

# Effect of a ZnO Addition on the Thermal Properties of Diopside-Based Glass Ceramics for LED Packages

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## Abstract

Diopside is known to be a ceramic phase with excellent thermal properties (~2.7 W/mK), but the thermal conductivity is not high enough to apply it as a LED packaging material. The chip and PCB (printed circuit board) will deteriorate if the heat is not released out of the LED device. In this study, glass-frit CaO-MgO-SiO<sub>2</sub> systems with a stoichiometric diopside phase composition containing ZnO of various types and amounts were fabricated. The thermal conductivity, density, and shrinkage as a function of the type of ZnO added were studied to investigate the feasibility of utilizing diopside-based glass ceramics in LED packaging applications. It was found that at temperatures below 1000°C, it is possible to fabricate diopside/ZnO composites with thermal conductivity values of approximately 5.7 W/mK, 2.1 times higher than that of pure diopside, by adding single-crystalline ZnO filler to the mother glass. The diopside/ZnO composites fabricated in this study can therefore be applied to LED packaging materials. They are also suitable for the LTCC process.

**Keywords:** Effect of a ZnO addition, Thermal properties, Diopside-based glass ceramics

## **1. Introduction**

At present, rapid growth in the LED (light-emitting diodes) illumination market continues due to the advantages of LEDs, such as their long times, high power generation, and energy saving potential [1]. Lately, LEDs with high power and luminescence levels have been in demand, making the release of heat-accumulating components in devices more important. If the generated heat inside the LED package cannot be efficiently dissipated, the properties of LEDs become unstable. LED packaging materials, therefore, should have high thermal conductivity as well as high chemical stability levels [2].

High thermal conductivity of these systems, therefore, is required, meaning that the thermal conductivity of each material constituting the LED package must be as high as possible. Moreover, the thermal resistance of the package system should be as low as possible [2].

The development of LTCC (low-temperature co-fired ceramic) technology has led to a decrease of the processing cost of many devices because, using this technology, devices can be made by processing a number of layers independently and assembling them into a device as a final step. LTCC devices are monolithic: the entire ceramic support structure and any components are fired in a kiln at the same time at a temperature below 1,000 °C.

Glass-ceramic materials are an excellent choice for the LTCC process; these materials can be fabricated at very lower sintering temperatures compared to the temperatures necessary for normal ceramic materials [3-6]. Compared to normal ceramic materials, LTCC packages prepared by the glass-ceramic process have been proven to demonstrate higher signal propagation speeds and better stability and chemical durability; they also have a low thermal expansion coefficient and a low cost [7,8] Glass ceramics are composed of materials with one or more crystalline phases immersed in a residual glassy phase. These materials have received increasing amounts of attention for various applications due to their improved properties compared to those of other types of glass and ceramic materials.

Recently, to fabricate a device with desired unique properties, glass frit and ceramic filler materials were combined to fabricate composites with more than two crystal phases. Selecting matrix materials with higher thermal conductivity levels, such as diopside ( $\text{CaO-MgO-2SiO}_2$ ) or cordierite ( $2\text{MgO-2Al}_2\text{O}_3\text{-5SiO}_2$ ) is also good choice; such materials have been the subjects of much active research of late [8-10]

Adding a more thermally conductive ceramic filler, such as  $\text{Al}_2\text{O}_3$ , to a glass-ceramic composite with a ceramic filler has been shown to lead to improved thermal conductivity; however, the thermal conductivity of these composites should still be enhanced to a value above 3 W/mK for practical applications. Some fillers of highly

thermally conductive materials, such as BN (~ 20 W/mK) or Si<sub>3</sub>N<sub>4</sub> (~ 27 W/mK), however, are expensive and may decompose during a sintering process in an oxidizing atmosphere.

The purpose of this study is therefore to develop a glass-ceramic composite that can be sintered at a temperature under 1000 °C, such that the composite can be applied to the LTCC process. Diopside has comparatively high thermal conductivity of about 2.7 W/mK [11] and ZnO has high thermal conductivity of about 60 W/mK, nearly twice as high as that of Al<sub>2</sub>O<sub>3</sub>. It is also less expensive than Al<sub>2</sub>O<sub>3</sub> [7, 8, 11-13]

For these reasons, in this study diopside and ZnO were chosen as the matrix and the filler, respectively, for the production of diopside/ZnO glass-ceramic composites. The effects of the ZnO content as a filler on the thermal conductivity, density, crystal phases generated, and microstructure were analyzed. Specifically, two types of ZnO filler, single- and poly-crystal types, were tested in an effort to increase the thermal conductivity of glass-ceramic diopside.

