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Effect of Al_2O_3 on thermal properties of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics

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Abstract

The thermal properties of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics with Al_2O_3 were investigated as a function of Al_2O_3 volume fraction (V_f). With increasing of Al_2O_3 content, the anorthite ($CaAl_2Si_2O_8$) phase was increased up to 0.08 V_f of Al_2O_3 and then decreased, while the diopside ($CaMgSi_2O_6$) phase was not changed remarkably. The coefficient of thermal expansion (CTE) of the sintered specimens was dependent on the degree of crystallization of glasses. The thermal conductivity of the sintered specimens was affected by the thermal diffusivity and density rather than the specific heat capacity (C_p). The thermal conductivity of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics was increased and the CTE was decreased with the addition of Al_2O_3.

Keywords: A. Sintering; C. Thermal properties; D. Al_2O_3; D. Glass ceramics

1. Introduction

The anorthite–diopside ($CaAl_2Si_2O_8$–$CaMgSi_2O_6$) mixture system has been extensively used for industrial applications because it is not only inexpensive and abundant raw materials in glass batches but also forms the glass–ceramics with wide range of crystalline mixtures between anorthite and diopside [1]. Anorthite–diopside mixture system is also one of good candidates applicable to the package materials for lighting–emitting diodes (LED) chips in view point of the fast heat dissipations and easy control of thermal expansion coefficient between LED chips and package materials.

Although $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics sintered at 950 °C for 3 h showed a thermal conductivity of 1.71 W/m °C from our preliminary experiment, it is not easy to apply this glass–ceramics for the practical application because the thermal conductivity is relatively low.

Generally, the thermal properties of glass–ceramics are dependent on the degree of crystallization. The crystallization of glasses can be achieved by the nucleation process of simple two-step heat treatment; the first step is an isothermal process to form embryo and to grow nucleus. The second step is necessary to enhance crystal growth up to the desired size homogeneously dispersed in the volume [1]. For the effective control of crystallization and thermal properties, the crystalline Al_2O_3 powders with high thermal conductivity (28–35 W/m °C) were added to $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics as impurities and the two-step heat treatment has been employed in this study.

Therefore, the dependences of thermal properties on the degree of crystallization of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glasses were investigated as a function of Al_2O_3 content. With the addition of Al_2O_3, the crystallization behaviors of glasses were also discussed with respect to the relative amount of anorthite ($CaAl_2Si_2O_8$) to diopside ($CaMgSi_2O_6$) phase of the sintered specimens.

2. Experimental procedures

High-purity oxide powders of $CaCO_3$ (99%), Al_2O_3 (99%), $MgCO_3$ (99.9%) and SiO_2 (99.9%) were used as starting materials. The powders were separately prepared according to the desired compositions of $CaAl_2Si_2O_8$ and $CaMgSi_2O_6$, and ground with ZrO_2 balls for 24 h in ethanol. The mixed powders were melted in a platinum crucible at 1550 °C for 3 h and quenched into distilled water. The cullets were pulverized and mixed according to the desired formula

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of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$, and then melted again at 1550 °C for 3 h. Pure glass frits were obtained by quenching of melts into distilled water. These glass frits were re-milled for 24 h with the addition of Al_2O_3, and pressed isostatically into pellets under the pressure of 147 MPa. These pellets were sintered from 900 °C to 1000 °C for 3 h after holding at 790 °C for 3 h in air.

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) and scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) were used to identify the phases developed during the sintering process and to evaluate the degree of crystallization of the sintered specimens. The thermal properties and thermal expansion coefficient (25–600 °C) of the sintered specimens were obtained by a laser flash apparatus (LFA 457, NETZSCH, Germany) and dilatometer (DIL 402 C, NETZSCH, Germany), respectively.

3. Results and discussion

The crystallization behavior of glasses can be determined from the thermal stability of glasses. A parameter usually employed to estimate the glass stability is the difference of onset temperature of crystallization (T_c) from glass transition temperature (T_g), ($T_c - T_g$) [2]. The larger $T_c - T_g$ delays the nucleation process. Also, the difference of peak temperature of crystallization (T_p) from T_c, ($T_p - T_c$) is related to the rate of devitrification transformation of glassy phases [2]. Saad and Poulain [3] suggested the thermal stability parameter (S) by the following equation.

$$S = \frac{(T_p - T_c)(T_c - T_g)}{T_g} \quad (1)$$

The S reflects the resistance to devitrification after the formation of glass.

