

## Thermal properties of glass-ceramics made with zircon and diopside powders

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Diopside is a ceramic material with excellent physical and chemical properties. However, when it is applied as an LED packaging material, heat dissipation of the LED element is not sufficient due to its relatively lower thermal conductivity, which may cause degradation of the LED function. In this study, glass-ceramics based on a  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system, in which diopside is the main crystal phase, were prepared by heat-treating the glass, which was composed of zircon ( $ZrO_2$ -SiO<sub>2</sub>) powders and diopside (CaO-MgO-2SiO<sub>2</sub>) powders. The possibility of using the glass-ceramics as a packaging material for LEDs was then investigated by analyzing the density, shrinkage, thermal conductivity, and phases generated according to the amount of zircon powder added. The density and shrinkage of specimens decreased slightly and then increased again with the amount of  $ZrO_2$ -SiO<sub>2</sub> added within a range of 0~0.38 mol. Even though the crystal phase of zircon does not appear in the  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system, the glass containing 0.38 mol zircon powder showed the highest thermal conductivity, 1.85 W/mK, among the specimens fabricated in this study: this value was about 23% higher than that of pure diopside. It was found that the thermal conductivity of the glass-ceramics based on a  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system was closely related to the density, but not to the phase type. Zirconia ( $ZrO_2$ ), a component oxide of zircon, plays an important role in increasing the density of the specimen. Furthermore the thermal conductivity of glass-ceramics based on a  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system showed a nearly linear relationship with thermal diffusivity.

**Key words:** Glass-ceramics, Zircon, LED Packaging, Diopside, Thermal conductivity.

### Introduction

In recent years, with rapidly accelerated development of LED (light emitting diode) technology, LEDs, which have been used mainly as information display devices, have been receiving widespread attention as an optimal form of lighting to spur green growth. In order to replace general lighting of several tens to several hundreds of watts with LEDs, a great deal of research is currently being carried out to increase the output of individual LED devices.

However, the first problem that arises when the output of the LED device improves is the amount of heat generated. It is important to release generated heat out of the device because 70 to 80% of the input power is converted to thermal energy. In the case of an LED package in which an LED chip is mounted, the package should protect the semiconductor chip from the external environment, electrically connect the terminal of the chip to a PCB (Printed Circuit Board) substrate, and transfer heat generated from the chip to the outside [1].

The heat transfer in the LED package depends mainly on the thermal conduction phenomenon. Therefore, the thermal conductivity of the materials constituting the package must be high to effectively dissipate heat. A

ceramic laminated package is widely used for this purpose [1-3], because the ceramic package has excellent heat dissipation performance, a thermal expansion coefficient similar to that of the LED chip, and long-term reliability despite continuous temperature change during the manufacture or use of the LED package.

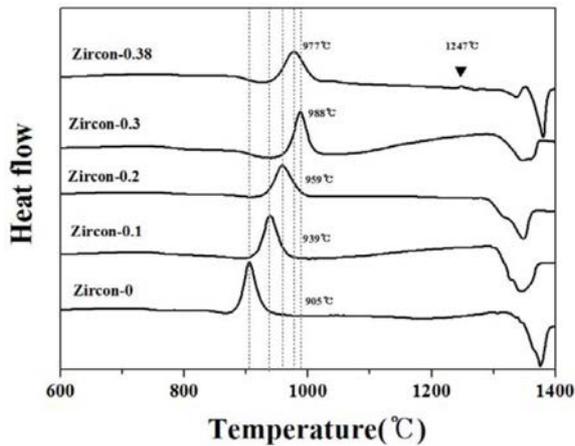
LTCC (low temperature co-fired ceramic) material is mainly used for ceramic laminated packages. The LTCC process is a material and process technology that sinters Cu and Ag electrodes with a ceramic substrate material at 1000 °C or less [4-9]. Ceramic materials such as diopside and anorthite are widely used as LTCC materials. Most of these materials are manufactured by the so-called 'glass-ceramics' process in which glass materials having various compositions transfer to crystalline materials through heat treatment.