## 2. Experimental procedures

In this study, SiO<sub>2</sub> (High Purity Chemicals, Japan, 99.9%), CaCO<sub>3</sub> (High Purity Chemicals, Japan, 99%), MgO (High Purity Chemicals, Japan, 99.9%), and ZnO (High Purity Chemicals, Japan, 99.9%) were used as reagents. Glass diopside with a composition of CaO-MgO-2SiO<sub>2</sub> was utilized as the matrix material. A batch of diopside with a stoichiometric composition was milled using zirconia balls for 24 h, after which the mixture was melted in an alumina crucible at 1450°C for 30 min and quenched in cold water to obtain a transparent glass frit. The glass was then crushed to a powder with a particle size of less than 45 μm

**Table 1. Composition of the Composites**

Matrix glass	Type of ZnO added	Amount of ZnO added(wt%)
Diopside (CaMgSiO <sub>6</sub> )	Powder	0-20
	Poly-crystal	0-40
	Single-crystal	

The ZnO in the single-crystal form was fabricated by sintering a green pellet body of ZnO containing 1 mol% of BaO pressed isostatically at 1.5 ton/cm<sup>2</sup> at 1400°C for 10h, followed by the dissolving of the grain boundary consisting of BaO with boiling water for 48h. The single-crystalline ZnO particles then were separated from the sintered body and screened to obtain single-crystalline ZnO particles 450~90μm in size. The method of the production of the polycrystalline ZnO particles

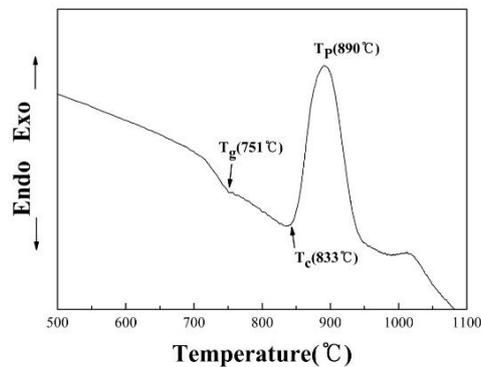
that were used as fillers was as follows. ZnO in polycrystalline particle form was fabricated by sintering a green pellet body pressed isostatically at 1.5 ton/cm<sup>2</sup> at 1400°C for 10 h with a heating speed of 10°C/min in air. The sintered ZnO body then was crushed and screened to obtain particles 45~90 μm in size.

The mother glass frit and ZnO filler were mixed uniformly using a stainless steel spatula and then formed into a pellet under isostatic pressure of 1.5 ton/cm<sup>2</sup>, followed by sintering at 890°C for 3hr at a heating speed of 10°C/min. Also, for comparison, diopside/ZnO glass-ceramic composites were fabricated by heat-treating glass of the ZnO-CaO-MgO-SiO<sub>2</sub> system with the same heat-treatment schedule as was used for the composite with the filler.

A DTA (differential thermal analysis, STA S 1500, Scinco Co., Korea) experiment on the glass frit under 45 μm in size was conducted. The identification of the crystal phases of the sintered body was carried out by means of XRD (MiniFlex II, Rigaku, Japan). The microstructure of the cross-section of the glass-ceramic material was analyzed using a FE-SEM device (field-emission scanning electron microscope, S-4800, Hitachi Co, Japan). The thermal conductivity, thermal diffusion coefficient, and specific heat capacity were measured using a LFA (laser flash apparatus, Netzsch, Germany).