Fig. 1 shows the DTA curves of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass powders with volume fraction (V_f) of Al_2O_3. The strong exothermic reaction peaked around 990 °C is attributed to the crystallization of glass. The thermal parameters obtained from the DTA curves are summarized in Table 1. With increasing of Al_2O_3 content, T_g of glasses was decreased up to 0.08 V_f and then increased, while T_c, T_p and $T_c - T_g$ were increased up to 0.08 V_f and then decreased. However, $T_p - T_c$ and S were decreased with the Al_2O_3 content except for the glass with 0.08 V_f of Al_2O_3. These results could be explained that the addition of Al_2O_3 induced the increase of glass stability and the decrease of resistance to devitrification after the formation of glass. For the glass with 0.08 V_f of Al_2O_3, the different behavior of thermal parameters could be attributed to the changes of relative amount of crystalline phases (anorthite and diopside) formed by the addition of Al_2O_3 (Table 2).

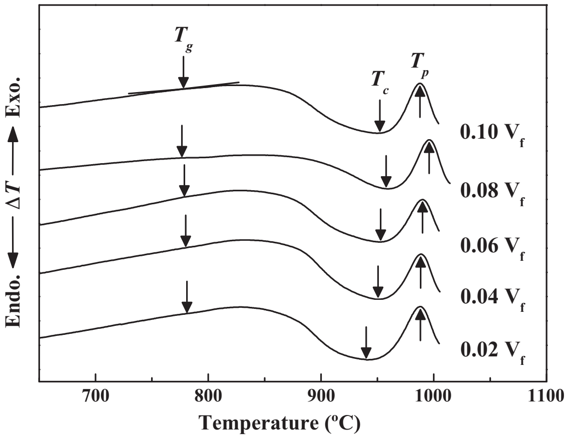

Fig. 1. DTA curves of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass powders with various volume fraction (V_f) of Al_2O_3.

To study the dependence of thermal properties on the crystallization behaviors of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glasses with Al_2O_3 content, the sintering temperatures from 900 °C (before T_c) to 1000 °C (around T_p) after holding at 790 °C (around T_g) for 3 h were determined from the results of DTA data. The optimal sintering temperature of 1000 °C was selected for the highest sintered density to reduce the effects of density on the thermal properties. The apparent (A_D) and relative (R_D) densities of the sintered specimens were remarkably decreased at 0.08 V_f of Al_2O_3, as shown in Table 2. These results could be attributed to the effect of crystalline phases on the sinterability which could be confirmed by XRD patterns of the specimens.

XRD patterns of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with various V_f of Al_2O_3 specimens sintered from 900 °C to 1000 °C for 3 h are shown in Fig. 2. The triclinic anorthite ($CaAl_2Si_2O_8$), monoclinic diopside ($CaMgSi_2O_6$) and rhombohedral α-Al_2O_3 phases were detected through the entire range of compositions. The degree of crystallization of the glasses with 0.02 V_f of Al_2O_3 was increased with increasing of sintering temperature from 900 °C to 1000 °C (Fig. 2(a)). For

Table 1
Thermal parameters of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass powders with various volume fraction (V_f) of Al_2O_3 obtained from DTA (T_g: glass transition temperature, T_c: onset temperature of crystallization, T_p: peak temperature of crystallization, S: thermal stability parameter).

Al_2O_3 (V_f)	T_g (°C)	T_c (°C)	T_p (°C)	$T_c - T_g$ (°C)	$T_p - T_c$ (°C)	S (°C)
0.02	781	940	988	159	48	9.79
0.04	780	951	989	171	38	8.31
0.06	779	953	990	174	37	8.27
0.08	776	958	996	182	38	8.93
0.10	778	952	988	174	36	7.96

Table 2
Degree of crystallization and physical properties of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with volume fraction (V_f) of Al_2O_3 specimens sintered at 1000 °C for 3 h (I_A and I_B: relative amount of anorthite and diopside, X_c, X_A and X_D: degree of crystallization of specimens, anorthite and diopside, A_D and R_D: apparent and relative densities, CTE: coefficient of thermal expansion, C_p: specific heat capacity).

