Phase development and dielectric properties of BaAl$_2$Si$_2$O$_8$-based low temperature co-fire ceramic material

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Low-temperature co-fired ceramics (LTCC) is a glass-ceramic composite, in which the glass crystallization occurs during firing. The amount and type of the crystalline and amorphous phases determine the final properties. A commercial glass-ceramic powder was selected in this study. The phase development was studied by XRD, and the dielectric properties were studied by DTA and dilatometry. The dielectric properties were measured by the Hakki and Coleman method. The results show that Al$_2$O$_3$, TiO$_2$, and Zn$_2$SiO$_4$ existed in the as-received powder and their quantities decreased as the firing temperature increased. BaAl$_2$Si$_2$O$_8$ appeared at 850°C and its quantity increased with temperature. At 900°C, Sr$_2$Al$_2$Si$_2$O$_7$, and (K$_{0.94}$Na$_{0.06}$)(Al$_{0.99}$Si$_{3.01}$)O$_8$ were formed. The degree of crystallinity of the as-received powder was around 53 mass% and gradually increased, reaching a maximum of ~96 mass% at 900°C. As the firing temperature increased, the dielectric constant of the fired specimens decreased, but the quality factor increased. The decrease in dielectric constant can be attributed to the porous microstructure and the increase of the quality factor can be attributed to the increasing degree of crystallinity at high temperatures. However, the porous microstructure deteriorates the mechanical strength of the fired specimens. So a trade-off between the dielectric properties and the mechanical strength should be made.

Key-words : Microwave, Glass-ceramic, Crystallization, LTCC, Celsian

1. Introduction

In recent years, low-temperature cofired ceramics (LTCC) have been widely applied in electronic, automotive, and medical industries. LTCC has several advantages, such as a low dielectric constant, low dielectric losses, high thermal conductivity, high mechanical strength, and the ability of integrating passive elements into the substrate.1–6) Compared with printed resin boards, LTCC is superior due to its high frequency characteristics, thermal stability, and its capacity for integrating passive components. Compared to HTCC (high temperature co-fired ceramics) technology, LTCC offers the advantage of using low resistivity conductors like silver, gold, copper, and alloys with palladium and platinum by co-firing at temperatures below 1000°C.6)

LTCC is a glass-ceramic composite that densifies via viscous-flow sintering.7–10) For this process, the glass must form a low-viscosity melt during firing. The ceramic filler is selected to optimize the dielectric, magnetic, thermal, and other properties. To improve the shape stability during firing and the dielectric as well as the mechanical properties of the composite, the glass amount is reduced after densification by crystallization.11,12) The amount and type of crystalline and amorphous phases in the microstructure of the composite after sintering determine the final properties. The purpose of this paper is to study the evolution of the crystalline and amorphous phases of commercial glass-ceramic powder during firing, as well as its dielectric properties.

2. Experimental procedure

2.1 Sample preparation

Commercially available glass-ceramic powder, Heraeus 40327°C (W.C. Heraeus GmbH, Germany), was used in this study. The supplier lists the dielectric constant ($\varepsilon_r$) in the range of 7.5–7.9 (1 kHz/25°C) and the dissipation factor to be 2.1 × 10$^{-3}$ (1 kHz/25°C). The as-received powder was put in a polyethylene jar containing yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) grinding balls ($\phi = 2$ mm). After being milled for 5 hours, the powder slurry was dried and then granulated by sieving through a 170-mesh with a suitable amount of 10% polyvinyl butyral (PVB) solution as the binder.

For dilatometry analysis, the granulated powder was compacted by uniaxially dry pressing at 50 MPa into disks of 6 mm in diameter and 5 mm in height. For dielectric properties analysis, the granulated powder was compacted by uniaxially dry pressing at 50 MPa into disks of 18 mm in diameter and 9 mm in height. After debinding, the disks were sintered in an air atmosphere with the chamber furnace (Nabertherm, Lilienthal, Germany) at various peak temperatures ranging from 800°C to 925°C for 30 min at a heating rate of 5°C/min.