The glass-ceramics process allows dense specimens to be produced at a lower temperature than the normal sintering process using crystal powder [10-13]. In this study, diopside was selected as the LED package material and the glass-ceramics process was applied to fabricate the diopside at low sintering temperature below 1000 °C. In order to further improve the thermal conductivity (about 1.5 W/mK) of the diopside, zircon, which has a theoretical thermal conductivity of 6.1 W/mK, was added. The generated phases and the thermal properties of the glass-ceramics of the  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system were evaluated and their suitability as an LED package material was examined [14-15].

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**Table 1.** Composition of specimens for glass-ceramic of ZrO<sub>2</sub>-CaO-MgO-SiO<sub>2</sub> system.

Specimen I.D.	Mol ratio	
	Zircon (ZrO <sub>2</sub> -SiO <sub>2</sub> )	Diopside (CaO-MgO-2SiO <sub>2</sub> )
Zircon-0	0	1
Zircon-0.1	0.1	1
Zircon-0.2	0.2	1
Zircon-0.3	0.3	1
Zircon-0.38	0.38	1

**Fig. 1.** DTA curve for ZrO<sub>2</sub>-CaO-MgO-SiO<sub>2</sub> glass system containing various amounts of zircon measured at a heating rate of 10 °C/min.

## Experimental

In this study, glass-ceramics based on a ZrO<sub>2</sub>-CaO-MgO-SiO<sub>2</sub> system were prepared by mixing a zircon, ZrO<sub>2</sub>-SiO<sub>2</sub>, powder with a diopside, CaO-MgO-2SiO<sub>2</sub>, powder. As shown in Table 1, the experiment was carried out by adding 0 to 0.38 mol of zircon to the diopside. When the amount of zircon added was more than 0.38 mol, the glass was not melted, and hence the maximum amount of zircon was set to 0.38 mol in this study. The reagents used were 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 ZrO<sub>2</sub> (Junsei Chemical, Japan, 99%).

The batch powder was dry-milled for 24 hrs using zirconia balls and then melted at 1600 °C for 2 hrs in a platinum crucible, and the melt was quenched in distilled water to produce the mother glass. The obtained glass was dried at a temperature of 100 °C for 24 hrs and then pulverized and only powders of 45 μm or less were used in the experiment. The prepared mother glass powder was weighed in 1.5 g portions, and then uniaxially pressed at a constant pressure of 25 MPa using a circular mold having a diameter of 20 mm, and then subjected to cold isostatic pressing at a constant pressure of 42000 kgf. The obtained green

body was then sintered at a heating rate of 10 °C/min for 2 hrs.

The sintering temperature of each specimen was obtained by a DTA analysis, as shown in Fig. 1. The main exothermic peak of the pure diopside glass (Zircon-0) specimen is 905 °C, which occurred due to heat generated by crystallization and is therefore referred to as the maximum crystal growth temperature (T<sub>pmax</sub>).

As the amount of zircon added increased, the T<sub>pmax</sub> tended to increase together except for the Zircon-0.38 specimen; the T<sub>pmax</sub> of each glass specimen was measured at 905 °C for Zircon-0, 939 °C for Zircon-0.1, 959 °C for Zircon-0.2, 988 °C for Zircon-0.3, and 977 °C for Zircon-0.38.

In this study, the shrinkage, density, thermal conductivity, and generated phase were measured to analyze the thermal properties of the crystallized glass. The diameter and the thickness of the circular specimens were measured before and after sintering using Vernier calipers. The density was measured using equation (1).

$$\frac{w_1}{w_2 - w_3} = \rho \quad (1)$$

where ω<sub>1</sub> = dry weight, ω<sub>2</sub> = water-containing weight, ω<sub>3</sub> = suspension weight, and ρ = density.

Thermal conductivity measurements were performed using an LFA (laser flash apparatus, NETZSCH, Germany). In order to observe the phase changes of the specimen after sintering, an X-ray diffraction analysis (XRD, Pan'alytical, X'pert pro, Netherland) was carried out with a scan speed of 4°/min. (5° ≤ 2θ ≤ 90°).