Al_2O_3 (V_f)	Relative amount		Degree of crystallization			A_D (g/cm^3)	R_D (%)	CTE (10^{-6}/°C)	C_p (J/g °C)
	I_A (%)	I_D (%)	X_c (%)	X_A (%)	X_D (%)				
0.02	70.2	29.8	83.4	58.5	24.9	2.827	93.7	6.32	0.772
0.04	70.5	29.5	83.9	59.1	24.8	2.835	93.3	6.48	0.742
0.06	71.0	29.0	83.5	59.3	24.2	2.843	93.0	6.37	0.732
0.08	72.4	27.6	83.2	60.2	23.0	2.763	89.8	6.30	0.731
0.10	71.8	28.2	83.0	59.5	23.4	2.836	91.6	6.27	0.749

the specimens sintered at 1000 °C, the amount of α-Al_2O_3 phase was increased with Al_2O_3 content (Fig. 2(b)). The XRD peak intensities of two crystalline phases (anorthite and diopside) were also changed with the sintering temperature and/or Al_2O_3 content. It has been reported [4] that anorthite resulted from the reaction between glass and crystalline Al_2O_3 powder is formed at the initial stage of sintering, and growing further until sintering is finished. With increasing of Al_2O_3 content, the integral intensity of the main XRD peak for diopside ($2\theta = 30°$) showed nearly a constant, while that for anorthite ($2\theta = 28°$) was increased up to 0.08 V_f and then decreased due to the imperfect dispersion of Al_2O_3 particles at 0.10 V_f. These results are agreed with the results for the anorthite–diopside system with Al_2O_3 reported by Kim et al. [5]. For the sintered specimens with 0.08 V_f of Al_2O_3, the decrease of density (Table 2) could be attributed to the increase of anorthite phase because the density of anorthite (2.761 g/cm^3) is smaller than those of diopside (3.236 g/cm^3) and/or Al_2O_3 (3.987 g/cm^3).

For the specimens sintered at 1000 °C for 3 h, SEM micrographs of the specimens with various V_f of Al_2O_3 are shown in Fig. 3. Characteristic lamellar crystals of anorthite ($CaAl_2Si_2O_8$) and bead of diopside ($CaMgSi_2O_6$) were observed, being cemented with residual glass in the glass–ceramics, as reported by Leonelli et al. [1]. With increasing of Al_2O_3 content, the lamellar crystals of anorthite was increased up to 0.08 V_f and then decreased. These results are in agreement with the results of density and XRD data (Table 2). Since the thermal properties of sintered specimens were affected by density resulted from the relative amount of each phase, the lamellar crystals of anorthite with fissure will have a decisive effect on the thermal properties.

According to Demirkesen et al. [6], the thermal properties of silica-based glass–ceramics with Al_2O_3 are dependent on the type and amounts of crystalline phases as well as the amount and composition of the residual glassy phase. Therefore, the degree of crystallization (X_c) of the specimens was calculated using the following equation reported by Challa–Hermans–Weidinger [7] and are summarized in Table 2.

$$X_c(\%) = \left[1 - ((I_a)_{2\theta}/(I_a)_{2\theta^*})\right] \times 100 \qquad (2)$$

where $(I_a)_{2\theta}$ and $(I_a)_{2\theta^*}$ are the amorphous intensities of the sintered specimens and glass powders at same range of 2θ (32–33°), respectively. The crystallization degrees of anorthite

