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Crystallization Behavior of Cordierite-Based Glass with Excess SiO_2 and Al_2O_3 at Initial Stage

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Crystallization behavior of cordierite-based glass with excess SiO_2 and Al_2O_3 (CM glass) was studied at the initial crystallization stage. Two kinds of glass-in-glass phase separation occurred during the heat treatment of glass powder. The secondary glass-in-glass phase separation, which consists of an SiO_2-rich phase and an Al_2O_3-rich phase significantly affects the crystallization of the glass and the resultant microstructures of the crystallized glass. Mullite nucleated first in the Al_2O_3-rich amorphous phase which is no longer a stable glass-forming region. Metastable μ-cordierite crystallized in the SiO_2-rich amorphous phase and grew rapidly. A fine-grained cordierite-mullite composite with mullite as the grain boundary phase was produced.

KEYWORDS: crystallization of glass, phase separation, cordierite-mullite composite, microstructures of glass ceramics

1. Introduction

The cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$)-based glass-ceramic system is a potential candidate for an alternative substrate material for high-speed circuits due to its low dielectric constant, low-temperature sintering capability and a thermal expansion coefficient matching that of Si chip.[1-3]

To improve the mechanical properties with the low dielectric constant, cordierite-mullite composite material has been studied. Previous studies have concentrated on the densification of cordierite-mullite ceramics at temperatures above 1465 °C, where the cordierite melts down to the liquid phase.[4-6] In order to fabricate a multilayered structure cofired with highly conductive electrodes such as Au, Cu and Ag–Pd, the sintering temperature should be reduced to below 1000 °C.

It was suggested that cordierite-mullite composite could be fabricated at temperatures below 1000 °C using glass precursor powder rather than colloidal precursor, since glass is a very homogeneous system on an atomic scale.[7] Many studies[8-11] have reported on the crystallization mechanism of cordierite glass or cordierite glass with excess SiO_2 and MgO, which is close to the ternary eutectic point, but limited study[12] has been carried out on the cordierite-mullite (cordierite with excess Al_2O_3 and SiO_2) system, since it is not within the stable glass-forming region.

The effect of the glass phase separation on the nucleation behavior has been associated with many factors, such as the formation of an amorphous phase with relatively high mobility, phase boundary as a nucleating site for the first crystalline phase and reduction of the energy barrier due to the compositional change. Fine-grained homogeneous composite glass ceramics can be produced by controlled phase separation in the range of 10–50 Å.[13]

The present study is concerned with the nucleation and crystallization behavior of cordierite-based glass with excess SiO_2 and Al_2O_3 (CM glass). Transmission electron microscopic studies on the microstructural evolution have been emphasized. Glass-in-glass phase separation and its effects on the nucleation and crystallization behavior of CM glass were examined.

2. Experimental Procedure

The $MgO–Al_2O_3–SiO_2$-based glass used in this study lies along the tie line between cordierite-mullite in the primary phase field of mullite. It contains $2MgO\ 3.38Al_2O_3\ 5.92SiO_2$ (the composition is equivalent to 75 wt% cordierite and 25 wt% mullite). Oxide raw materials were mixed and milled by using alumina jar with isopropyl alcohol for 24 h. Glass was prepared by melting the premixed oxides in a Pt crucible at 1600 °C for 5 h. The glass melt was quenched rapidly by pouring it into a water bath. Since some devitrification occurred during quenching, crystal-free glass cullets were selected for further processing.

Glass powder was prepared by grinding the quenched glass cullets to a fine powder (average particle size: 3.5 μm) using an alumina ball mill with isopropyl alcohol. The slurry was dried and the powder was mixed with 0.5 wt% stearic acid as a pressing aid in a mortar and pestle and pressed at 1 ton/cm^2 using a cylinder type mold with 1/2-inch diameter. The glass powder was heat-treated in the range of 700 and 1000 °C for various durations. Differential thermal analysis (DTA: Perkin Elmer DTA 1700, Norwalk, CT) studies of the glass powder were performed in air at the heating rate of 10 °C/min up to 1200 °C.

