

Dependence of Thermal Properties on Crystallization Behavior of CaMgSi₂O₆ Glass-Ceramics

Chang Jun Jeon, Won Jae Yeo and Eung Soo Kim[†]

Department of Materials Engineering, Kyonggi University, Suwon 443-760, Korea

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Abstract The effects of thermal properties on the crystallization behavior of CaMgSi₂O₆ glass-ceramics were investigated as a function of sintering temperature from 800°C to 900°C. The crystallization behavior of the specimens depended on the sintering temperature, which could be evaluated from the differential thermal analysis, X-ray diffraction and Fourier transform infrared spectroscopy. With increasing sintering temperature, the thermal conductivity of the sintered specimens increased, while the coefficient of thermal expansion (CTE) of the sintered specimens decreased. These results could be attributed to the increase of crystallization, confirmed from the estimation by density measurements. Also, the thermal diffusivity and specific heat capacity of the sintered specimens were discussed with relation to the sintering temperature. Typically, a thermal conductivity of 3.084 W/m°C, CTE of 8.049 ppm/°C, thermal diffusivity of 1.389 mm²/s and specific heat capacity of 0.752 J/g°C were obtained for CaMgSi₂O₆ specimens sintered at 900°C for 5 h.

Key words diopside, crystallization, thermal properties, sintering temperature.

1. Introduction

Due to the significant advantages such as high efficiency, long lifetime and low power consumption, the lighting-emitting diodes (LEDs) are played an important role in many applications.¹⁾ To obtain more lumen, the driving electric current of LED chips has been grown gradually recently. However, nearly 80% of the input power is transformed into heat and the rest is transformed into light. Temperature of LEDs is a primary parameter influencing the durability and reliability, and high temperature and temperature gradient by the mismatch of Young's moduli and coefficients of thermal expansions (CTEs) will generate significant stresses for the packaging and substrate materials. Therefore, the materials with high thermal conductivity and low CTEs should be studied to dissipate heat and prevent mismatch of CTEs in LED multilayer packages.

However, the most of materials with high thermal conductivity have a sintering temperature above 1600°C. For the application of LED multilayer devices, it is necessary to reduce the sintering temperature of materials which can be co-fired with metallic electrodes such as silver (960°C) and copper (1050°C). An efficient way to reduce the sintering temperature is to use crystallized glass.²⁾ And

the transition temperature (T_g) of glass plays an important role in reducing sintering temperature. It is well known that diopside (CaMgSi₂O₆) has high mechanical properties (bending strength of 300 MPa, Mohs hardness of 5-6), good chemical resistivity and proper dielectric properties ($K=6$, $Qf=300$ GHz)³⁾ which could be available to the various applications such as electronics, biomedicine and sealants for solid oxide fuel cells (SOFC).⁴⁾ Typically, the electric, mechanical and thermal properties of glass-ceramics such as diopside (CaMgSi₂O₆) depend on the degree of crystallization. Therefore, the glass-ceramics should be controlled the crystallization behaviors to reduce the sintering temperature effectively without any degradation of thermal properties.

In this study, the dependences of thermal properties on the crystallization behavior of CaMgSi₂O₆ glass-ceramics were investigated as a function of sintering temperature. The degree of crystallization in glass-ceramics was also evaluated by density measurements.

2. Experimental Procedure

High-purity oxide powders of CaCO₃ (99%, high purity chemicals, Japan), MgCO₃ (99.9%, high purity chemicals, Japan) and SiO₂ (99.9%, high purity chemicals, Japan) were used as starting powders. The powders were prepared according to the desired composition CaMgSi₂O₆ and

[†]Corresponding author
E-Mail : eskim@kyonggi.ac.kr (E. S. Kim)

ground with ZrO₂ balls for 24h in ethanol. The mixed powders were first melted in a platinum crucible at 1500°C for 3h and quenched into distilled water. Then the cullet was pulverized and melted again 1500°C for 3h for homogeneity. The pure diopside glass frits were prepared after quenching and ball milling. These glass frits were re-milled for 24h and pressed into pellets isostatically under the pressure of 1500 kg/cm². These pellets were sintered from 800°C to 900°C for 5h in air at heating rate of 5°C/min.

