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Microwave dielectric properties of diopside glass-ceramics

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Abstract

The effect of crystallization behaviors on the microwave dielectric properties of $CaMgSi_2O_6$ (diopside) glass-ceramics was investigated as a function of the particle size of the glass frit. The crystallization behaviors of the specimens were evaluated by differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis by the combined Rietveld and reference intensity ratio (RIR) methods. With increasing particle size of the glass frit, the dielectric constant (K) and the temperature coefficient of resonant frequency (TCF) decreased. However, the quality factor (Qf) of the specimens increased up to 6.88 μm and then decreased with increasing particle size. These results could be attributed to the degree of crystallization.

Keywords: C. Dielectric properties; D. Glass ceramics; Crystallization behaviors

1. Introduction

The considerable progress in the wireless communication and electronics industries has led to an increasing demand for lightweight, miniaturized, multifunctional electronic devices. Recently, low-temperature co-fired ceramic (LTCC) technology has been developed to meet the demand for electronic devices, and it is necessary to reduce the sintering temperature of microwave dielectric ceramics that can be co-fired with metallic electrodes (Ag, Cu, or Au).

The desired LTCC substrate materials are required to have a low dielectric constant ($K < 10$) in order to avoid signal propagation delay, and a high quality factor (Qf), as well as a small temperature coefficient of resonant frequency (TCF) [1]. Diopside ($CaMgSi_2O_6$)-based glass-ceramics are attractive materials for LTCC substrates because they have a low dielectric constant, high quality factor, and high mechanical strength at low sintering temperatures [2].

In the fabrication of a desirable glass-ceramic used in LTCC substrate materials, complete densification and sufficient crystallization must be achieved in order to obtain good mechanical and dielectric properties. The particle size of the glass frit has a significant influence on the formation of glass-ceramics, affecting the densification, crystallization behavior, and microwave dielectric properties of the resulting glass-ceramics [3].

Therefore, the dependence of the microwave dielectric properties on the degree of crystallization of diopside ($CaMgSi_2O_6$) glass-ceramics with various particle sizes was investigated using the combined Rietveld and reference intensity ratio (RIR) methods.

The activation energy of crystallization and the Avrami constant are also discussed to evaluate the crystallization behaviors of the glass.

2. Experimental procedures

High-purity oxide powders of $CaCO_3$ (99%), $MgCO_3$ (99.9%), and SiO_2 (99.9%) were used as starting materials. The powders were prepared according to the desired composition of $CaMgSi_2O_6$ and ground with ZrO_2 balls for 24 h in ethanol. The mixed powders were melted in a platinum crucible at 1500 °C for 3 h. Pure glass frits were obtained by quenching the melts in distilled water. These glass frits were re-milled from 3 h to 48 h to obtain different particle-size distributions and then isostatically pressed into pellets under a pressure of 1500 kg/cm^2. These pellets were sintered from 800 °C to 950 °C for 1 h in air.

The particle-size distributions of the diopside glass frit were measured by a laser diffraction particle size analyzer

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(Mastersizer-2000, Malvern Instruments, UK). Diopside glass frits have a median particle size in the range of 3.35–19.89 μm. The densities of the sintered specimens were measured by Archimedes's method. The differential thermal analysis (DTA) curves were obtained using a simultaneous thermal analyzer-mass spectrometer (STA 409PC-QMS 403C, NETZSCH, Germany) at different heating rates (5–20 K/min). Powder X-ray diffraction analysis (XRD, D/Max-2500 V/PC, RIGAKU, Japan) was used to evaluate the crystalline phase and crystallization behavior of glass-ceramics. The degree of crystallization of the specimens was determined by the combined Rietveld and RIR methods [4,5]. A sample of 10 wt% α-Al_2O_3 (annealed at 1500 °C for 24 h to increase the crystallinity up to 100 wt%) was added to all specimens as an internal standard [5]. Rietveld refinements of the XRD patterns were performed using the FullProf program [6]. The degree of crystallization (α) of the specimens in relation to the internal standard was evaluated from Eq. (1) [4]:

$$\alpha = \left(W_c/W_{std}\right)\left(W_{std}/W\right) \quad (1)$$

Where W, W_c, and W_{std} are the weights of the specimens, the crystalline component, and the internal standard, respectively. The value of W_c/W_{std} calculated by the Rietveld quantitative analysis under the condition of $W_c + W_{std} = 1$ and W_{std}/W was obtained by measuring the weights of the specimens and the internal standard [4]. The microwave dielectric properties were measured by Hakki and Coleman's method [7] with the TE_{011} mode at 12 GHz. The TCF of specimens was measured by the cavity method [8] in the temperature range 20–80 °C.