The phase of the sintered body was characterized by means of X-ray diffraction (XRD; Philips APD 1700 Automated Powder Diffractometer, Mahwah, NJ) at a

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scan rate of 0.1°/min in order to detect small amounts of crystalline phase formed in the initial stage. The intensities of μ-cordierite (101), mullite (210) and α-cordierite (211) were used to create a plot for the examination of crystalline phase development in the glass. To investigate macroscopic features of the sintered composite glass, scanning electron microscopy (SEM) was used. The samples were prepared for SEM examination by mounting and polishing samples with alumina powders (15, 5 and 1 μm) and etching in 5% HF solution for 30 s.

The microstructural evolution of the heat-treated glass samples was investigated with a transmission electron microscope (TEM). A Philips 430T equipped with an LaB_6 filament was used in the TEM operating mode at 200 kV, along with a liquid-nitrogen-cooled double-tilt holder (Model 636, Gatan Inc., Warrendale, PA). The sample preparation involved cutting with a diamond saw to 250-μm-thick foil. Cut foil was attached to a disc grinder (Disc Grinder, Model 623, Gatan Inc., Warrendale, PA) and polished with diamond paste of 30, 6 and 1 μm size until the thickness of the foil was reduced to less than 10 μm. The thinned wafer was attached to a 3-mm-diameter Cu grid having an oval-shaped hole with colloidal silver paint. Ion beam milling (Model 600, DuoMill, Gatan Inc., Warrendale, PA) was used for final thinning of the sample, and conditions for the milling were 6 kV, Ar ions at a milling angle of 15° with liquid nitrogen cooling. Powder sample was suspended on a carbon film attached on a 100-mesh Cu grid for TEM characterization.

Chemical analyses were performed by utilizing energy-dispersive X-ray spectroscopy (EDS: EDAX PV9800) for the examination of compositional change

