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The thermal properties of cordierite/diopside composites fabricated by glass–ceramics process for LED packages

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Abstract

Cordierite/diopside composites were manufactured by the heat-treatment of green compacts composed of diopside (CaO–MgO–2SiO$_2$) and cordierite (2MgO–2Al$_2$O$_3$–5SiO$_2$) glass frits. The thermal properties were analyzed as a function of the type and intensity of the crystalline phases generated and the microstructure. The composites contained 0–30 wt% diopside glass frits had α-cordierite as the major phase and the μ-cordierite as the minor phase (designated as α-series). In the composites containing 40–80 wt% of diopside frit, the μ-cordierite and diopside crystals were generated as the major and minor phase, respectively (designated as μ-series). Adding diopside glass frit decreased the thermal conductivity of the α-series specimens but increased that of the μ-series specimens. The density of the composites showed a linearly proportional relationship with the thermal conductivity. At an equal density, the α-series specimens had higher thermal conductivity than the μ-series specimens. 30–50 nm crystals were sparsely observed in the microstructures of the μ-series specimens and 30–100 nm crystals were formed compactly in the α-series specimens. The cordierite/diopside composites manufactured in this research can be applied as LED packaging materials due to their adequate thermal conductivity of 1–3 W/mK and their diffusivity of 0.5–1.3 mm^2/s.

Keywords: A. Sintering; C. Thermal conductivity; C. Thermal properties; D. Glass ceramics

1. Introduction

LEDs (light-emitting diodes) are currently used as indicator lamps in many devices and are increasingly used as other lighting device owing to their many advantages over incandescent light sources, including lower energy consumption, longer lifetime, improved robustness, smaller size, and faster switching [1]. Presently, technological developments are enhancing the power of LEDs so that they can replace all other lighting devices [2]. High-power LED elements, however, cause the increase in temperature of the chip due to the heat generated. If this heat is not removed, the LEDs run at high temperatures, not only lowering their efficiency but also making them more dangerous and less reliable [3–5].

In this research, diopside and cordierite, which are known to have excellent thermal and mechanical properties, were selected as the target phases to be formed as the composites for LED packaging materials [6–9]. First, glass frits of cordierite and diopside compositions were fabricated by a conventional process for glass, melting and quenching, and these two frits were mixed at various ratios, molded, and sintered to fabricate cordierite/diopside composites. Then analysis of thermal properties of the composite fabricated were performed based on the results of the phase analyses and microstructure observation. Finally, the applicability of the cordierite/diopside composites fabricated in this study for LED packaging material was studied.

2. Experimental procedures

The composition of the cordierite/diopside composites fabricated in this study is shown in Table 1. The capital letters ‘C’ and ‘D’ in the specimen I.D. refer to the cordierite (2MgO–2Al$_2$O$_3$–5SiO$_2$) and the diopside (CaO–MgO–2SiO$_2$), respectively. The reagents used were oxides of high purity over 99.9%. The uniformly mixed powders were melted in a platinum crucible and quenched in cold

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Table 1
Composition of cordierite/diopside composites (wt%)

Specimen I.D	Cordierite glass frit	Diopside glass frit
C10-D0	100	0
C7-D3	70	30
C6-D4	60	40
C4-D6	40	60
C2-D8	20	80
C0-D10	0	100

water to prepare the glass frits. The melting temperatures for the formation of the cordierite and diopside glass frits were 1600 °C and 1450 °C, respectively. The glass frits obtained were transformed onto pallets with diameter of 10 mm and height of 3 mm using cold isostatic press. The pellets formed were sintered at 940 °C for 2 h at a heating rate of 10 °C/min.

The crystalline phases of the sintered body were identified by XRD (X-ray diffraction analysis, Pan'alytical, X'pert Pro, The Netherlands) in which the Cu*K*α line was used. The microstructures of the composites were observed by FESEM (Field Emission Scanning Electron Microscope, JSM-6700F, JEOL, and Japan) after mirror polishing and etching in a 3 vol% HF solution for 20 s. The thermal conductivity and thermal diffusion coefficient were measured using a LFA (laser flash apparatus, NETZSCH, Germany).

3. Results and discussion

The XRD results of the cordierite/diopside composites as a function of mixing ratio between the cordierite and the diopside glass frits are shown in Fig. 1. The C10-D0 specimen manufactured with 100% cordierite frit had the α-cordierite as the major phase and the μ-cordierite as a minor phase.