The densities of the sintered specimens were measured by Archimedes method. The differential thermal analysis (DTA) curve was obtained by a simultaneous thermal analyzer-mass spectrometer (STA 409PC + QMS 403C, NETZSCH, Germany). Powder X-ray diffraction analysis (XRD, D/Max-2500V/PC, RIGAKU, Japan), scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) and Fourier transform infrared spectroscopy (430FT-IR, JASCO, Japan) were used to determine the degree of crystallization. The thermal properties and thermal expansion coefficient (25-200°C) of the sintered specimens were obtained by a laser flash apparatus (LFA 457, NETZSCH, Germany) and dilatometer (DIL 402C, NETZSCH, Germany), respectively.

3. Results and Discussion

The values of glass transition temperature (T_g), onset temperature of crystallization (T_c) and the peak temperature of crystallization (T_p) of CaMgSi₂O₆ glass powders were obtained from the DTA curve at heating rate of 5°C/min, as shown in Fig. 1. The strong exothermic reaction peak at 900°C is attributed to the crystallization of glass.

The crystallization kinetics parameters were determined using the modified John-Mehl-Avrami (JMA) equation.⁵⁾

$$\ln\left(\frac{T_p^2}{\varphi}\right) = \left(\frac{E}{RT_p}\right) + \ln\left(\frac{E}{R\nu}\right) \quad (1)$$

where φ is the heating rate (5-20°C/min), R is the gas constant, E is the activation energy for crystallization, and ν is the frequency factor. The Avrami parameter, n , which is related to the mechanism of the crystallization process, is determined from crystallization exotherm using the equation

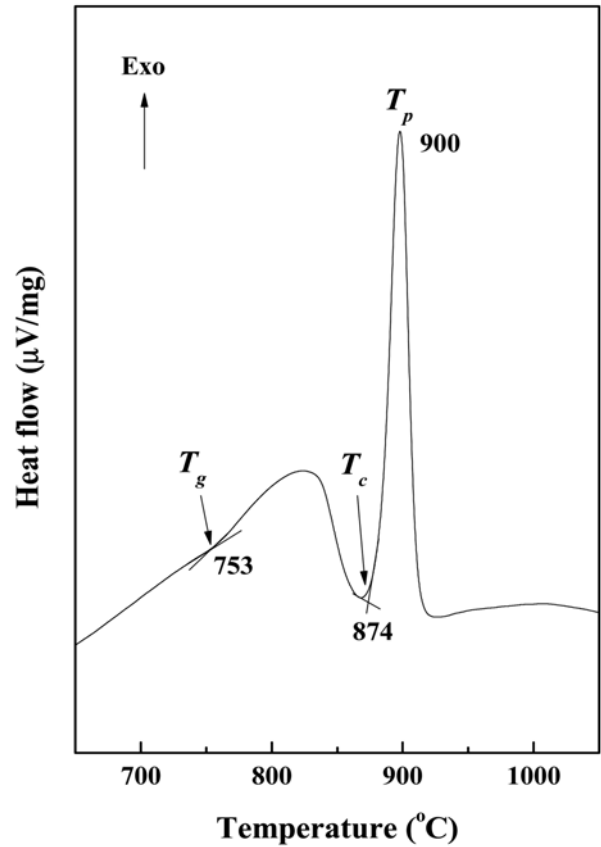


Fig. 1. DTA curve of CaMgSi₂O₆ glass powders at heating rate of 5°C/min.

given by Augis and Bennett.⁶⁾

$$n = \frac{2.5RT_p^2}{E\Delta T} \quad (2)$$

where ΔT is the width of the crystallization peak at half maximum. A value of n close to 3 supports bulk or three-dimensional crystallization and value close to 1 indicates surface crystallization. The $\ln(T_p^2/\varphi)$ versus $1/T_p$ was plotted from T_p with φ , and the kinetic parameters E and ν were determined from the slop and intercept of solid line by least squares fit of the data point, respectively. Also, the value of n was calculated from Eq. (2). The values of the kinetic parameters for CaMgSi₂O₆ (diopside) glasses are showed in Table 1. The value of activation energy was similar to the value (392 kJ/mol) for glasses with composition of diopside reported by Branda et al.⁷⁾

Table 1. T_p with φ , E , ν , ΔT and n of CaMgSi₂O₆ glass.