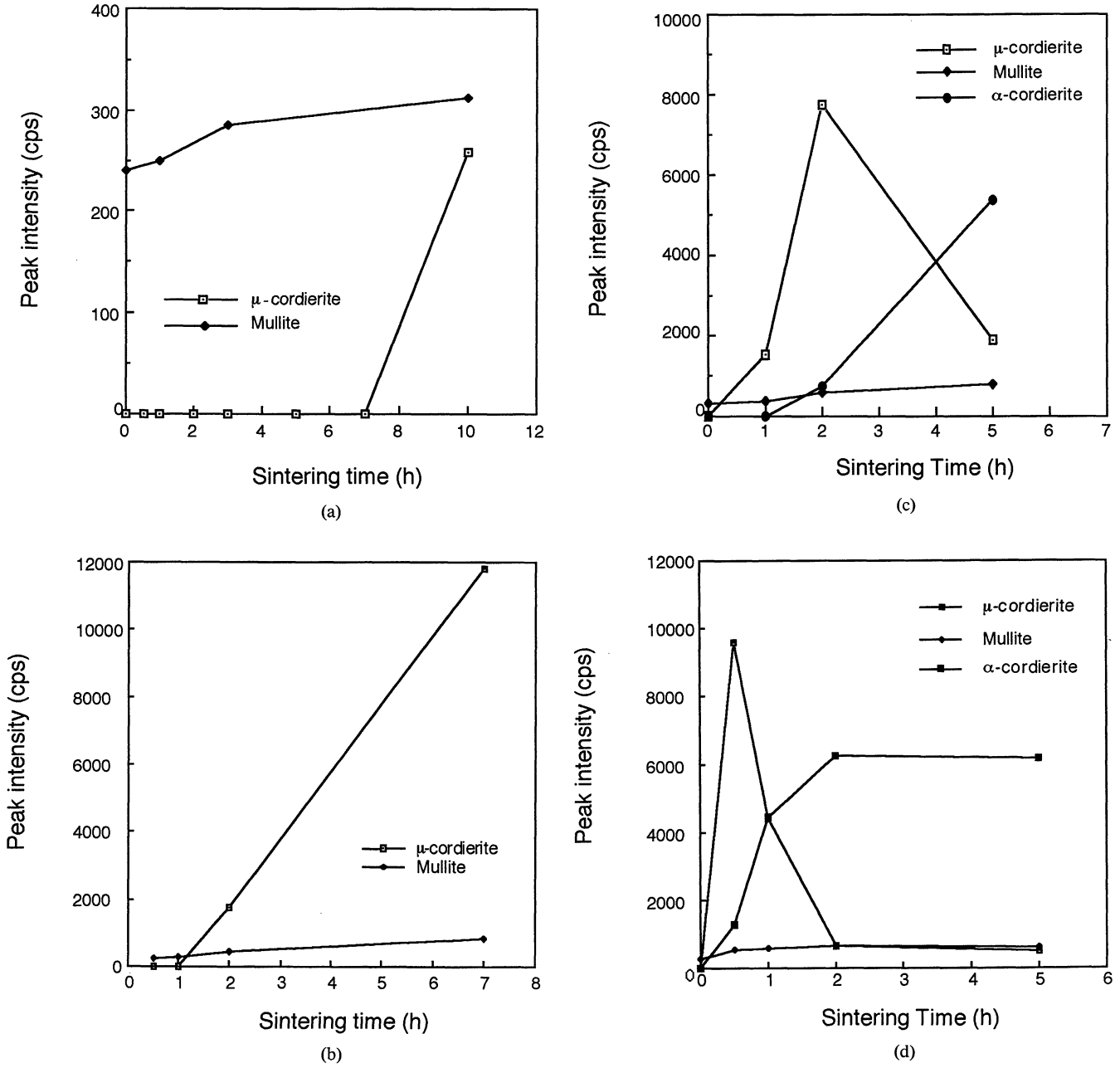


Fig. 1. The variation of XRD peak intensities in CM glass powder depending on sintering temperature and time.

in the crystalline phase at different sintering temperatures. All data for EDS analyses were acquired with specimens tilted 35° toward the detector and with a 200-Å-sized probe for reproducibility.[14]

3. Results

3.1 *XRD analyses*

The phase evolution in glass samples heat-treated in the range of 850 and 925°C is clearly shown in the X-ray diffraction spectra (Fig. 1). There was no crystalline phase in the original glass powder. A small amount of mullite had already formed below 850°C at zero duration time, whereas μ-cordierite began to crystallize after soaking for 10 h at 850°C. The peak intensity of mullite increased slowly with the sintering time. At 875°C, the intensity of the μ-cordierite peak increased rapidly.

The phase transformation of μ-cordierite to α-cordierite started after heating for 2 h at 900°C, whereas it started after 30 min at 925°C. Mullite did not increase in intensity at these temperatures. The XRD results for a sample crystallized at 925°C show almost complete transformation of μ-cordierite to α-cordierite after a soaking time of 2 h (Fig. 1(d)).

3.2 *DTA analyses*

The results of DTA analyses of cordierite-based glass are shown in Fig. 2. Stoichiometric cordierite glass was examined for the comparison with CM glass used in this study. Significant difference was observed between the two samples. Two separated peaks which represented metastable μ-cordierite and α-cordierite phases were revealed in the stoichiometric cordierite glass precursor, but only one peak appeared for CM glass.

3.3 *SEM examinations*

The samples sintered at 900°C for 30 min and 10 h were investigated by means of SEM for the examination of the microstructures at the initial crystallization stage (Figs. 3(a), 3(b)). It was observed that the crystallization of glass powder began at the surface or interface between the glass grains, and that the crystals grew toward the center of the glass grains. Residual glass grains can be observed in the sample of 900°C/30 min (Fig. 3(a)). After a long treatment (10 h) at 900°C, crystallization of residual glass was almost complete

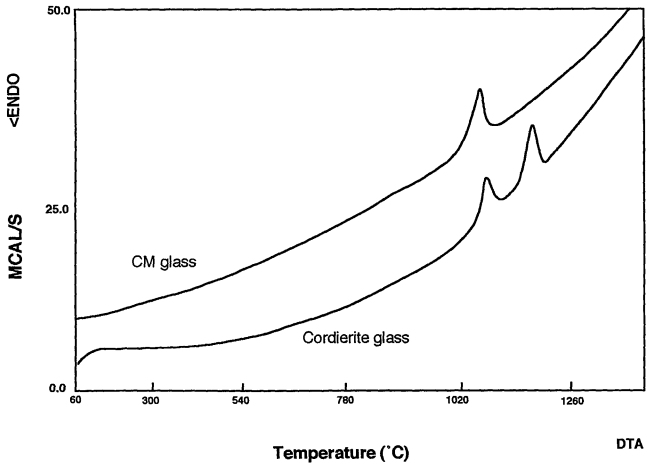


Fig. 2. DTA curves of cordierite glass and CM glass. The exothermic peak temperatures of the cordierite glass samples were 1005°C for metastable μ-cordierite and 1091°C for α-cordierite. The peak temperature of CM glass was 997°C for μ- and α-cordierite. The rapid transformation of μ- to α-cordierite could be observed in CM glass.