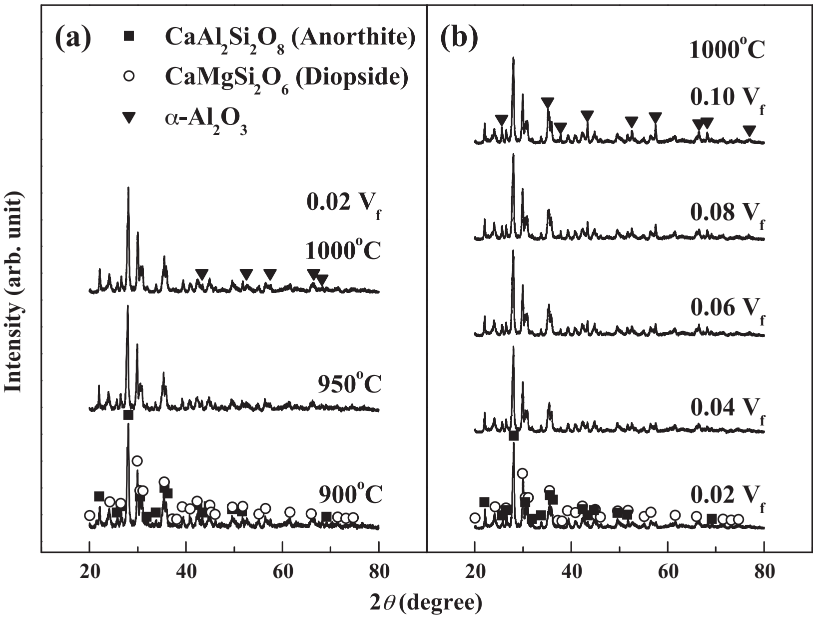

Fig. 2. XRD patterns of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with 0.02 volume fraction (V_f) of Al_2O_3 specimens sintered from 900 °C to 1000 °C for 3 h (a) and those with various V_f of Al_2O_3 specimens sintered at 1000 °C for 3 h (b).

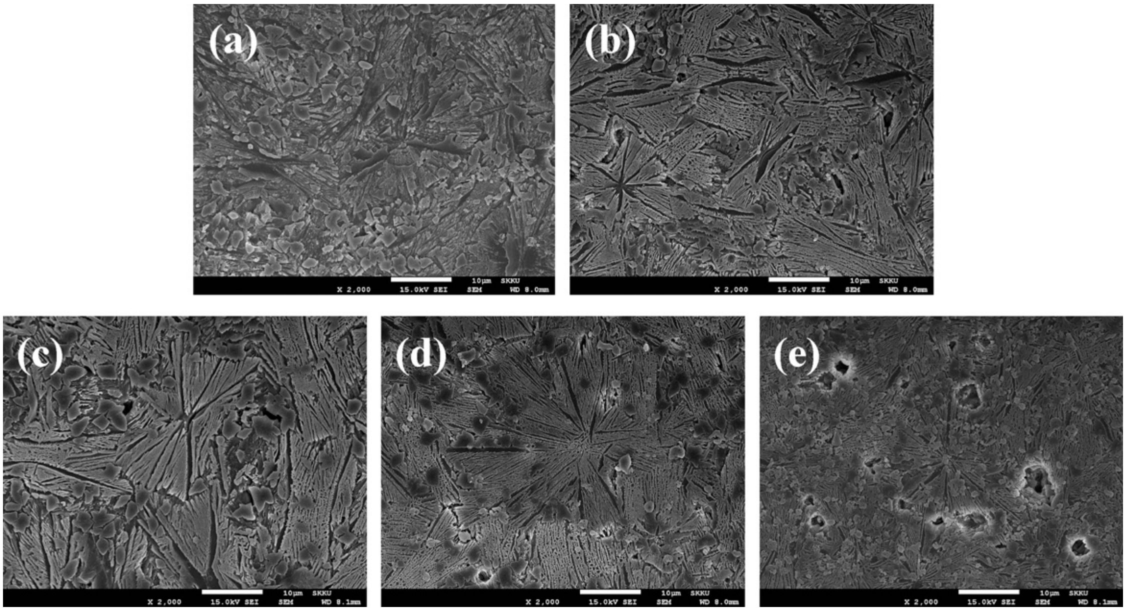

Fig. 3. SEM micrographs of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with volume fraction (V_f) of Al_2O_3 specimens sintered at 1000 °C for 3 h (bar = 10 μm); (a) 0.02 V_f, (b) 0.04 V_f, (c) 0.06 V_f, (d) 0.08 V_f and (e) 0.10 V_f.