T_p (°C)				E (kJ/mol)	ν	ΔT	n
$\varphi = 5^\circ\text{C}/\text{min}$	$\varphi = 10^\circ\text{C}/\text{min}$	$\varphi = 15^\circ\text{C}/\text{min}$	$\varphi = 20^\circ\text{C}/\text{min}$				
870.4	883.9	892.2	891.2	359.1	9.97×10^{20}	47	1.0

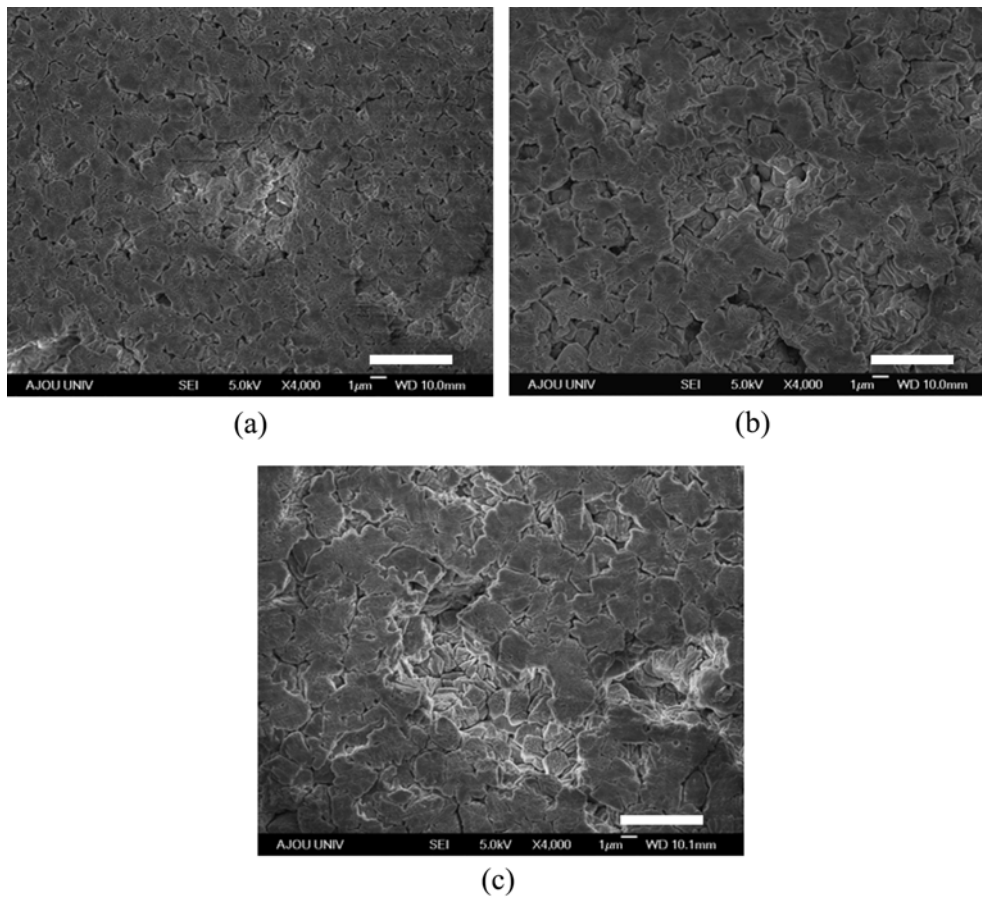


Fig. 2. SEM micrographs of $\text{CaMgSi}_2\text{O}_6$ specimens sintered at (a) 800°C, (b) 850°C and (c) 900°C for 5h (bar = 5µm).