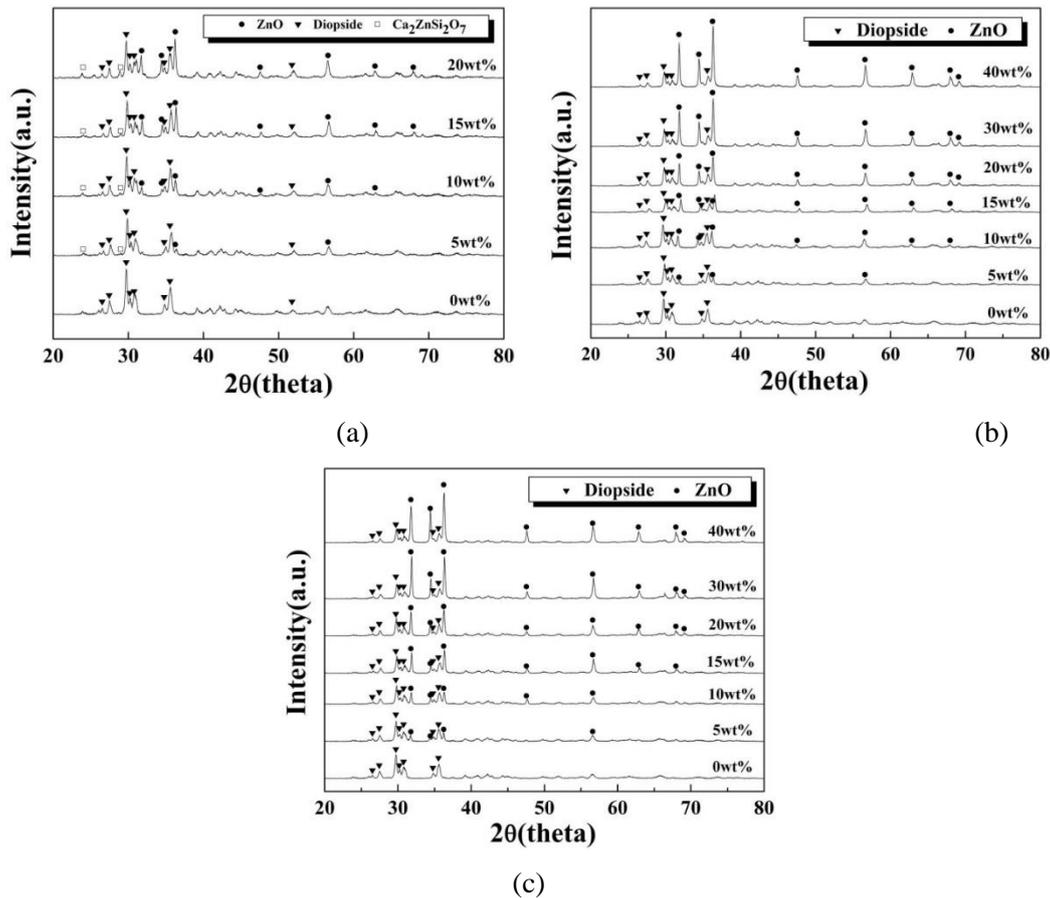
### 3. Result and Discussion

The glass-transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ) of the mother glass of the stoichiometric diopside (CaO-MgO-2SiO<sub>2</sub>) composition were measured and found to be 751°C and 890°C, respectively, from the DTA curve obtained, as shown in Fig. 1. The temperature of 890°C is sufficient for application to the LTCC process; thus, the glass ceramics with the ZnO filler were sintered at 890°C for 3 h in this study.



**Fig. 1.** DTA curve of CaO-MgO-SiO<sub>2</sub> glass frit system measured at a heating rate of 10°C/min.

The XRD patterns of the glass ceramics containing various types of ZnO are shown in Fig. 2. When the specimen was made with a batch of the ZnO-CaO-MgO-SiO<sub>2</sub> system, i.e., with ZnO not added as a filler, the main phase was diopside for the specimen containing 0~15 wt% ZnO. The main phase of diopside became the ZnO phase for the specimen containing 20wt% ZnO. In addition, all specimens containing ZnO above 5 wt% had a small amount of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub> in the crystal phase. For the specimen containing ZnO in the single-crystalline and polycrystalline form as a filler, however, the XRD results were quite different from that of the specimen made with a batch of the ZnO-CaO-MgO-SiO<sub>2</sub> system. None of the specimens had any crystal phase of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>. The specimen containing single-crystalline and polycrystalline ZnO filler of less than 10 wt% had a peak for diopside as the main phase. Above 10% of ZnO filler, the main phase changed to ZnO in the specimen.



**Fig. 2.** XRD pattern of glass ceramics of the CaO-MgO-SiO<sub>2</sub> system containing ZnO of various types. The ZnO was contained (a) in the batch powder, (b) in the polycrystalline filler, and (c) in the single-crystal filler.