## Results and discussion

### Physical properties

Fig. 2 shows the change of shrinkage of glass-ceramics based on a ZrO<sub>2</sub>-CaO-MgO-SiO<sub>2</sub> system depending on the amount of zircon added. As the amount of zircon increased, the shrinkage ratio increased. The maximum crystal growth temperature in the DTA curve is higher in the specimens containing larger amounts of zircon, and therefore the shrinkage rate is also higher in these specimens due to the generation of more liquid phase because of higher sintering temperature.

Fig. 3 shows the variation of the density of glass-ceramics based on a ZrO<sub>2</sub>-CaO-MgO-SiO<sub>2</sub> system depending on the amount of zircon added. As the amount of zircon added increases, the density also increases. These results could be understood as follows: first, with higher sintering temperature, densification during the sintering process is accordingly easier and a higher shrinkage rate was obtained; second, zirconia (ZrO<sub>2</sub>), a component oxide of zircon, acts as a nucleating agent

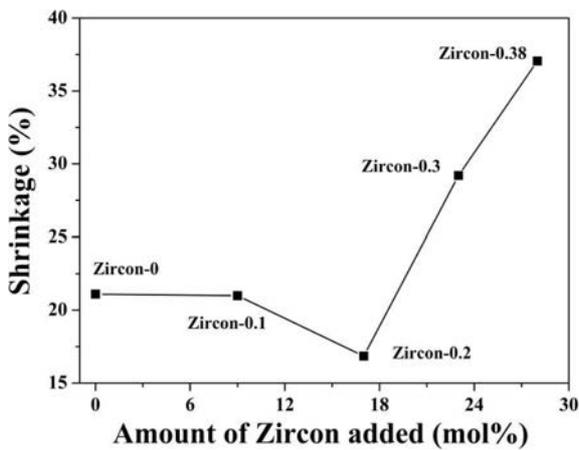


Fig. 2. Shrinkage of glass-ceramic specimens of  $ZrO_2$ -CaO-MgO- $SiO_2$  system containing various amounts of zircon.

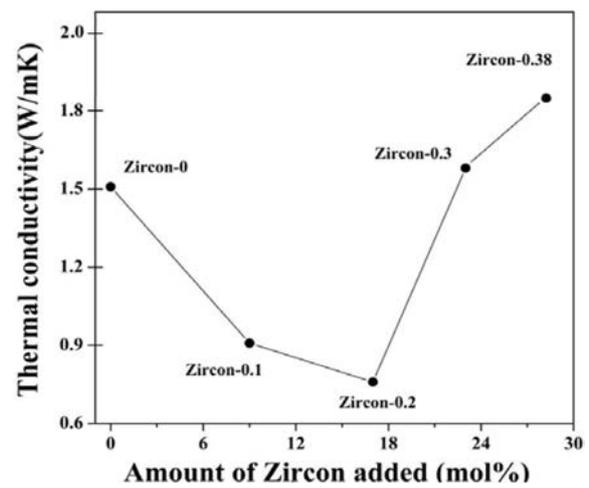


Fig. 4. Thermal conductivity of glass-ceramics of  $ZrO_2$ -CaO-MgO- $SiO_2$  system containing various amounts of zircon.

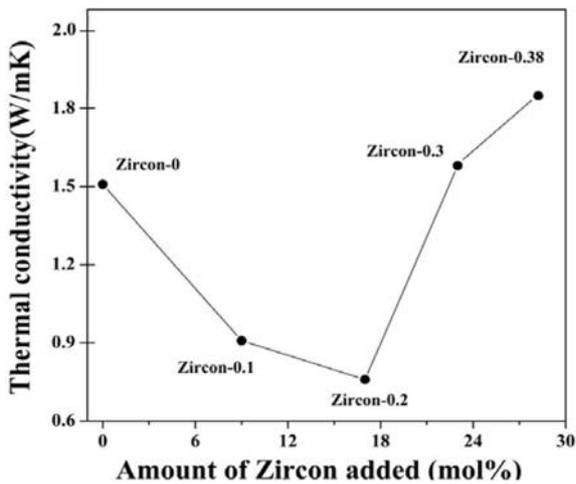


Fig. 3. Density of glass-ceramic specimens of  $ZrO_2$ -CaO-MgO- $SiO_2$  system containing various amounts of zircon.

in the  $ZrO_2$ -CaO-MgO- $SiO_2$  system glass and hence the diopside crystal phase is better formed and the density of the specimen is increased [16].