To study the dependence of thermal properties on the crystallization behaviors of $\text{CaMgSi}_2\text{O}_6$ glass-ceramics, the sintering temperature from 800°C to 900°C was determined from the results of DTA data. With increasing of sintering temperature from 800°C to 900°C, the apparent density of $\text{CaMgSi}_2\text{O}_6$ specimens was increased from 2.892 g/cm³ to 2.955 g/cm³, which was also confirmed by the increase of grain size with the sintering temperature, as shown in Fig. 2.

XRD patterns of $\text{CaMgSi}_2\text{O}_6$ specimens sintered from 800°C to 900°C for 5h are shown in Fig. 3. A single phase with monoclinic diopside ($\text{CaMgSi}_2\text{O}_6$) was confirmed through the entire range of the sintering temperatures. In general, the intensity of diffraction peak of a phase depends on the content of crystalline phase. With increasing of sintering temperature, the intensity of diffraction peaks was increased due to the increase of crystalline $\text{CaMgSi}_2\text{O}_6$ phase.

Fig. 4 shows the FTIR spectra of $\text{CaMgSi}_2\text{O}_6$ specimens sintered at 800°C and 900°C for 5h. The bands in the region of 400-1200 cm⁻¹ for diopside were confirmed to

be in accordance with the report of Omori.⁸⁾ The transmittance bands in the 400-800 cm⁻¹ region are due to the bending vibrations of Si-O-Si and Si-O-Al linkages. The broad bands in the 800-1300 cm⁻¹ are assigned to the stretching vibrations of the SiO_4 tetrahedron with a different number of bridging oxygen atoms. With increasing of sintering temperature, any shift of all bands was not observed, while the intensity of all bands was increased due to the increase of crystallization of $\text{CaMgSi}_2\text{O}_6$ glass-ceramics.⁹⁾ These results are in agreement with the results of XRD in Fig. 3.

It has been reported¹⁰⁾ that the diopside ($\text{CaMgSi}_2\text{O}_6$) without nucleation agents is formed only by surface crystallization because there is a big density difference between the crystal and amorphous structure of diopside. Therefore, the degree of crystallization, x (wt.%), was evaluated by density measurements using the following equation.¹¹⁾

$$x = \frac{1/\rho_g - 1/\rho_{gc}}{1/\rho_{g(cr)} - 1/\rho_{cr}} \times 100, \quad (\text{wt.}\%) \quad (3)$$

where ρ_g is absolute density of parent glass, ρ_{gc} is the

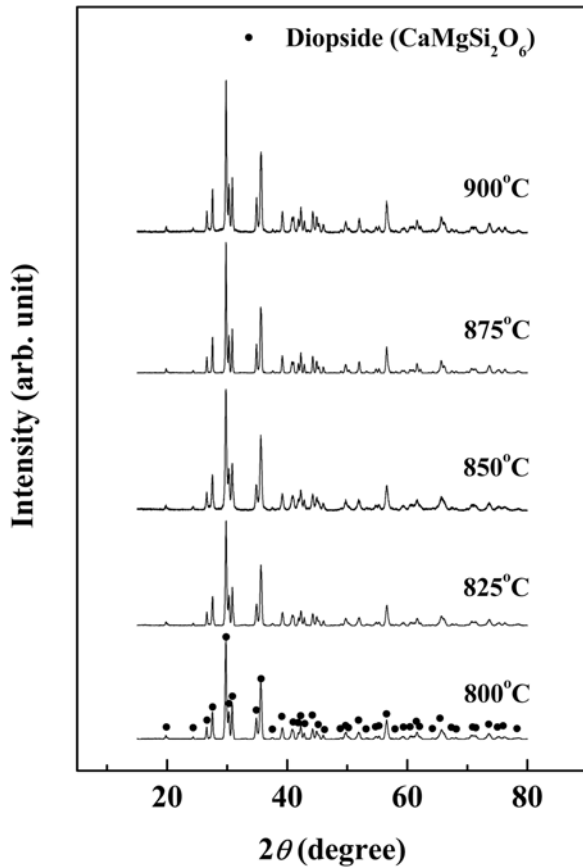


Fig. 3. XRD patterns of CaMgSi₂O₆ specimens sintered from 800°C to 900°C for 5h.