(X_A) and diopside (X_D) were determined from the relative amount of each phase (anorthite (I_A) and diopside (I_D)) obtained by the integral intensity of main XRD peaks for anorthite and diopside, as shown in Table 2. With increasing of Al_2O_3 content, the coefficient of thermal expansion (CTE) of the specimens was increased up to 0.04 V_f and then decreased. This result is agreed with the tendency of the degree of crystallization (X_c) of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics with Al_2O_3 content (Table 2).

Fig. 4 shows the thermal conductivity and diffusivity of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with various V_f of Al_2O_3 specimens sintered at 1000 °C for 3 h. In general, the thermal conductivity can be obtained from thermal diffusivity, density and specific heat capacity (C_p). The thermal diffusivity of the specimens was increased with Al_2O_3 content. These results are due to the fact that Al_2O_3 affects the diffusion mechanism at the initial stages of sintering, causing a decrease of activation energy of diffusion [8]. With increasing of Al_2O_3 content, the thermal conductivity of the specimens was increased due to the higher thermal conductivity of Al_2O_3 (28–35 W/m °C) than that of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics (1.71 W/m °C) except for specimens with 0.08 V_f of Al_2O_3. The decrease of thermal conductivity at 0.08 V_f is due to the decrease of sintered density resulted from the increase of anorthite ($CaAl_2Si_2O_8$) phase with lower thermal conductivity than that of diopside ($CaMgSi_2O_6$) (Table 2). However, the C_p with Al_2O_3 content was not changed remarkably from 0.731 J/g °C (0.08 V_f) to 0.772 J/g °C (0.02 V_f) (Table 2). Therefore, the thermal conductivity of the specimens was affected by the thermal diffusivity and density rather than C_p in this study. By the addition of Al_2O_3, the thermal conductivity of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ glass–ceramics was effectively increased (Fig. 4) and CTE was decreased (Table 2). Comparing to the soda-lime glass (thermal conductivity = 0.9–1.3 W/m °C, CTE = 9×10^{-6}/°C) and FR-4 glass epoxy (thermal conductivity = 0.2 W/m °C, CTE = 12–16×10^{-6}/°C), the thermal conductivity (2.07 W/m °C) and CTE (6.27×10^{-6}/°C) of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with 0.10 V_f of Al_2O_3 could be applicable to the LED multilayer ceramic packages with low temperature co-fired ceramic (LTCC) technology.

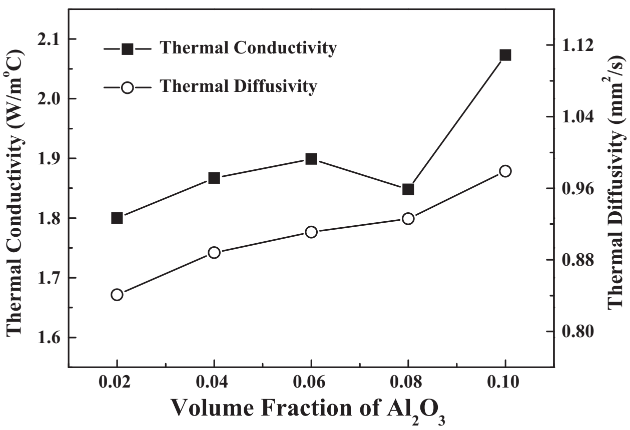

Fig. 4. The thermal conductivity and diffusivity of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with various volume fraction of Al_2O_3 specimens sintered at 1000 °C for 3 h.

4. Conclusions

For the sintered specimens of $0.5CaAl_2Si_2O_8$–$0.5CaMgSi_2O_6$ with Al_2O_3, the triclinic anorthite ($CaAl_2Si_2O_8$), monoclinic diopside ($CaMgSi_2O_6$) and rhombohedral α-Al_2O_3 phases were confirmed through the entire range of compositions.

With increasing of Al_2O_3 content, the coefficient of thermal expansion (CTE) of the specimens sintered at 1000 °C for 3 h was increased up to 0.04 volume fraction (V_f) and then decreased, which could be attributed to the degree of crystallization of the specimens with Al_2O_3 content. The thermal conductivity of sintered specimens was increased due to the increase of thermal diffusivity with Al_2O_3 content. For the specimens with 0.08 V_f of Al_2O_3, the decrease of thermal conductivity is due to the increase of relative amount of anorthite to diopside phase.

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