3. Results and discussion

Fig. 1 shows the differential thermal analysis (DTA) curves of diopside glass powders with different particle sizes heated at rates of 5–20 K/min. The strong exothermic reactions peaked at 886–926 °C, and these are attributed to the crystallization of the glass at different particle sizes and heating rates. For the glasses with the same heating rate of 5 K/min [Fig. 1(a)], the peak temperature of crystallization (T_p) increased with increasing particle size because larger particles have greater heat transfer resistance compared to the smaller particles [9]. However, the glass transition temperature (T_g) is nearly constant regardless of the particle size because the increase in the specific surface area does not significantly influence the glass transition temperature [10]. The T_p of glasses with the same particle size (6.88 μm) increased with increasing heating rate [Fig. 1(b)]. A similar tendency was confirmed for all particle sizes with the different heating rates. From the T_p of glasses with different heating rates, the activation energy of crystallization (E_a) was calculated using the following modified form of the Kissinger equation [11]:

$$\ln\frac{T_p^2}{\beta^n} = \frac{E_a}{RT_p} + \text{constant} \quad (2)$$

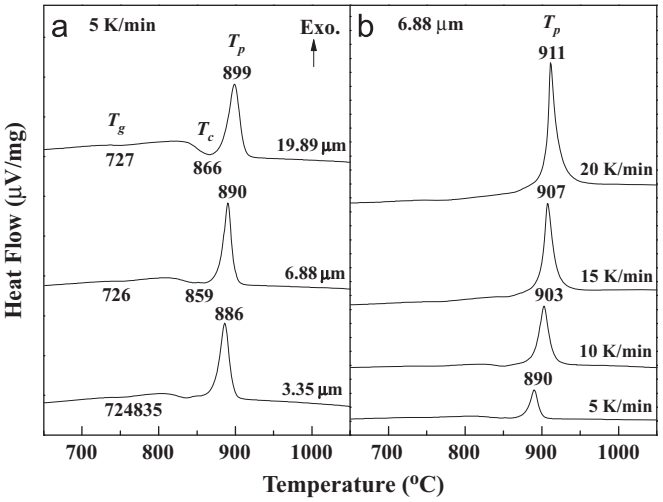

Fig. 1. DTA curves of (a) $CaMgSi_2O_6$ glass powders with different particle sizes heated at a rate of 5 K/min and (b) with the same particle size of 6.88 μm at different heating rates.

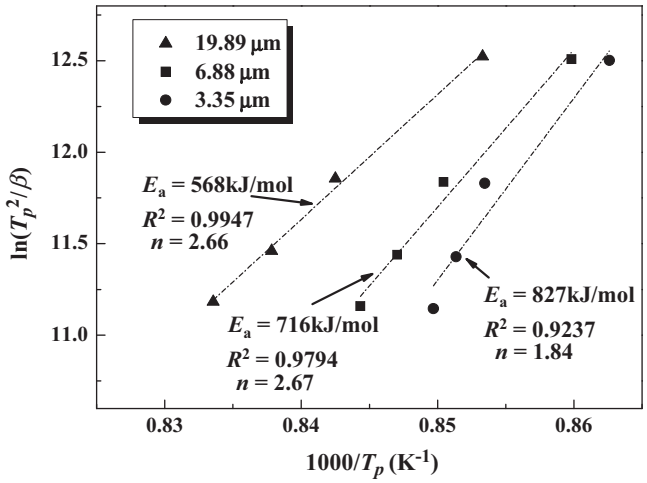

Fig. 2. Plots of activation energy for crystallization (E_a) of $CaMgSi_2O_6$ glasses (R^2=correlation coefficients).