The density and shrinkage of the glass ceramics containing various types of ZnO are shown in Fig. 3. The density and shrinkage of glass ceramics made with a batch of the ZnO-CaO-MgO-SiO<sub>2</sub> system decreased with the amount of ZnO added. This

is considered to be due to the generation of the crystal phase of  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ , which may interrupt the densification of the specimen during the sintering process.

For the specimens containing the single-crystalline and polycrystalline ZnO filler materials, the density increased greatly with the content of the ZnO filler, while the shrinkage of the specimen decreased with the ZnO filler content. Although the shrinkage decreased with the ZnO filler content, the density of the specimens increased due to the high theoretical density of ZnO of  $5.65 \text{ g/cm}^3$ , which is much higher than that of diopside, at  $3.27 \text{ g/cm}^3$  [8,14].

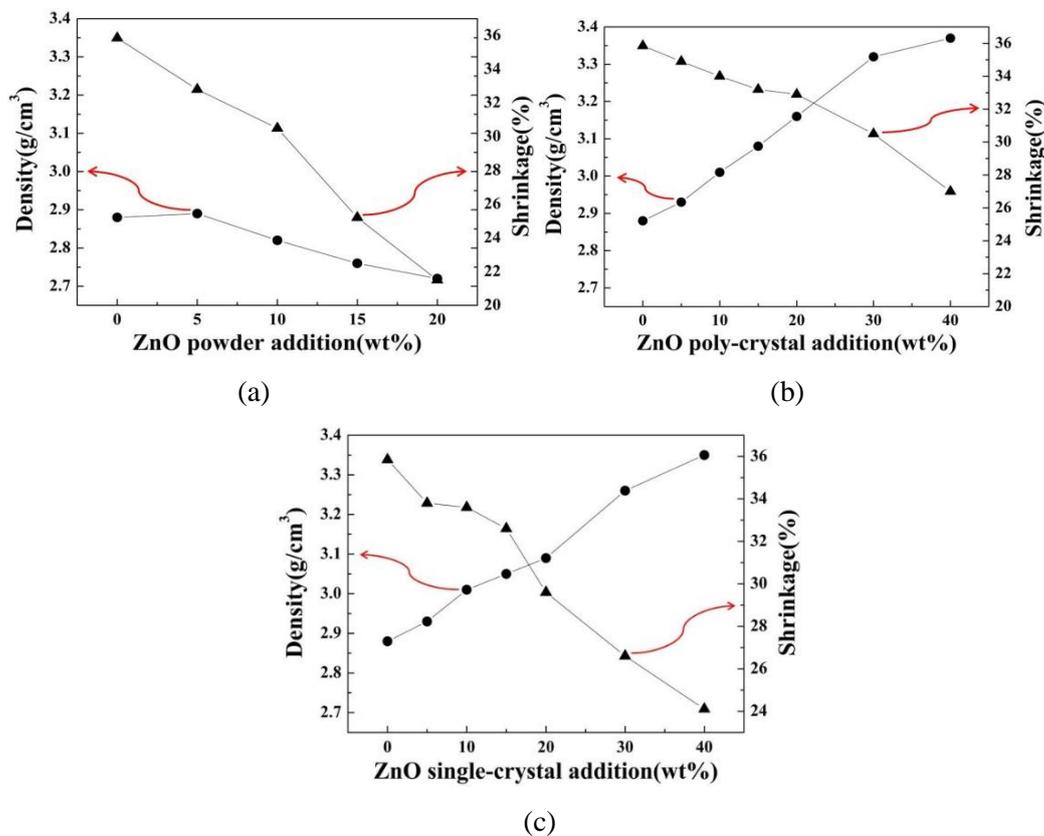


Fig. 3. Density and shrinkage of glass ceramics of the  $\text{CaO-MgO-SiO}_2$  system containing ZnO of various types. The ZnO was contained (a) in the batch powder, (b) in the polycrystalline filler, and (c) in the single-crystal filler.

The thermal conductivity values of glass ceramics containing various types of ZnO are shown in Fig. 4. The thermal conductivity of the glass ceramics of the  $\text{ZnO-CaO-MgO-SiO}_2$  system decreased with the ZnO content. This is considered to be due to the generation of the crystal phase of  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ , which has a thermal conductivity value of approximately  $1 \text{ W/mK}$ , much lower than that of ZnO at about  $60 \text{ W/mK}$ . The thermal conductivity of the glass ceramics of the  $\text{ZnO-CaO-MgO-SiO}_2$  system containing 20wt% ZnO was  $1.8 \text{ W/mK}$ , which is 32% lower than that

of pure diopside. The specimen containing 20 wt% of single-crystalline or polycrystalline ZnO filler, however, had very high values of about 4.2 W/mK in both cases. Specifically, the specimen containing 40 wt% had the highest thermal conductivity of 5.7 W/mK among the glass-ceramics samples produced in this study. Unlike the glass ceramics of the ZnO-CaO-MgO-SiO<sub>2</sub> system, there was no minor phase, such as Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>, which formed in the diopside-based glass-ceramic/ZnO filler composites. This is why adding ZnO as a filler is more advantageous for developing higher thermal conductivity.