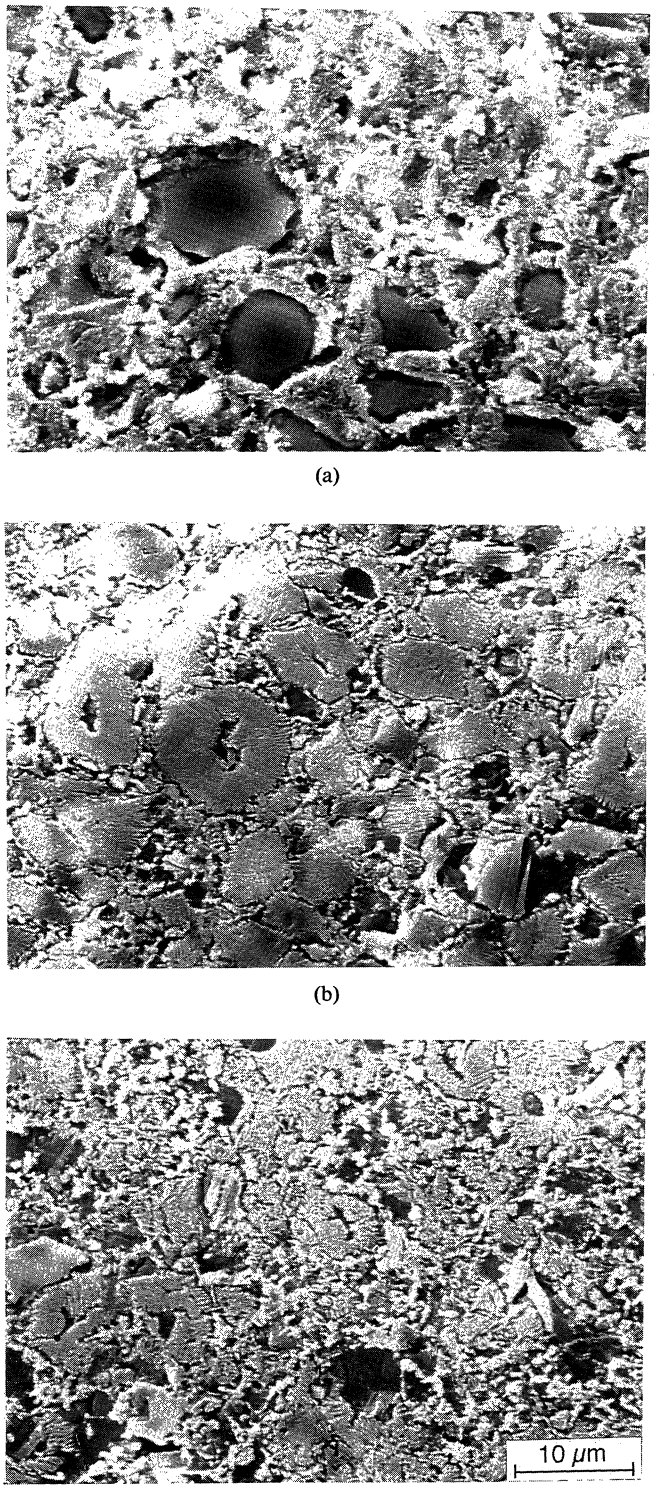


Fig. 3. SEM micrographs of CM glass sintered at various temperatures and times: (a) 900°C/0.5 h, (b) 900°C/10 h and (c) 950°C/10 h.

(Fig. 3(b)). The microstructure of a sample sintered at 950°C for 10 h (Fig. 3(c)) exhibits the dendritic growth of α-cordierite with a spongelike structure.