### Thermal properties

Fig. 4 shows the thermal conductivity of glass-ceramics based on a  $ZrO_2$ -CaO-MgO- $SiO_2$  system according to the amount of zircon added. The thermal conductivity of the specimen was improved only when the amount of added zircon exceeded 0.3 mol. When the amount of zircon was below 0.2 mole, the thermal conductivity of the specimen was even lower than that of the pure diopside. The thermal conductivity of the Zircon-0.38 specimen was 1.85 W/mK, which is 23% higher than that of the Zircon-0 specimen.

This result can be explained in relation to the density change graph according to the amount of zircon that is added, as shown in Fig. 3. The thermal conductivity, one of the most important factors determining the thermal property of the crystallized glass for LED packaging, is affected by the density. Increasing the

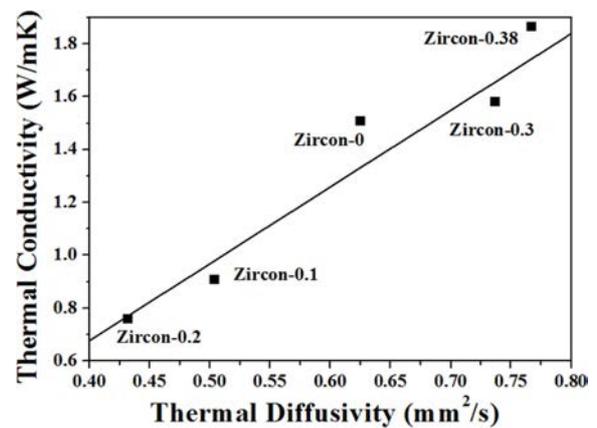


Fig. 5. The linear relationship between thermal conductivity vs. thermal diffusivity for the  $ZrO_2$ -CaO-MgO- $SiO_2$  glass-ceramics system.

amount of zircon increased the density of the glass-ceramic and consequently the thermal conductivity of the crystallized glass increased as well.

The thermal conductivity (K) of the solid can be calculated by the formula (2).

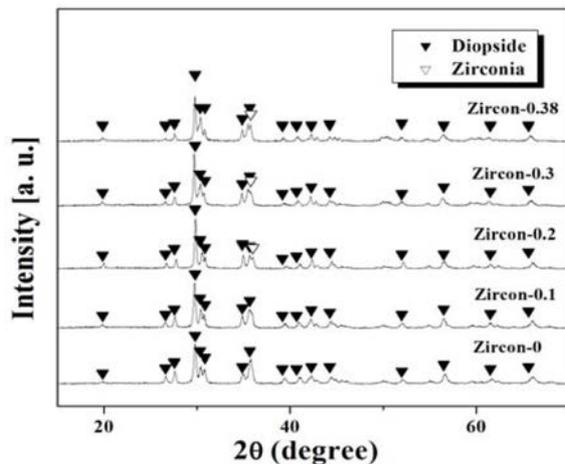
$$K = k \times \rho \times C_p \quad (2)$$

where  $k$ ,  $\rho$ , and  $C_p$  represent the thermal diffusivity ( $mm^2/s$ ), the density ( $g/cm^3$ ), and the heat capacity ( $J/gK$ ), respectively.

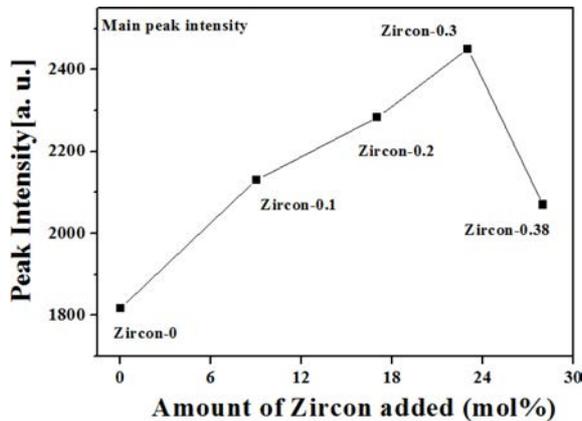
The relationship between the thermal diffusivity and the thermal conductivity of the  $ZrO_2$ -CaO-MgO- $SiO_2$  glass-ceramics is plotted as a function of the amount of zircon added in Fig. 5: the thermal conductivity of the glass-ceramic is linearly proportional to the thermal diffusivity.