Where β is the heating rate (5–20 K/min), R is the idealgas constant, and n is the Avrami constant. The plots of $\ln(T_p^2/\beta)$ versus $1000/T_p$ for the crystallization of $CaMgSi_2O_6$ glasses are shown in Fig. 2. The E_a values were obtained from the slope of the solid line by least-squares fit of the data points. The validity of the Kissinger method [12] is supported by the high values of the correlation coefficients (R^2). From the value of the activation energy, the Avrami parameter (n) was calculated by the Augis–Bennett equation [13]:

$$n = \frac{2.5RT_p^2}{E_a\Delta T} \quad (3)$$

Where ΔT is the full width of the exothermic peak at the half-maximum intensity. A crystallization value of n close to 1 means that surface crystallization dominates the overall crystallization, whereas a bulk or three-dimensional

crystallization process corresponds to values close to 3. The value of the activation energy decreased with increasing particle size from 827 to 568 kJ/mol. The value of n was 1.84–2.67, which indicates that primary crystallization started from the surface.

To investigate the dependence of the microwave dielectric properties on the crystallization behaviors of $CaMgSi_2O_6$ glass-ceramics with different particle sizes of the glass frit, the sintering temperature from 800 °C to 950 °C was determined from the results of the DTA data. With increasing sintering temperature, the apparent density of the specimens increased. However, the apparent densities of specimens sintered at 900 °C and 950 °C were almost the same, and their relative densities were above 91%. Therefore, the effects of the crystallization behaviors on the microwave dielectric properties of specimens sintered at 900 °C were investigated for practical applications.

Fig. 3 shows the Rietveld refinement plots of the XRD data for the $CaMgSi_2O_6$ with 6.88 μm particle size specimens sintered at 900 °C for 1 h. Dots indicate the observed intensities, overlying solid lines are calculated intensities, and the dotted lines at the bottom are the difference between the observed and calculated intensities. Short vertical bars indicate the Bragg reflections that were allowed for the monoclinic diopside (top) and rhombohedral α-Al_2O_3 (bottom) phases. All peaks in the XRD patterns fit well with the monoclinic diopside ($C12/c1$) and rhombohedral α-Al_2O_3 ($R\bar{3}c$) structures. The results obtained from the Rietveld–RIR quantitative analysis of XRD data are summarized in Table 1. With increasing particle size of the glass frit, the degree of crystallization increased up to 6.88 μm and then decreased for the specimen sintered at 900 °C for 1 h. The validity of the Rietveld–RIR quantitative analysis was supported by the low values of the refinement parameters for each specimen.

The dependence of the quality factor (Qf) on the degree of crystallization of $CaMgSi_2O_6$ specimens with different particle sizessintered at 900 °C for 1 h are shown in Fig. 4. In general, the dielectric properties of the material are affected mainly by the density, porosity, crystalline phase, and the degree of crystallization [2]. The degree of crystallization of the glass matrix has significant effects on the Qf of the glass-ceramics. It has been reported that single crystals always have a higher Qf value than the corresponding glass [14]. Therefore, a high Qf value would be expected for the specimens with a high degree of crystallization. With an increase in particle size, the Qf increased

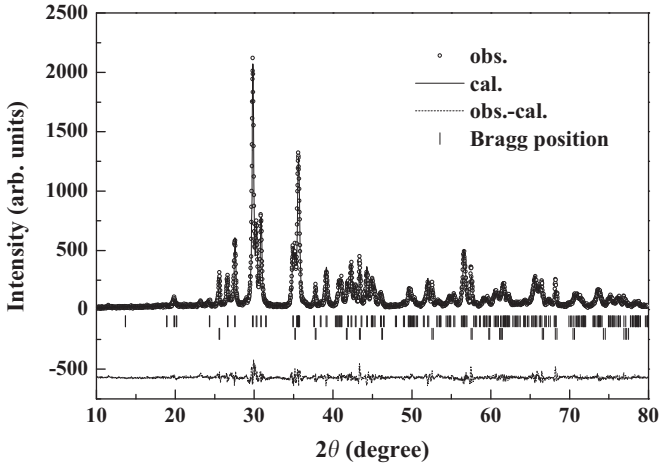

Fig. 3. Rietveld refinement patterns with 6.88 μm particle size of $CaMgSi_2O_6$ specimens sintered at 900 °C for 1 h. Markers representing the phase reflections correspond to Al_2O_3 and diopside (from bottom to top).