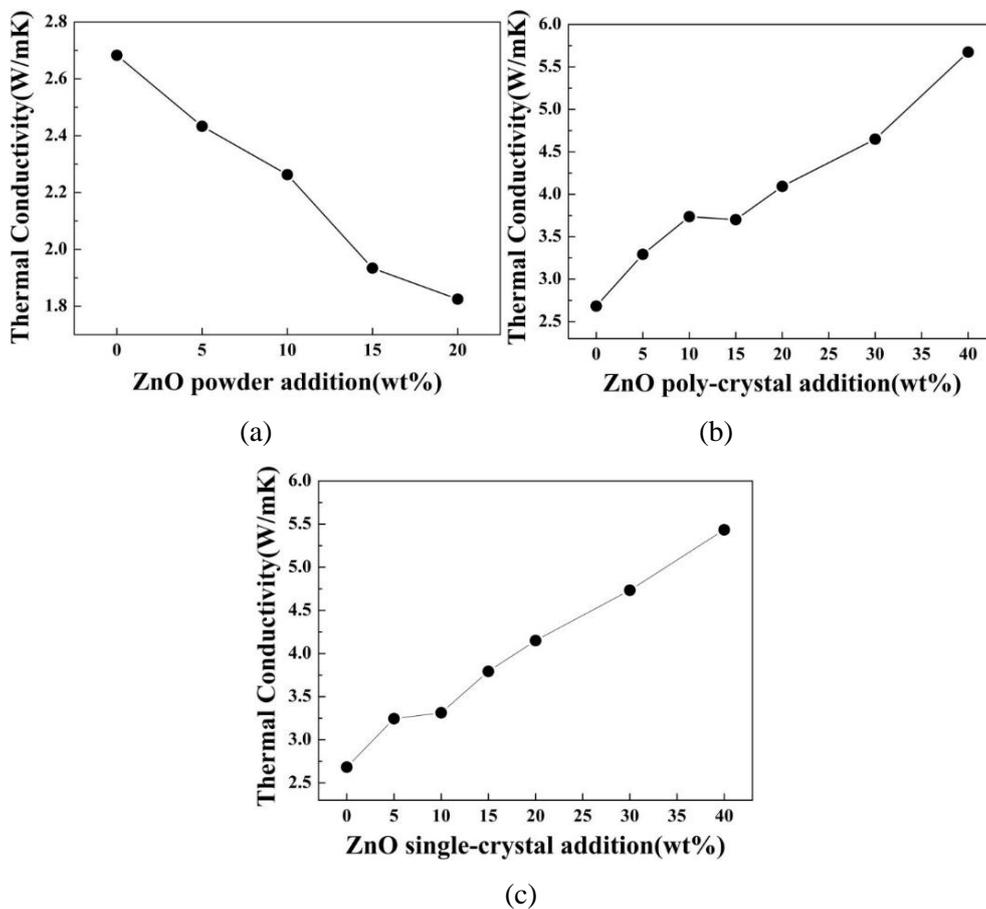


Fig. 4. Thermal conductivity of the glass ceramics of the CaO-MgO-SiO<sub>2</sub> system containing ZnO of various types. The ZnO was contained (a) in the batch powder, (b) in the polycrystalline filler, and (c) in the single-crystal filler

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

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

where  $D$  is the thermal diffusivity [ $\text{cm}^2/\text{s}$ ],  $\rho$  is the density [ $\text{g}/\text{cm}^3$ ], and  $C_p$  is the specific heat capacity [ $\text{J}/\text{gK}$ ].

The density and thermal diffusivity of the specimens as a function of the thermal conductivity are shown in Figs. 5 and 6, respectively. Fig. 5 shows that the density was the dominant factor among these three parameters in terms of the thermal conductivity of the anorthite/ZnO composites fabricated in this study.