The sample used for semi-quantitative analysis by XRF (X-ray fluorescence) spectrometer was prepared in the form of a pressed disk. The as-received powder was mixed with wax (Hoechstwax, Fluxana, Germany) in a weight ratio of 6:4. The mixture was then ground by a disk mill (HSM–50H, Herzog, Germany) at 1600 rpm for 30 seconds. It was then pressed uniaxially at 50 MPa into a disk of 4 cm in diameter and 3 mm in height.

2.2 Thermal properties analysis

The thermal behavior of the as-received glass-ceramic powder was analyzed by differential thermal analysis (DTA, STA 449C,
Netzsch, Germany). A sample with a weight of around 50 mg was placed into an Al₂O₃ crucible pan. The measurement was performed in air with a flow rate of 50 ml/min. The heating rate in the DTA measurement was 5°C/min and alumina powder was used as an inert reference material.

The sintering shrinkage behavior of the compacted disk was studied using dilatometry (DIL 402C, Netzsch, Germany). The measurement was performed in air by placing the testing sample in between two alumina disks and heating them at a rate of 5°C/min.

2.3 Composition and crystalline phase analysis

The chemical analysis of the as-received powder was conducted by an XRF spectrometer (S8, Bruker, Germany) equipped with a rhodium X-ray tube, 4 kW generator. The fluorescence radiation emitted was filtered through the programmable collimator and detected simultaneously by a proportional flow counter and a scintillation counter. The spectral scan was carried out from 5° to 140° (2θ) for the elements between potassium to uranium. The analyzer crystal was LiF(200) and 60 kV, 67 mA excitation conditions were used. For the light elements, spectral scans were carried out around the fluorescence angle of every element using suitable crystals: PET for analyzing elements from aluminium to chlorine and XS–55 with a synthetic multilayer structure for the analysis of oxygen to magnesium.

The crystalline phases of the sintered disks were identified by an X-ray diffractometer (XRD, XPert Pro, Philips, the Netherlands). The angular range was from 20° to 80°(2θ), with a step width of 0.01° and a step time of 5 s. A copper tube was used with 50 kV/40 mA. The degree of crystallinity was determined using the Archimedes method. In addition, the true density of each specimen sintered at various temperatures was determined using the Archimedes method. The apparent densities of sintered samples were measured using the Archimedes method. Finally, the samples were ground with progressively finer sand paper and polished to obtain a mirror finish.

Table 1. Chemical Analysis of the as-received Powder by XRF

<table>
<thead>
<tr>
<th>Element</th>
<th>Ba</th>
<th>Si</th>
<th>Al</th>
<th>Sr</th>
<th>Zn</th>
<th>Zr</th>
<th>Co</th>
<th>Ca</th>
<th>Ti</th>
<th>Mg</th>
<th>K</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>22.4%</td>
<td>17.1%</td>
<td>12.6%</td>
<td>6.6%</td>
<td>5.7%</td>
<td>3.2%</td>
<td>2.6%</td>
<td>2.5%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>1.6%</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

2.4 Density measurement

The apparent densities of sintered samples were measured using the Archimedes method. In addition, the true density of each specimen sintered at various temperatures was determined by a helium pycnometer (AccuPyc 1330, Micromeritics, USA). The samples for helium pycnometry measurement were prepared by crushing and grinding the fired disks with alumina mortar and pestle. The ground powder was forced to pass through a 325-mesh sieve before measurement.

2.5 Dielectric properties measurement

Microwave dielectric properties were calculated from the resonant frequency using the Hakki and Coleman dielectric resonator method(13) as modified and improved by Courtney.(14) A cylindrical dielectric resonator was positioned between two brass plates connected to the measuring system. A HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement. The dielectric constant εᵣ was approximated using the values of resonant frequency and the size of the fired disk. Since the shrinkage of all the specimens was not uniform, the Q values were measured at different frequencies (9–10 GHz).

2.6 Microstructure analysis

The microstructure of the specimens’ cross-sectioned view was characterized by a scanning electron microscope (SEM, S–4100, Hitachi, Japan). All samples were examined at an accelerating voltage of 15 kV. The specimens were ground with progressively finer sand paper and polished to obtain a mirror finish. The samples were cleaned by sonication in D. I. Water for three minutes to remove any unwanted debris from the surface. The surfaces were then platinum sputter coated for 2 min in order to eliminate surface charging.