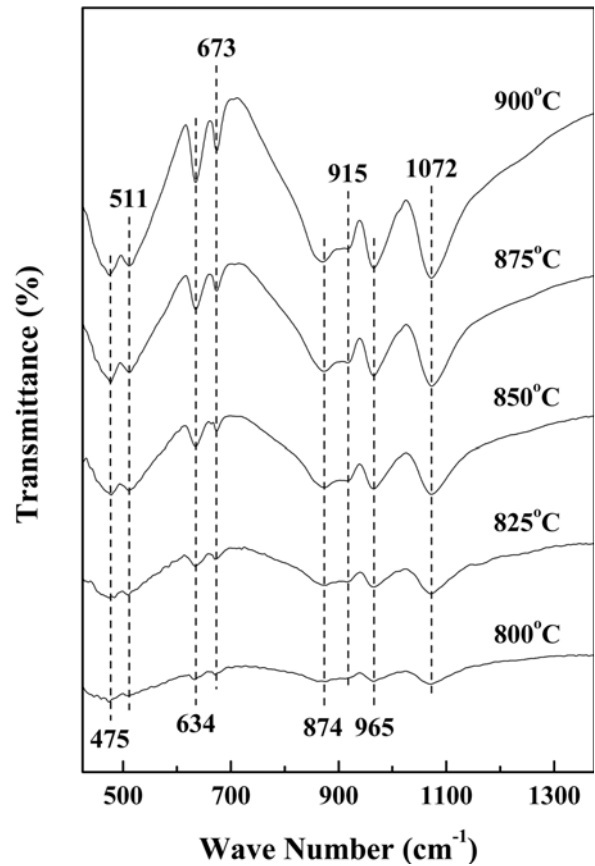


Fig. 4. FTIR spectra of CaMgSi₂O₆ specimens sintered from 800°C to 900°C for 5h.

sintered density of the glass-ceramics, $\rho_{g(cr)}$ is the density of a hypothetical glass with the composition of the formed crystal phase and ρ_{cr} is the density of the crystalline phase. For the case of diopside ρ_g , $\rho_{g(cr)}$ and ρ_{cr} have values of 2.601, 3.27 and 2.75 g/cm³, respectively.^{11,12)} The experimental associated error to the measurements of ρ_{gc} was evaluated as ± 0.0002 g/cm³. As shown in Table 2, the degree of crystallization (x) of CaMgSi₂O₆ specimens was increased with the sintering temperature.

The dependences of thermal conductivity and coefficient of thermal expansion (CTE) on the degree of crystallization (x) of CaMgSi₂O₆ sintered specimens are shown in

Fig. 5. In general, the thermal conductivity and CTE of glasses are not only dependent on the temperature, but also on the composition and structures of the glasses.¹³⁾ With increasing of sintering temperature from 800°C to 900°C, the thermal conductivity of the specimens was increased, while the CTE of the specimens was decreased due to the increase of the degree of crystallization (x). The thermal expansion of crystalline solids can be markedly different from those of the parent glasses. The crystallization process greatly altered the thermal expansion of the glasses. Therefore, the glass-ceramics may have high or low CTE depending on the CTE and elastic properties of

Table 2. The degree of crystallization (x) of CaMgSi₂O₆ specimens sintered from 800°C to 900°C for 5h.

Sintering temperature (°C)	ρ_g (g/cm ³)	ρ_{gc} (g/cm ³)	$\rho_{g(cr)}$ (g/cm ³)	ρ_{cr} (g/cm ³)	x (wt.%)
800	2.601	2.892	2.75	3.27	66.90
825	2.601	2.908	2.75	3.27	70.19
850	2.601	2.934	2.75	3.27	75.46
875	2.601	2.944	2.75	3.27	77.46
900	2.601	2.955	2.75	3.27	79.65

