Effects of Crystallization Behavior on Microwave Dielectric Properties of CaMgSi$_2$O$_6$ Glass-Ceramics

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ABSTRACT

Dependence of microwave dielectric properties on the crystallization behavior of CaMgSi$_2$O$_6$ (diopside) glass-ceramic was investigated with different heat treatment methods (one and/or two-step). The crystallization behaviors of the specimens, crystallite size and degree of crystallization, were evaluated by differential thermal analysis (DTA), scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis by combined Rietveld and reference intensity ratio (RIR) methods. With an increase in heat treatment temperature, the dielectric constant ($K$) and the quality factor ($Q_f$) increased due to the increase of the crystallite size and degree of crystallization. The specimens heat-treated by the two-step method had a higher degree of crystallization than the specimens heat-treated by the one-step method, which induced improvement in the quality factor ($Q_f$) of the specimens.

Key words : Two-step heat treatment, Microwave dielectric properties, CaMgSi$_2$O$_6$ Glass-ceramics

1. Introduction

With the rapid growth of wireless communication and the electronics industries, the operating frequencies of electronic application systems have increased. Due to the increase of operating frequency, it is essential that substrates should have a low dielectric constant ($K < 10$) to avoid signal propagation delay, and obtain a high quality factor ($Q_f$) and near zero temperature coefficient of resonant frequency ($T_C$) to ensure the stability of frequency against temperature changes. Low-temperature cofired ceramics (LTCC) technology is one of the most promising approaches to meet the demand for integration of component to electronic devices with high quality. ¹

Diopside (CaMgSi$_2$O$_6$) glass-ceramics have been extensively investigated and considered as a potential material in LTCC technology because of its low dielectric constant, high quality factor, high mechanical strength and low sintering temperatures.²

It has been reported that single crystals always have a higher $Q_f$ value than the corresponding glass and the degree of crystallization of the glass matrix has significant effects on the microwave dielectric properties of the glass-ceramics.³ A high $Q_f$ value would be expected for the specimens with a high degree of crystallization. Therefore, the nucleation and growth of glass should be controlled to improve the degree of crystallization of glass-ceramics applicable to microwave dielectric materials with a high quality factor.

The heat treatment method to control the crystallization of glass-ceramics is to devitrify a glass by a two-step heat treatment. The first step is a low temperature heat treatment at a nucleation temperature ($T_n$) that forms a high density of nuclei throughout the interior of the glass. A high density of nuclei is important as it leads to a desirable microstructure consisting of a large number of small crystals. The second step is a high temperature heat treatment at a peak temperature of crystallization temperature ($T_p$) to allow crystal growth of the nuclei.⁴

In this study, the dependence of the microwave dielectric properties on the crystallization behavior of diopside (CaMgSi$_2$O$_6$) glass-ceramics was investigated with different heat treatment methods (one and/or two-step). The crystallite size and degree of crystallization were studied to evaluate the crystallization behavior of glass-ceramics.

2. Experimental Procedure

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$_2$O$_6$ 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 for 12 h and then isostatically pressed into pellets under a pressure of 1500 kg/cm$^2$. These pellets were heat treated from 800°C to 950°C for 1 h after holding at 763°C for 3 h in air.

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). The dilatometer (DIL 402, Netzch, Germany) were performed to determine the suitable nucleation and crystallization temperatures. The rate of heating for DTA and dilatometer was 5°C/min. Scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) and powder X-ray diffraction analysis (XRD, D/MAX-2500V/PC, RIGAKU, Japan) were used to evaluate the crystalline phase and crystallization behavior of the glass-ceramic samples. The degree of crystallization of the specimens was determined by the combined Rietveld and reference intensity ratio (RIR) methods. A sample of 10 wt% α-Al₂O₃ (annealed at 1500°C for 24 h to increase the crystallinity up to 100 wt%) was added to all specimens as an internal standard. Rietveld refinements of the XRD patterns were performed using the Full-Profil program. The degree of crystallization (α) of the specimens in relation to the internal standard was evaluated from Eq. (1).

\[
\alpha = \frac{W_c}{W_c + W_{std}}
\]

Where \(W_c\), \(W_{std}\) are the weights of the specimens, the crystalline component, and the internal standard, respectively. The value of \(W_c/W_{std}\) calculated by 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. The microwave dielectric properties were measured by Hakki and Coleman’s method with the TE₀₁₁ mode at 12 GHz.