3. Results and discussion

3.1 Phase development analysis

Table 1 shows the main elements of the as-received powder obtained by XRF semi-quantitative analysis. The XRD patterns of the as-received powder and the specimens fired at various temperatures from 20° to 40°(2θ) are shown in Fig. 1. Table 2 summarizes the crystalline phases detected at various temperatures. Three crystalline phases, Al₂O₃, TiO₂, and Zn₂SiO₄, existed in the as-received powder. They existed at all temperatures up to a maximal temperature of 925°C. It has been reported that Al₂O₃ ceramics have an ultrahigh Qf of 360,000 GHz, a low εᵣ of 9.8, and a negative τf of -60 ppm/°C, while TiO₂ ceramics have a high Qf of 48,000 GHz, a εᵣ of 100, and a positive τf of +450 ppm/°C.(15–17) Therefore, the temperature coefficient of the resonant frequency can be improved by adding TiO₂. Besides being a τf modifier, TiO₂ also acts as the nucleating agent in the glass-ceramic system. The amount of TiO₂ utilized greatly controls the crystalline content of the fired glass-ceramic.(16,17) Zn₂SiO₄ (willenite) ceramics also possess excellent dielectric properties; a dielectric constant εᵣ of 6.6, a quality factor Qf of 219,000 GHz, and a temperature coefficient of resonant frequency τf of -61 ppm/°C.(20)

In Fig. 1, at 850°C the diffraction lines of a new crystalline phase, identified as BaAl₂Si₂O₈, can be seen. At 900°C, Sr₂Al₂Si₂O₈ and (K₀.₉₄Na₀.₀₆)(Al₀.₉₉Si₃.₀₁)O₈ were also formed. Eventually, Al₂O₃, BaAl₂Si₂O₈, TiO₂, Zn₂SiO₄, Sr₂Al₂Si₂O₈ and (K₀.₉₄Na₀.₀₆)(Al₀.₉₉Si₃.₀₁)O₈ co-exist in the 925°C-fired specimen. BaAl₂Si₂O₈ is the major crystalline phase formed during firing.

![Fig. 1. XRD patterns of the as-received powder and the specimens fired at various temperatures.](image-url)
paracelsian) are monoclinic, while orthorhombic (low temperature) and hexagonal (high temperature) forms are the usual products of synthesis. Monoclinic celsian is the most desirable form for many ceramic applications, since it is stable to 1590°C, whereas hexagonal celsian undergoes a polymorphic phase transformation at 300°C with an associated volume change which leads to mechanical instability. It has been reported that BaAl2Si2O8 possess some superior characteristics, such as a low dielectric constant, a highly refractory property, high mechanical resistance, low thermal expansion, and great chemical stability. It is therefore a potential matrix material in the LTCC process.24)–26)

Besides the crystalline phases, there are background-bump phenomena in the angular range of 20° to 35°(2θ) of the specimens fired at temperature less than 900°C, as can be seen in Fig. 1. The background-bump phenomena reveals the existence of the amorphous phase in these specimens. As the firing temperature increased, the background-bump phenomena became less significant. This implies a decrease in the quantity of the glass phase in specimens as the firing temperature increased. Figure 2 shows the temperature dependence of the quantity of the major crystalline phases and the degree of crystallinity of the fired specimens. The quantities of Al2O3, TiO2, and Zn2SiO4 decreased as the firing temperature increased. In particular, when the firing temperature was higher than 850°C, Al2O3, TiO2, and Zn2SiO4 all decreased rapidly. In contrast, after BaAl2Si2O8 was formed at 850°C, its quantity increased rapidly and reached a maximum at 900°C. In addition, the variation of the degree of crystallinity showed a trend similar to that of BaAl2Si2O8. The degree of crystallinity of the as-received powder was 53 mass%; it increased to 63 mass% at 850°C, 75 mass% at 875°C, and reached its maximum of 96 mass% at 900°C.