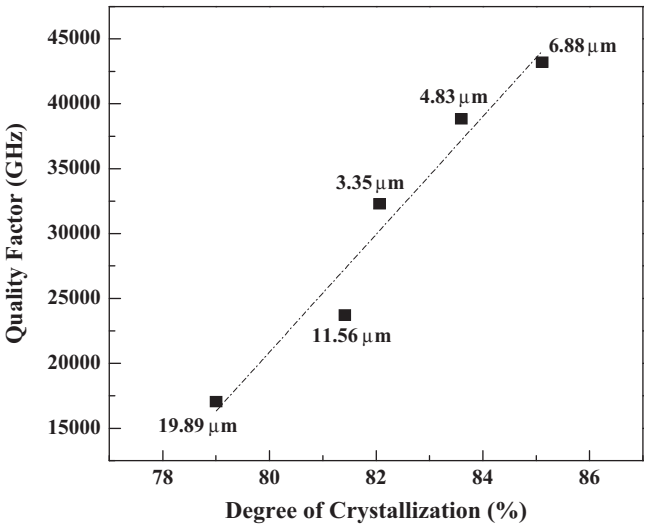

Fig. 4. Dependence of quality factor (Qf) on degree of crystallization with different particle sizes of $CaMgSi_2O_6$ specimens sintered at 900 °C for 1 h.

Table 1
Degree of crystallization and Rietveld refinement parameters with different particle sizes of $CaMgSi_2O_6$ specimens sintered at 900 °C for 1 h.

Sintering temperature (°C)	900				
Particle size of glass (μm)	3.35	4.83	6.88	11.56	19.89
Diopside crystalline (wt%)	82.06	83.59	85.11	81.41	79.00
R_{Bragg}					
Diopside	3.58	3.69	3.72	3.9	4.01
Al_2O_3	4.72	5.15	6.24	4.47	5.64
GoF	1.2	1.3	1.2	1.2	1.3
R_p	12.2	12.0	12.0	11.4	12.5
R_{wp}	15.9	15.8	15.7	15.2	16.3

R_{Bragg} is the Bragg R-factor, GoF is the goodness of fit, R_p is the profile factor and R_{wp} is the weighted profile factor.

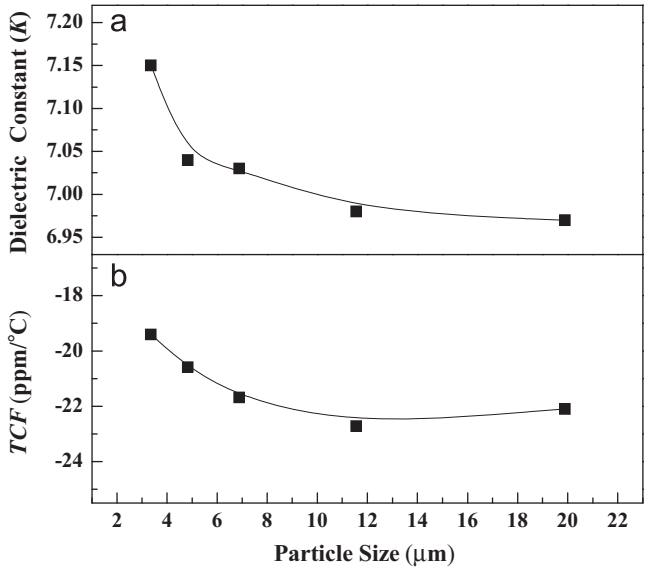

Fig. 5. (a) Dielectric constant (K) and (b) temperature coefficient of resonant frequency (TCF) with different particle sizes of $CaMgSi_2O_6$ specimens sintered at 900 °C for 1 h.

up to 6.88 μm and then decreased. These results could be attributed to the degree of crystallization.

Fig. 5 shows the dielectric constant (K) and the temperature coefficient of the resonant frequency (TCF) of $CaMgSi_2O_6$ specimens with different particle sizes sintered at 900 °C for 1 h. With increasing particle size of the glass frit, the K and TCF of the sintered specimens decreased due to an increase of porosity.

4. Conclusions

For $CaMgSi_2O_6$ specimens with different particle sizes sintered at 900 °C for 1 h, a single crystalline phase of a monoclinic diopside structure was confirmed. With increasing particle size of the glass frit, the dielectric constant (K) and the temperature coefficient of resonant frequency (TCF) decreased, while the quality factor (Qf) increased up to 6.88 μm and then decreased due to the degree of crystallization. Typically, $K=7.03$, $Qf=43$, 197 GHz, and $TCF=-21.68$ ppm/°C were obtained for the specimens sintered at 900 °C for 1 h.

Acknowledgments

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