensity of the diopside in the XRD patterns. The CM1.0 specimen had the highest thermal conductivity and peak intensity of diopside. The diopside-based glass-ceramics with CaO/MgO = 0.7 ~ 1.0 containing 2 wt% Li_2O had a thermal conductivity of 3.3 ~ 3.4 W/mK. However, the thermal conductivity decreased to below 3.0 W/mK for CaO/MgO < 0.7 and CaO/MgO > 1.5 due to the formation of forsterite and

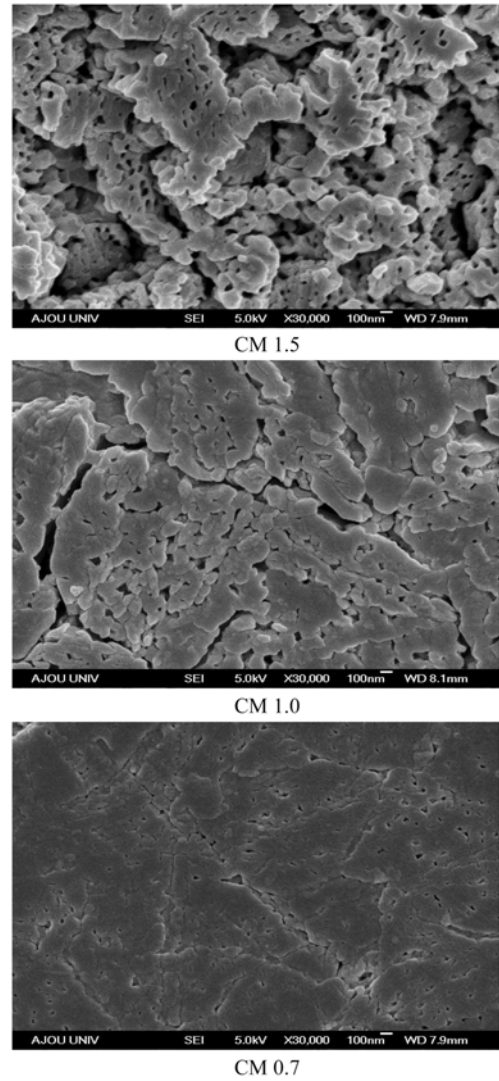


Fig. 6. Microstructures magnified 30,000 times for diopside-based glass-ceramics of various CaO/MgO ratios after etching at 5 vol. % HF solution for 20 sec. The white bar indicates 100 nm.

β -wollastonite, respectively. The CM2.3 specimen had the smallest peak intensity of diopside among all specimens, and the lowest thermal conductivity (2.2 W/mK), which is 34% lower than that of the CM1.0 specimen. The thermal conductivity of CM0.4 (2.92 W/mK) is about 14% lower in comparison with CM1.0. The CM0.7 specimen had better thermal conductivity compared to the CM1.5 due to the formation of forsterite crystal, which has a superior thermal conductivity to β -wollastonite.⁹⁻¹⁰

The relationship between the thermal diffusivity and the thermal conductivity of diopside-based glass-ceramics is plotted as a function of CaO/MgO ratios in Fig. 5. The thermal conductivity, (K), is determined using Equation (1):

$$K = D \cdot \rho \cdot C_p \quad (1)$$

where D , ρ , and C_p indicate the thermal diffusivity, density, and heat capacity, respectively. The thermal

conductivity is linearly proportional to the thermal diffusivity, showing that the thermal diffusivity is dominant among these three factors.

The microstructures for diopside-based glass-ceramics with various CaO/MgO ratios are shown in Fig. 6. All specimens were mirror-polished and etched in 5 vol.% HF solution for 20 sec before observation. The chemical resistance to the HF solution of the specimen was clearly shown in the microstructure, which was magnified 30,000 times. The specimen with higher CaO/MgO ratio had a more porous microstructure. Many voids, left by being dissolved out of some phases, showed the weak resistance of the specimens of high CaO/MgO ratio against HF solution. The CM1.5 specimen had wollastonite as a minor phase, which is a material known to be soluble in acidic solution.¹¹

The CM0.7 specimen containing forsterite showed denser microstructure without corrosion, because the forsterite crystal is more durable against acid than wollastonite. In addition, the CM0.7 specimen had thermal conductivity comparable to pure diopside. From this study, the diopside glass-ceramics with good thermal conductivity and chemical durability can be fabricated in a CaO-MgO-SiO₂-(Li₂O) system by controlling the secondary phases. In conclusion, the diopside-based glass-ceramics from the CaO-MgO-SiO₂-(Li₂O) system is very promising for use in high-generating-power LED packaging materials.

Conclusion

Diopside-based glass-ceramics were manufactured from CaO-MgO-SiO₂-(Li₂O) systems. The major phase was observed to be the diopside in all glass-ceramics with CaO/MgO ratios in the range of 0.4 ~ 2.3. The forsterite phase was formed as the minor phase in the specimen with CaO/MgO ratio = 0.4 ~ 0.7, and β -wollastonite was formed with CaO/MgO ratio = 1.5 ~ 2.3. The thermal conductivity was proportional to the intensities of the major peaks of diopside. The lowest thermal conductivity and chemical resistance against

HF solution were found in the specimen of CaO/MgO = 2.3 due to the formation of β -wollastonite phase. The thermal conductivity was linearly proportional to the thermal diffusivity, showing that the thermal diffusivity is the main factor, rather than the density or the heat capacity. The diopside-based glass-ceramics of CaO/MgO = 0.7 from the CaO-MgO-SiO₂-(Li₂O) system sintered at 823°C had a thermal conductivity of 3.3 W/mK, which is as high as in pure diopside, and higher chemical durability than that of the pure diopside glass-ceramics. In conclusion, the diopside-based glass-ceramics with CaO/MgO ratio < 1.0 showed a high possibility for these materials to be applied in LED packaging materials through LTCC processing.

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