Increasing the diopside frit added to the composites decreased the α-cordierite crystalline peaks. In the composites containing diopside frit of more than 40%, the α-cordierite disappeared and μ-cordierite and diopside crystals were generated as the major and minor phases, respectively. Only diopside crystalline was generated in the C0-D10 specimen, which was manufactured with 100% of diopside frit. The composites that contained 0–30 wt% diopside glass frit were designated as 'α-series' because the main crystalline phase was α-cordierite. The composites containing 40–80 wt% diopside glass frit were designated as 'μ-series' because the main crystalline phase was μ-cordierite. The thermal conductivity of the cordierite/diopside composites as a function of the added diopside frit content is shown in Fig. 2.

Increasing the diopside frit content added decreased the thermal conductivity of the α-series specimen and increased that of the μ-series specimens.

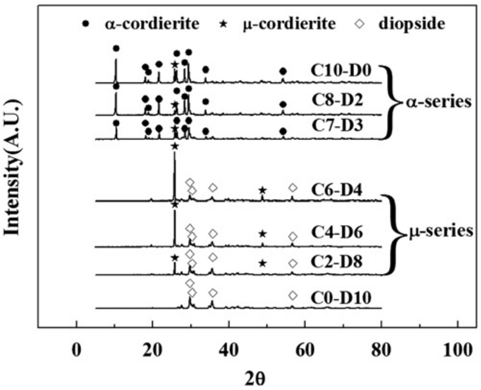


Fig. 1. XRD patterns of cordierite/diopside composites heat-treated at 940 °C/2 h as a function of ratio of cordierite and diopside glass frit content.

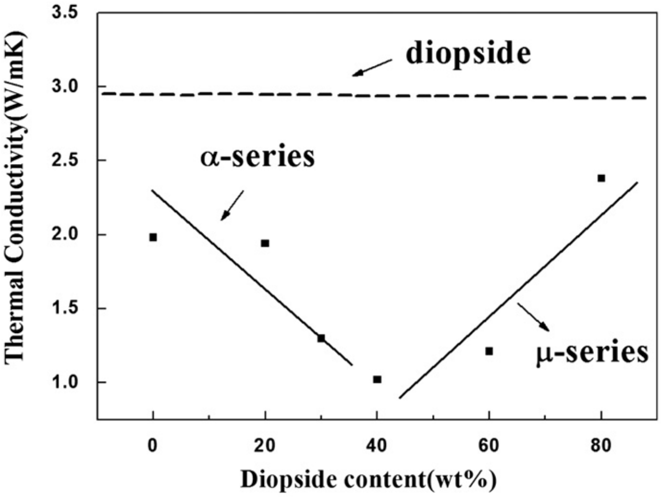


Fig. 2. Thermal conductivity vs. diopside frit content added relationship in cordierite/diopside composites.

From the XRD results shown in Fig. 1, the peak intensities of the α-cordierite were decreased in the α-series specimens while those of the μ-cordierite samples were increased by increasing the amount of added diopside frit content. In addition, in the μ-series specimens, the peak intensities of μ-cordierite decreased as the added diopside frit content increased. From these results, it could be concluded that the α-cordierite phase is superior to the μ-cordierite phase for enhancing the thermal conductivity of these types of composites.

The densities of the composites were closely related to the XRD peak intensity ratio of the major/minor peak intensities in Fig. 3. In the μ-series specimens, the density decreased with the major/minor peak intensity ratio to converge to the theoretical density of μ-cordierite. In contrast, in the α-series specimens, the density increased with the major/minor peak intensity ratio and approaches the theoretical density of α-cordierite. A density vs. thermal conductivity graph of the cordierite/diopside composites is shown in Fig. 4.

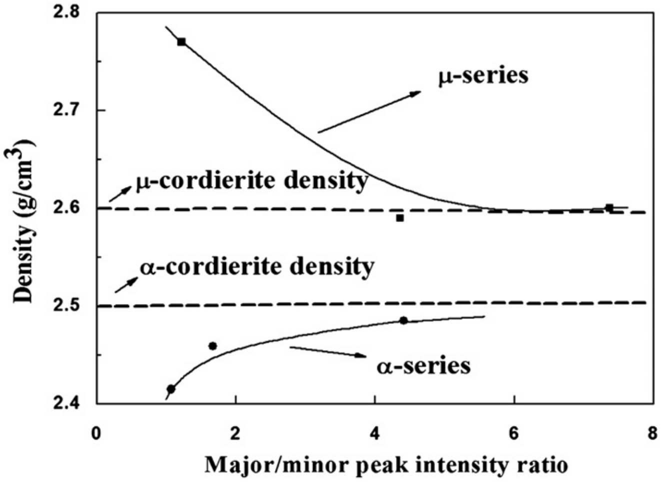


Fig. 3. Density vs. major/minor crystal peak ratio identified from the XRD patterns in Fig. 1. The density of the μ-series and α-series specimens converged to the theoretical density of μ-cordierite ($=2.6$ g/cm^3) and of α-cordierite ($=2.5$ g/cm^3), respectively.