### 3. Results and Discussion

Fig. 1 shows the dilatometric and differential thermal analysis (DTA) curves of diopside (CaMgSi₂O₆) glass powder heated at rates of 5°C/min. The crystal nucleation and growth (crystallization) temperatures of diopside (CaMgSi₂O₆) glass-ceramics were determined by dilatometric and DTA curves. A dilatometric curve of the glass powders, represented in Fig. 1(a) shows the exact locations of the glass transition temperature (\(T_g\)) at around 740°C and the softening point temperature (\(T_s\)) at around 775°C. As shown in Fig. 1(b), a DTA curve of the glass powder shows the onset temperature of crystallization (\(T_p\)) at around 859°C and a strong exothermic reaction peak at around 890°C (\(T_n\)), which are attributed to the crystallization of the glass. However, the exact nucleation temperature (\(T_n\)) values could not be confirmed through the dilatometric and DTA curves. The \(T_n\) is usually determined in the nucleation range between \(T_g\) and \(T_s\). According to Marghussian and Dayi Niaki, \(T_n\) can be estimated by Eq. (2).

\[
T_n = T_g + \frac{2}{3} (T_s - T_g)
\]

From the result of Eq. (1), the \(T_n\) value of diopside glasses was determined at about 763°C.

To investigate the dependence of the microwave dielectric properties on the crystallization behaviors of diopside (CaMgSi₂O₆) glass-ceramics with different heat treatment methods (one and/or two-step), diopside specimens were heat treated at 800-950°C for 1 h after holding at 763°C for 3 h, based on the results of the dilatometric and DTA data.

The apparent and relative densities of diopside glass-ceramics with different heat treatment methods are summarized in Table 1. With an increase of the heat-treatment

### Table 1. Apparent Density, Relative Density, and Average Crystallite Size of Diopside (CaMgSi₂O₆) Glass-Ceramics with Different Heat Treatment Methods (One and/or Two-step)

<table>
<thead>
<tr>
<th>Heat treatment temperature (°C)</th>
<th>Heat treatment method</th>
<th>Apparent density (g/cm³)</th>
<th>Relative density (%)</th>
<th>Average crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1 step</td>
<td>2.822(15)</td>
<td>87.21</td>
<td>26.05(4)</td>
</tr>
<tr>
<td>850</td>
<td>1 step</td>
<td>2.952(31)</td>
<td>91.22</td>
<td>25.49(5)</td>
</tr>
<tr>
<td></td>
<td>2 step</td>
<td>2.947(2)</td>
<td>91.08</td>
<td>25.49(5)</td>
</tr>
<tr>
<td>900</td>
<td>1 step</td>
<td>2.982(0)</td>
<td>92.16</td>
<td>31.18(6)</td>
</tr>
<tr>
<td></td>
<td>2 step</td>
<td>2.955(12)</td>
<td>91.33</td>
<td>27.77(2)</td>
</tr>
<tr>
<td>950</td>
<td>1 step</td>
<td>2.988(6)</td>
<td>92.34</td>
<td>31.42(9)</td>
</tr>
<tr>
<td></td>
<td>2 step</td>
<td>2.960(8)</td>
<td>91.48</td>
<td>28.09(5)</td>
</tr>
</tbody>
</table>

\[\text{Data were obtained by }\]

\[\text{Hakki and Coleman’s method with the TE_011 mode at 12 GHz.}\]
temperature from 800°C to 950°C, the apparent and relative densities of the specimens increased up to 850°C, and then were almost the same. However, the densities of specimens with two-step heat treatment were slightly smaller than those of specimens with the one-step heat treatment. These results may be due to the difference in the density of glass and crystalline phase, which leads to the formation of the crystallization induced porosity.

Fig. 2 shows the XRD patterns of diopside (CaMgSi$_2$O$_6$) specimens with different heat treatments (one and/or two-step) (b).

The crystallite size ($L$) of the diopside (CaMgSi$_2$O$_6$) specimens was calculated from the FWHM of the peaks with strong intensities of XRD patterns using Scherrer’s Eq. (3):\n
$$L = \frac{0.89\lambda}{B\cos\theta}$$  \hspace{1cm} (3)$$

where $\lambda$ is the wavelength of the CuK$_\alpha$-radiation ($\lambda = 0.154$ nm), $\beta$ is the FWHM of the peak (radians) corrected for instrumental broadening, and $\theta$ is the Bragg angle.

With an increase of heat-treatment temperature from 850°C to 950°C, the average crystallite size ($L$) of the specimens increased as confirmed in Table 1 and Fig. 3. However, the average crystallite size of the specimens with two-step heat treatment (nucleation and growth) was relatively smaller than that of specimens with one-step heat treatment (growth) due to the formation of more nuclei induced by holding at nucleation temperature ($T_n$).