### Analysis of crystal phases

Although the thermal conductivity value was not significantly improved by the addition of zircon, the



**Fig. 6.** XRD patterns of glass-ceramics of  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system containing various amounts of zircon. The temperatures of heat-treatment for each specimens were obtained from DTA curves: 905 °C for Zircon-0, 939 °C for Zircon-0.1, 959 °C for Zircon-0.2, 988 °C for Zircon-0.3, and 977 °C for Zircon-0.38.



**Fig. 7.** The intensity of the main peak of diopside phase in XRD patterns shown in Fig. 6.

addition of zircon contributed to the increase of the thermal conductivity of the glass-ceramics of diopside.

Fig. 6 shows the XRD graph of the glass-ceramics of  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system sintered at each maximum crystal growth temperature obtained from the DTA curve as a function of the amount of zircon added. The XRD analysis revealed that diopside phase was detected in all specimens. It is considered that the added  $ZrO_2$  serves as a nucleating agent in the glass structure and thus contributed to the formation of smaller size diopside crystals. A maximum thermal conductivity value of 1.85 W/mK was measured for Zircon-0.38, which is 23% higher than that of the pure diopside specimen, Zircon-0. As shown Fig. 7, the main peak intensity of the diopside phase increased with the amount of zircon added, showing a maximum value in the Zircon-0.3 specimen.

When we compare the results of Fig. 4 and Fig. 7, the thermal conductivity of the Zircon-0.38 specimen with lower main peak intensity of diopside crystal is

higher than that of the Zircon-0.3 specimen. It is clear that the addition of zircon increased the thermal conductivity of the specimen. However, since the zircon phase does not appear in the specimen, it is considered that zirconia, which is a component of zircon, acts as a nucleating agent, and consequently the diopside crystal size is smaller, resulting in densification of the specimen, or zirconia induced the formation of a liquid phase during the sintering process to densify the specimen.

Zirconia phase was found in the specimen containing more than 0.2 mol  $ZrO_2$ . No other phase was identified, indicating that the added powder containing zircon remained in a glassy state, not a crystalline phase.

Even though the diopside phase was generated in all specimens, the thermal conductivity of the specimens was not high, falling below 2 W/mK for all specimens due to the residual glassy matter. Thermal conductivity of glassy matter is normally below 1.0 W/mK. Therefore, it is necessary to sinter the specimen at precisely the optimal temperature to eliminate the remaining glassy matter and crystallize the zircon phase. Appropriate experiments should be performed in further work.

## Conclusions

In this study, glass-ceramics based on a  $ZrO_2$ -CaO-MgO-SiO<sub>2</sub> system were fabricated by heat-treating glass and their thermal properties were evaluated. The heat-treatment temperature for fabricating the glass-ceramic specimens could be obtained from a DTA analysis. As the amount of added zircon powder was increased, the crystallization peak temperature in the DTA curve increased, falling in a range of 905~977 °C. The percent shrinkage of heat-treated body decreased with the amount of zircon up to 0.2 mole and increased rapidly up to 0.38 mole added. The density of the heat-treated body with the amount of zircon added showed a similar trend with the percent shrinkage. The thermal conductivity of the specimens fabricated in this study is proportional with their density. The relationship between the thermal conductivity versus thermal diffusivity showed quite good linearity. It is considered that the added  $ZrO_2$  serves as a nucleating agent in the glass structure and thus contributed to densification of the specimen due to the formation of smaller crystal size: also  $ZrO_2$  induced liquid-phase-sintering to readily densify the specimen. A thermal conductivity value of 1.85 W/mK was measured for the Zircon-0.38 specimen, which is 23% higher than that of Zircon-0, the pure diopside specimen. It is considered that the zircon powder added to glass did not show a remarkable effect in increasing the thermal conductivity: zircon powder in the glass could not be crystallized, but remained in a glassy state. Further studies should be carried out to remove residual glassy matter that cause a decrease of the thermal conductivity of the specimens.

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