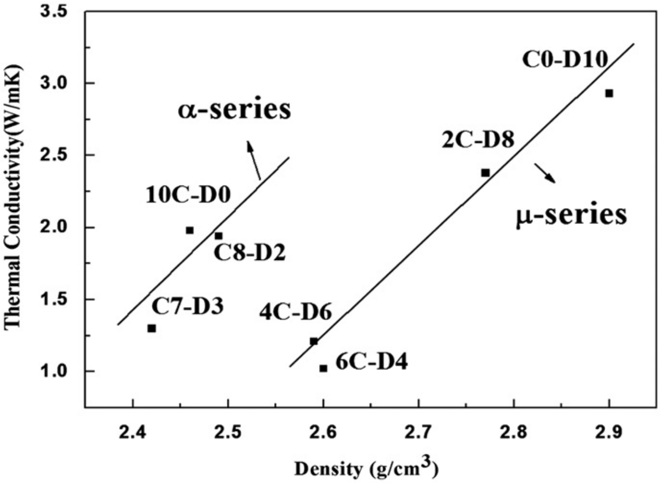
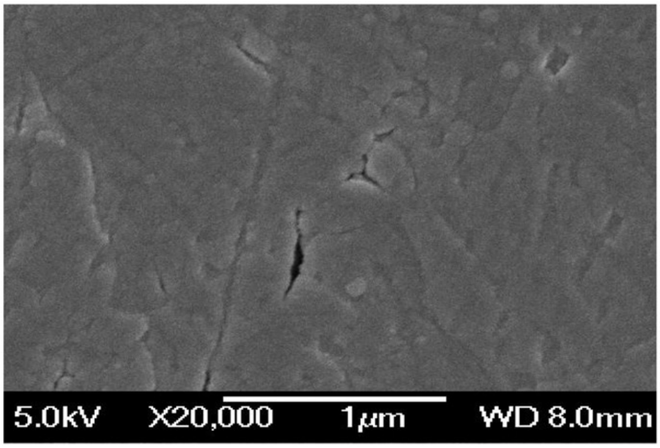
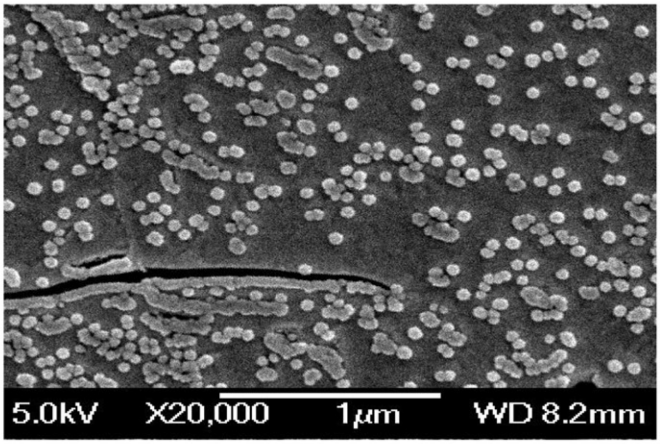


Fig. 4. Thermal conductivity vs. density of cordierite/diopside composites.

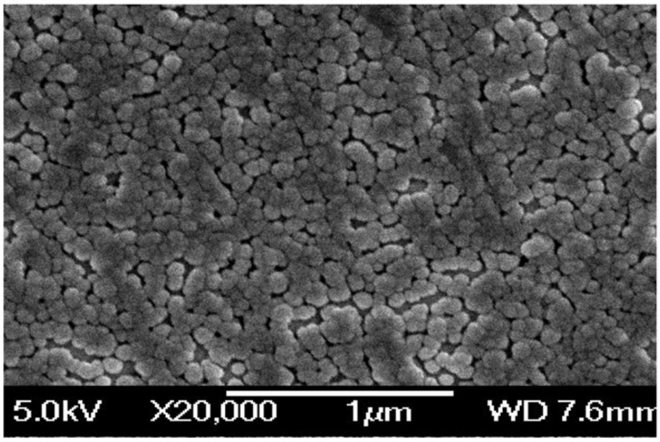
The density of the cordierite/diopside composites showed a linear relationship with the thermal conductivity regardless of the type of crystalline phase that formed. The α-series specimens are positioned at higher coordinates than the μ-series specimens. This indicates that even with the same density, the α-series specimen has higher thermal conductivity than the μ-series specimen. This behavior arose due to the higher thermal conductivity of the α-cordierite compared to that of the μ-cordierite as discussed early.