In addition, a linear relationship between the thermal conductivity and the thermal diffusivity of the glass ceramics of the (ZnO-)CaO-MgO-SiO<sub>2</sub> system was confirmed, as shown in Fig. 6.

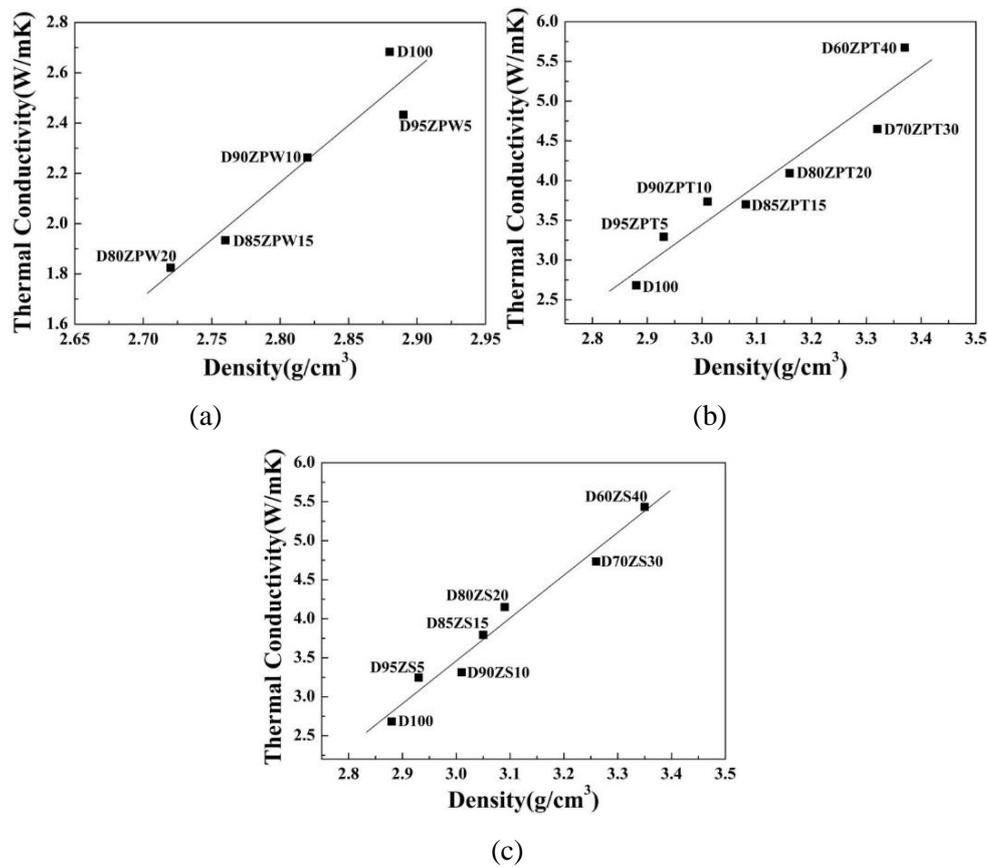


Fig. 5. Thermal conductivity vs. density plot showing a linear relationship of the glass ceramics of the diopside system containing ZnO of various types. The ZnO was contained (a) in the batch powder, (b) in the polycrystalline filler, and (c) in the single-crystal filler