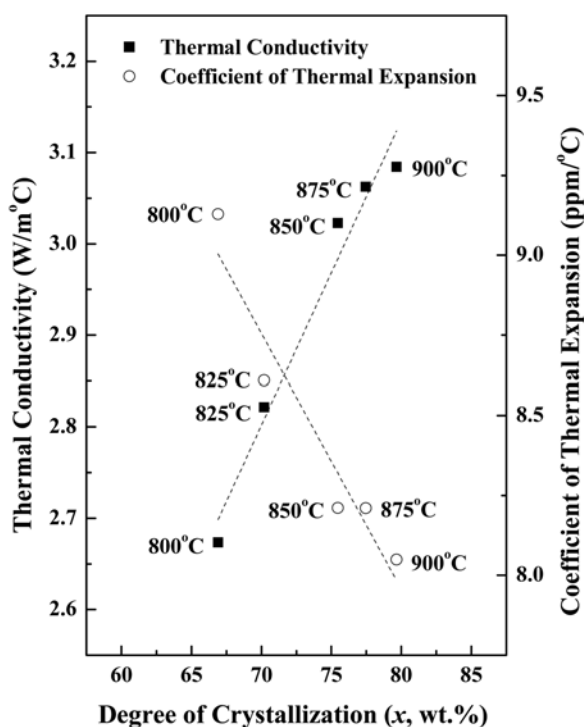


Fig. 5. Dependences of the thermal conductivity and coefficient of thermal expansion on the degree of crystallization (x) of $\text{CaMgSi}_2\text{O}_6$ specimens sintered from 800°C to 900°C for 5h.

the crystal phases formed, including the residual glass matrix. In most cases, the CTE of the crystalline phase generally decrease with decreasing of glassy phase contents in the materials.¹³⁾

Fig. 6 shows the thermal diffusivity and specific heat capacity of $\text{CaMgSi}_2\text{O}_6$ specimens sintered from 800°C to 900°C for 5h. The thermal diffusivity of the specimens was increased with the sintering temperature. However, the specific heat capacity of the specimens was increased up to 850°C, and then decreased. The reasons why the specific heat capacity of the specimens sintered at 850°C for 5h showed the maximum value are under investigation at present.

4. Conclusions

A single phase with monoclinic diopside ($\text{CaMgSi}_2\text{O}_6$) was confirmed through the entire sintering temperature range from 800°C to 900°C. The intensity of diffraction peaks (XRD) and transmittance bands (FTIR) of the sintered specimens were increased with the sintering temperature due to the increase of crystallization of $\text{CaMgSi}_2\text{O}_6$ glass-ceramics.

With increasing of sintering temperature from 800°C to

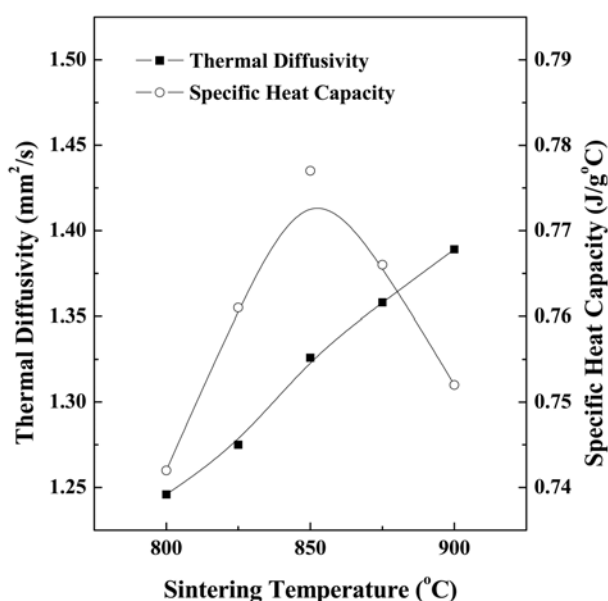


Fig. 6. Thermal diffusivity and specific heat capacity of $\text{CaMgSi}_2\text{O}_6$ specimens sintered from 800°C to 900°C for 5h.

900°C, the thermal conductivity of the sintered specimens was increased, while the coefficient of thermal expansion (CTE) of the sintered specimens was decreased. These results could be attributed to the increase of crystallization confirmed from the estimation by density measurements. The thermal diffusivity of the sintered specimens was increased with the sintering temperature. However, the specific heat capacity of the sintered specimens was increased up to 850°C, and then decreased.

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