![Fig. 2. XRD patterns of diopside (CaMgSi$_2$O$_6$) specimens after one-step heat treatment (a) and specimens heat-treated at 950°C with different heat treatments (one and/or two-step) (b).](image)

![Fig. 3. SEM micrographs of diopside (CaMgSi$_2$O$_6$) specimens with one step heat treatment at (a) 850°C, (b) 900°C, and (c) 950°C; with two step heat treatment at (d) 850°C, (e) 900°C, and (f) 950°C (bar = 0.1 µm).](image)
heat treatment at 950°C. 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$_2$O$_3$ (bottom) phases. All peaks in the XRD patterns fit well with the monoclinic diopside (C12/c1) and rhombohedral α-Al$_2$O$_3$ (R-3c) structures. The results obtained from the Rietveld-RIR quantitative analysis of XRD data are summarized in Table 2. For the specimens with heat treatment of the same step, the degree of crystallization increased with an increase of heat-treatment temperature from 850°C to 950°C. The degree of crystallization of specimens with two-step heat treatment was greater than that of specimens with one-step heat treatment. The validity of the Rietveld–RIR quantitative analysis was supported by the low values of the refinement parameters for each specimen.

Fig. 6 shows dependence of the quality factor ($Q_f$) on the degree of crystallization of diopside (CaMgSi$_2$O$_6$) specimens with different heat treatment methods. In general, glass-ceramics with a low degree of crystallization have relatively poor mechanical and dielectric properties, and a $Q_f$ value at microwave frequency would be detrimental to the residual glass. Therefore, a higher degree of crystallization should be achieved in order to improve $Q_f$ value. With an increase of heat-treatment temperature from 850°C to 950°C, the $Q_f$ increased. In addition, the $Q_f$ of specimens with two-step heat treatment was greater than that of specimens with

<table>
<thead>
<tr>
<th>Heat treatment method</th>
<th>1 step</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sintering temperature (°C)</strong></td>
<td>850</td>
<td>900</td>
<td>950</td>
<td>850</td>
<td>900</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td><strong>Diopside crystalline (wt.%)</strong></td>
<td>(0.56)</td>
<td>(0.55)</td>
<td>(0.57)</td>
<td>(0.43)</td>
<td>(0.43)</td>
<td>(0.41)</td>
<td></td>
</tr>
<tr>
<td>Glass (wt.%)</td>
<td>(0.21)</td>
<td>(0.20)</td>
<td>(0.21)</td>
<td>(0.15)</td>
<td>(0.15)</td>
<td>(0.14)</td>
<td></td>
</tr>
<tr>
<td>$R_{Bragg}$</td>
<td>3.19</td>
<td>3.82</td>
<td>3.73</td>
<td>3.51</td>
<td>3.73</td>
<td>3.43</td>
<td></td>
</tr>
<tr>
<td>$R_{Al_2O_3}$</td>
<td>5.66</td>
<td>6.58</td>
<td>5.56</td>
<td>4.37</td>
<td>5.90</td>
<td>5.31</td>
<td></td>
</tr>
<tr>
<td>$R_T$</td>
<td>10.90</td>
<td>11.80</td>
<td>11.40</td>
<td>8.94</td>
<td>9.21</td>
<td>8.75</td>
<td></td>
</tr>
<tr>
<td>$R_{mp}$</td>
<td>14.40</td>
<td>15.60</td>
<td>14.90</td>
<td>11.50</td>
<td>12.00</td>
<td>11.30</td>
<td></td>
</tr>
</tbody>
</table>
one-step heat treatment. These results could be attributed to an increase in the degree of crystallization. In particular, the \( Q' \) value (47,712 GHz) of specimens with two-step heat treatment at 900°C was greater than that (46,870 GHz) of specimens with one-step heat treatment at 950°C. Even though the heat-treatment temperature is reduced, the \( Q' \) value was improved through two-step heat treatment.

4. Conclusions

For diopside (CaMgSi\(_2\)O\(_4\)) glass-ceramics with different heat treatment methods (one and/or two-step), a single crystalline phase of diopside with monoclinic structure was confirmed. The dielectric constant (\( K \)) of the specimens was dependent on the density and the average crystallite size of the diopside phase. However, the quality factor (\( Q' \)) of the specimens was affected by the degree of crystallization. With an increase of heat-treatment temperature from 850°C to 950°C, the dielectric constant (\( K \)) and the quality factor (\( Q' \)) increased. The \( Q' \) of the specimens was increased more by the two-step heat treatment (crystal nucleation and growth) than by the one-step heat treatment (crystal growth). Typically, \( K = 7.03 \) and \( Q' = 43,197 \) GHz were obtained for the specimens with two-step heat treatment at 950°C.

Acknowledgment

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