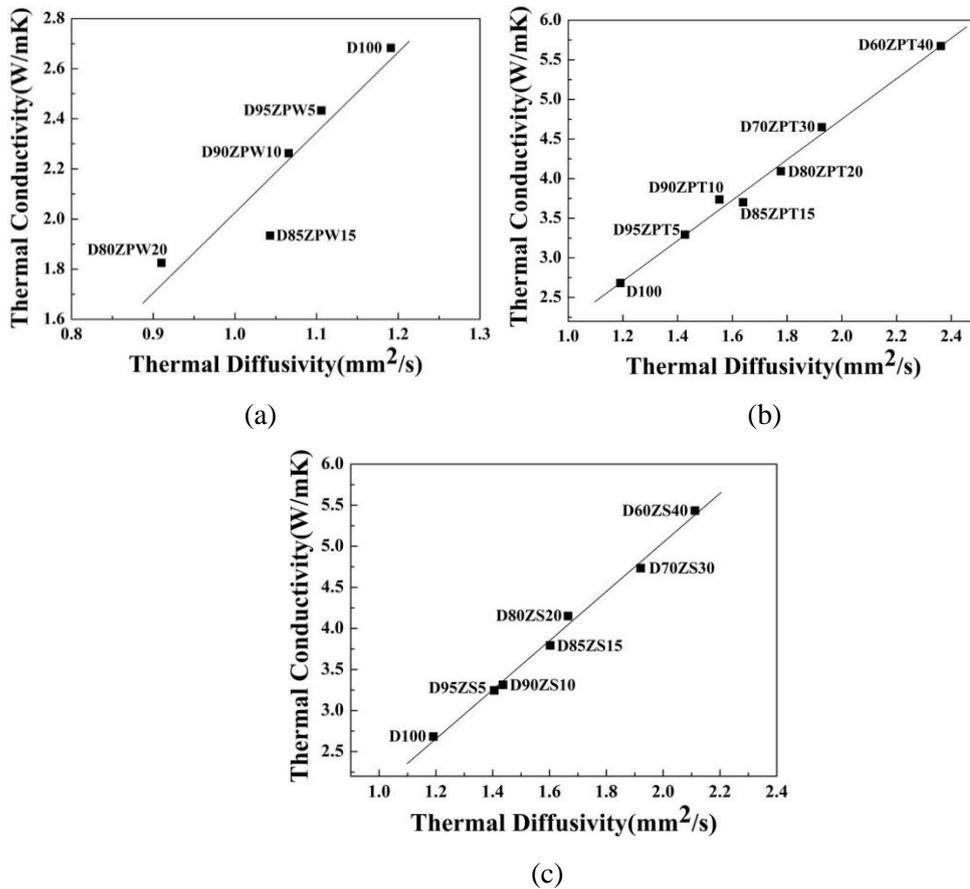


Fig. 6. Thermal diffusivity vs. thermal conductivity plot showing a linear relationship of the glass ceramics of the diopside system containing ZnO of various types. The ZnO was contained (a) in the batch powder, (b) in the polycrystalline filler, and (c) in the single-crystal filler

A SEM micrograph of the glass ceramics of the diopside system containing ZnO of various types is shown in Fig. 7. The microstructure of the glass ceramics of the ZnO-CaO-MgO-SiO<sub>2</sub> system containing 20 wt% reagent ZnO was very porous (b), while a dense microstructure was noted in the pure diopside specimen (a).

The glass ceramics of the CaO-MgO-SiO<sub>2</sub> system containing two types of ZnO fillers, single- and poly-ZnO, have relatively uniform microstructures, as shown in (c) and (d). The small image at the right below the larger picture is magnified by 1,000 times, in which the larger particles are the ZnO filler. The poly-ZnO filler (c) consists of many small ZnO grains, while the single-ZnO filler (d) had no boundary.