### 3.2. Thermal analysis results

Figure 3 shows the DTA results of the as-received glass-ceramic powder. There is an endothermic reaction starting from 778°C, which corresponds to the glass softening point of the glass-ceramic powder. There was another exothermic reaction starting at 874°C, which corresponds to the glass crystallization reaction of the glass-ceramic powder. Compared to the findings in Fig. 2, the degree of crystallinity started to increase rapidly at 850°C. This reveals that the crystallization reaction detected by

### Table 2. Crystalline Phases of Specimens Fired at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crystalline Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received</td>
<td>Al2O3, TiO2, Zn2SiO4</td>
</tr>
<tr>
<td>800</td>
<td>Al2O3, TiO2, Zn2SiO4</td>
</tr>
<tr>
<td>825</td>
<td>Al2O3, TiO2, Zn2SiO4</td>
</tr>
<tr>
<td>850</td>
<td>Al2O3, BaAl2Si2O6, TiO2, Zn2SiO4</td>
</tr>
<tr>
<td>875</td>
<td>Al2O3, BaAl2Si2O6, TiO2, Zn2SiO4</td>
</tr>
<tr>
<td>900</td>
<td>Al2O3, BaAl2Si2O6, TiO2, Zn2SiO4, (K0.92Na0.08)(Al0.98Si3.02)O8, Sr2Al2SiO7</td>
</tr>
<tr>
<td>925</td>
<td>Al2O3, BaAl2Si2O6, TiO2, Zn2SiO4, (K0.92Na0.08)(Al0.98Si3.02)O8, Sr2Al2SiO7</td>
</tr>
</tbody>
</table>

Fig. 2. Temperature dependence of the quantity of the major crystalline phases and the degree of crystallinity of the fired specimens.

Fig. 3. DTA results of the glass-ceramic powder.

Fig. 4. Sintering-shrinkage curve of the glass-ceramic compact.
DTA occurred at a temperature higher than that of the XRD results. The specimens for XRD analysis were fired at evaluated temperatures for 30 min, while the DTA was measured with a constant heating rate to the evaluated temperature. The difference in thermal history is responsible for the temperature discrepancy between DTA and XRD results.

Figure 4 shows the sintering–shrinkage curve of the glass-ceramic compact. The onset temperature of the sintering shrinkage starts from 765°C. It corresponds well to the glass softening point of 778°C found in Fig. 3. The glass ceramics densify via the viscous-flow sintering mechanism. During firing, the glass melts first, followed by the filling of the pores by viscous glass flow. Therefore, as the glass melts, the specimen densifies rapidly.

3.3 Microstructure analysis

Figure 5 shows the SEM photographs of specimens fired at various temperatures. As can be seen in Fig. 5, when the sintering temperature increases, the microstructure contains more closed pores. These pores are spherical instead of having an angular appearance. According to Imanaka, there are two possible causes of these spherical pores. (1) During sintering, the surface of the sample is sintered first, and after a well-sintered film is formed on the surface, the pores are formed when gas is left inside the material or when residues of organic binder are expelled at high temperatures. (2) The gas dissolved in the raw glass powder used in LTCC’s is released at a high temperature forming the pores. On the other hand, the specific volume of the crystalline phase is smaller than that of the glass phase. Therefore, when the crystallization of the glass proceeds during firing, it gradually makes the microstructure porous.

Figure 6 shows the variation of true density and relative density of the fired specimens as a parameter of the firing temperature. The relative density was obtained from the apparent density divided by the true density at each temperature. As can be seen in Fig. 6, the relative density of the fired specimens decreased as the firing temperature increased. This is consistent with the SEM images, which show a more porous microstructure as the firing temperature increased.

From the true density of the specimens fired at various temperatures, it can be determined that the density decreases as the firing temperature increases.
Fig. 6. True density and relative density of the sintered specimens at various temperatures.