C0-D10



C4-D6



C10-D0

Fig. 5. Microstructures magnified 20,000 times observed by scanning electron microscope for the cordierite/diopside composites.

The microstructures observed by SEM for the cordierite/diopside composites are shown in Fig. 5. Fine particles of 30–50 nm in size were observed in the microstructures of the composites containing cordierite above 40 wt%. These nanometer-sized particles were μ-cordierite, as identified from the XRD result shown in Fig. 1. These types of nanometer-sized crystals were not clearly observed in the C0-D10 specimen made with diopside glass frit at 100%. The fine nano-particles were more closely packed as the cordierite content increased. These particles were confirmed as α-cordierite, as shown in Fig. 1. In the C10-D0 specimen manufactured with 100% cordierite glass frit, particles of 80–100 nm in size were densely formed. These

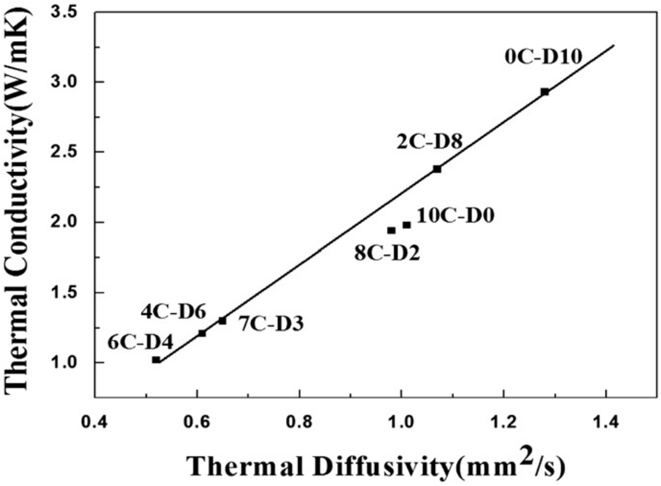


Fig. 6. Thermal conductivity vs. thermal diffusivity of the cordierite/diopside composites fabricated in this study, showing a remarkable linear relationship.

were α-cordierite, as confirmed from the XRD result in Fig. 1. The linear relationship between the thermal conductivity and the thermal diffusion coefficient of the cordierite/diopside composites regardless of the type of crystalline generated and XRD crystal peak intensity shown in Fig. 6. The thermal conductivity (K) is determined by Eq. (1)

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

where D is the thermal diffusivity, ρ is the density and C_p is the specific heat capacity.

Fig. 6. shows that the thermal diffusivity was identified as the dominant factor among these three parameters in terms of expressing the thermal conductivity of the cordierite/diopside composites fabricated in this study.

4. Conclusion

Cordierite/diopside composites for LED packaging materials were manufactured using a glass–ceramics process in which a green compact composed of diopside ($CaO–Al_2O_3–2SiO_2$) and cordierite ($2MgO–2Al_2O_3–5SiO_2$) glass frits was heat-treated. The composites contain 0–30 wt% diopside glass frits had α-cordierite as the major phase and the μ-cordierite as a minor phase, whereas the composites containing diopside frit of 40–80 wt% had μ-cordierite and diopside crystals as the major and minor phase, respectively. Adding diopside glass frit decreased the thermal conductivity of the specimens with main crystal of α-cordierite but increased that of the specimens with the major crystal of μ-cordierite.

The density of the cordierite/diopside composites showed a linear correlation with the thermal conductivity regardless of the type of crystalline phase that formed. The α-cordierite phase was superior to the μ-cordierite phase in enhancing the thermal conductivity of the composites. 30–50 nm crystals were sparsely observed in the microstructures of the specimens with major crystal of μ-cordierite, and 30–100 nm crystals were formed compactly in the specimens with the major crystal of α-cordierite. The cordierite/diopside composites fabricated in this study could be applied as components in LED packaging materials due to the adequate thermal conductivity of 1–3 W/m, and thermal diffusivity of 0.5–1.3 mm^2/s.

Acknowledgements

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