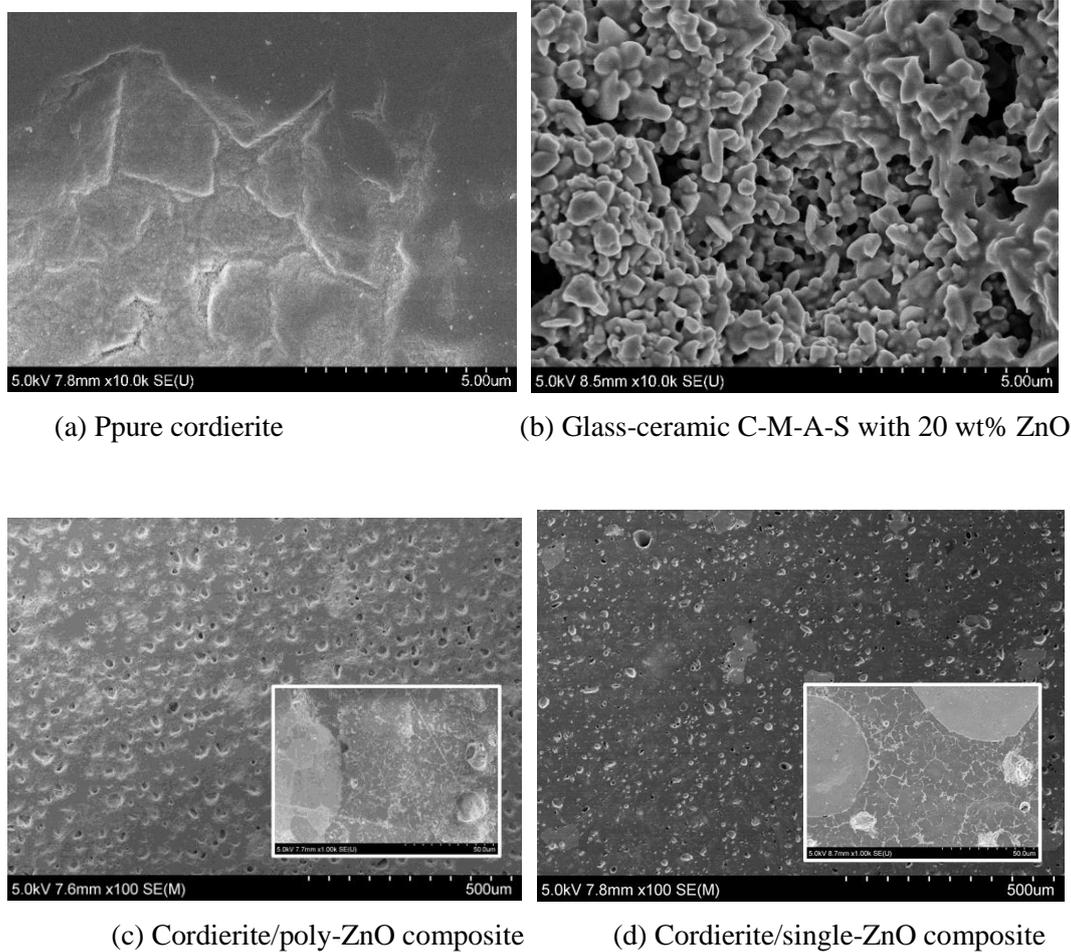


Fig. 7. SEM micrograph of the glass ceramics of the diopside system containing various amounts and types of ZnO: (a) pure diopside, (b) 20 wt% reagent ZnO powder, (c) 5 wt% poly-ZnO filler, and (d) 5 wt% single-ZnO filler

#### 4. Conclusion

To produce diopside/ZnO glass-ceramic composites, diopside and ZnO were chosen as the matrix and the filler in this study, respectively. The effects of the ZnO content as a filler on the thermal conductivity, density, crystal phases generated, and microstructures were then analyzed.

The specimen containing more than 10% of the single-crystalline or polycrystalline ZnO filler had a main phase of ZnO. For the glass ceramics made with a batch of the ZnO-CaO-MgO-SiO<sub>2</sub> system, the main phase was the ZnO phase when the ZnO content exceeded 20 wt%, and all specimens containing ZnO at more than 5 wt% had a small amount of the crystal phase of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>. For the specimen containing the single-crystalline and polycrystalline ZnO filler, the density increased greatly with the content of ZnO filler, while the shrinkage of the

specimen decreased with the ZnO filler content. Although the shrinkage decreased with the ZnO filler content, the density of the specimen increased. This arose due to the high theoretical density of ZnO of  $5.65 \text{ g/cm}^3$ , which is 1.7 times higher than that of diopside. The thermal conductivity of the glass ceramics of the ZnO-CaO-MgO-SiO<sub>2</sub> system decreased with the ZnO content. This is considered to have been due to the generation of the crystal phase of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub> with very low thermal conductivity. The specimen containing single-crystalline or polycrystalline ZnO filler, however, greatly increased with the amount of the ZnO filler content. For example, the thermal conductivity of the specimens containing ZnO filler of 40 wt% had the highest thermal conductivity of 5.7 W/mK among the glass ceramics produced in this study. Unlike the glass ceramics of the ZnO-CaO-MgO-SiO<sub>2</sub> system, no minor phase, such as Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>, formed in the diopside-based glass-ceramic/ZnO filler composites. This is why the adding ZnO as a filler is more advantageous for developing higher thermal conductivity. The microstructure of the glass ceramics made with a batch of the ZnO-CaO-MgO-SiO<sub>2</sub> system became more porous with the amount of ZnO added, while a dense microstructure was noted in the pure diopside specimen.

In conclusion, at a temperature below 1000°C, it is possible to fabricate diopside/ZnO composites with thermal conductivity values of approximately 5.7 W/mK, which is 2.1 times higher than that of pure diopside, by adding single-ZnO filler to the mother glass. The diopside/ZnO composites fabricated in this study can therefore be applied to LED packaging materials and are suitable for the LTCC process as well.

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