Table 3. True Density, Theoretical Volume Shrinkage Rate, and Porosity Ratio of the Specimens Fired at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>True Density (g/cm³)</th>
<th>Theoretical volume shrinkage rate(*)</th>
<th>Porosity %, SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received</td>
<td>3.2421</td>
<td>–</td>
<td>0.1%</td>
</tr>
<tr>
<td>800°C</td>
<td>3.3101</td>
<td>0%</td>
<td>0.7%</td>
</tr>
<tr>
<td>825°C</td>
<td>3.3274</td>
<td>0.51%</td>
<td>2.8%</td>
</tr>
<tr>
<td>850°C</td>
<td>3.3862</td>
<td>2.20%</td>
<td>3.3%</td>
</tr>
<tr>
<td>875°C</td>
<td>3.3983</td>
<td>2.54%</td>
<td>5.0%</td>
</tr>
<tr>
<td>900°C</td>
<td>3.4375</td>
<td>3.63%</td>
<td>5.9%</td>
</tr>
<tr>
<td>925°C</td>
<td>3.4493</td>
<td>3.95%</td>
<td></td>
</tr>
</tbody>
</table>

*: with respect to the true density of 800°C specimen.

Fig. 7. Variation of dielectric constant and quality factor of the specimens fired at various temperatures.

3.4 Electric properties

Figure 7 shows the variation of the dielectric constant and quality factor of the specimens fired at various temperatures. The data of the specimens fired at 800°C and 825°C are not shown. As can be seen in Fig. 2, the degree of crystallinity of these two specimens is lower than those of the others. The high glass content in these two specimens causes a higher dielectric loss, so no obvious resonant peaks are found in the measurement. It is also noteworthy that as the firing temperature increased, the dielectric constant decreased, while the quality factor increased. The decrease in dielectric constant with an increasing temperature is ascribed to the density drop of the fired specimens. As can be seen in Fig. 5, when the firing temperature increased, the microstructure of the fired specimens became more porous. The increasing porosity level in the fired specimens decreases the dielectric constant.

Unlike the dielectric constant, the quality factor increased as the firing temperature increased. From Fig. 2, the degree of crystallinity increased with an increasing firing temperature. Glass phases have a higher dielectric loss than the crystalline phases in the microwave region. Therefore, the increasing degree of crystallinity is responsible for the higher quality factor of the specimens fired at high temperatures. Though the increasing porosity level in the fired specimens deteriorates the quality factor, it is widely accepted that a low level of porosity (< 5 vol%) significantly decreases the permittivity but does not affect the microwave dielectric losses dramatically. As can be seen in Fig. 6, the fired specimens all had relative densities higher than 95%. Therefore, the increasing porosity level in the high-fired specimens did not deteriorate the quality factor dramatically. However, the porosity in the fired specimens is detrimental to the mechanical strength so a trade-off between the dielectric properties and the mechanical strength, should be made.

4. Conclusion

The phase development, thermal properties, and dielectric properties of a commercial glass-ceramic powder were studied. The results show that there were three crystalline phases, Al₂O₃, TiO₂, and Zn₂SiO₄, in the as-received powder. They decreased as the firing temperature increased. During firing, BaAl₂Si₂O₈ was formed at 850°C. It increased rapidly with temperature and reached a maximum at 900°C. At 900°C, Sr₂Al₂SiO₄ and (K₀.₉₄Na₀.₀₆)(Al₉₀Si₁₀O₃)O₃ were formed and eventually Al₂O₃, BaAl₂Si₂O₈, TiO₂, Zn₂SiO₄, Sr₂Al₂SiO₇, and (K₀.₉₄Na₀.₀₆)(Al₁₀₀Si₁₀O₃)O₃ coexisted in the 925°C-fired specimen. In addition to the crystalline phases, the amorphous phase existed in the specimens fired at temperatures less than 900°C. The degree of crystallinity of the glass-ceramic powder increased with an increasing firing temperature and reached its maximum of 96 mass% at 900°C.

The DTA and dilatometry results indicate that the glass softening point of the glass-ceramic powder occurred at 778°C, and the glass crystallization occurred at 874°C. Significant sintering shrinkage started at 765°C, which corresponds well to the glass softening point of the glass-ceramic powder.

Moreover, as the sintering temperature increased, the microstructure of the fired specimens became more porous, decreasing the dielectric constant. Nevertheless, the quality factor of the fired specimens increased with an increasing firing temperature. The increase of the quality factor is ascribed to the better degree
of crystallinity in the fired specimens as the firing temperature increased. However, the porosity in the fired specimens is detrimental to the mechanical strength, so a trade-off between the dielectric properties and the mechanical strength should be made.

References