3.4 *TEM examinations*

The initial nucleation procedure of μ-cordierite is clearly shown in Fig. 4 (850°C/10 h). Small dark spots (30–50 Å) with the same dimensions as primary phase separation grew and coagulated into large crystals.

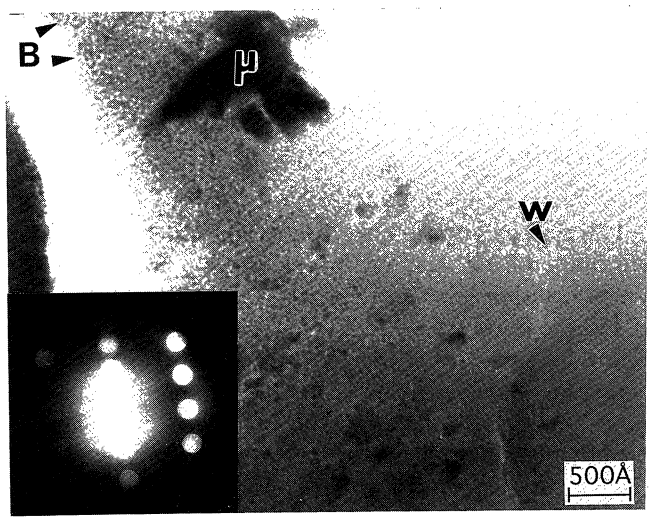
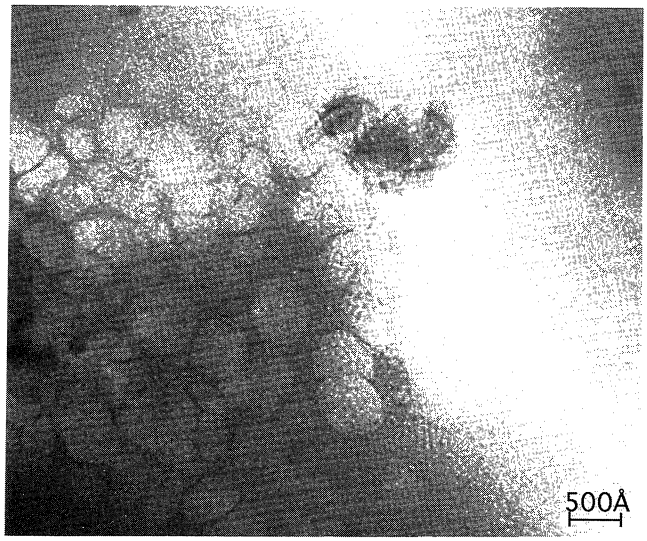
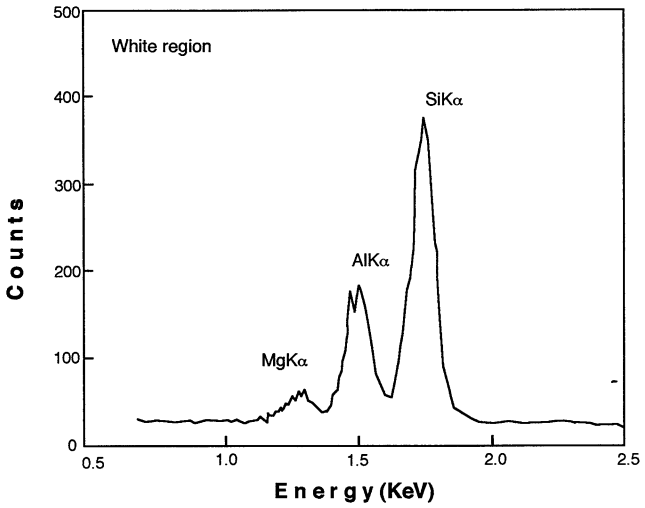


Fig. 4. TEM micrograph of the glass heat-treated at 850°C for 10 h; microdiffraction pattern of the large crystal reflected the $Z=[\bar{3}123]$ zone axis orientation of μ-cordierite. It is observed that the μ-cordierite phase begins to nucleate in the white spots (arrow; W), which are believed to reflect secondary phase separation. Very small black spots (30 Å, arrow; B) were confirmed by tilting to be the crystalline phase.



(a)



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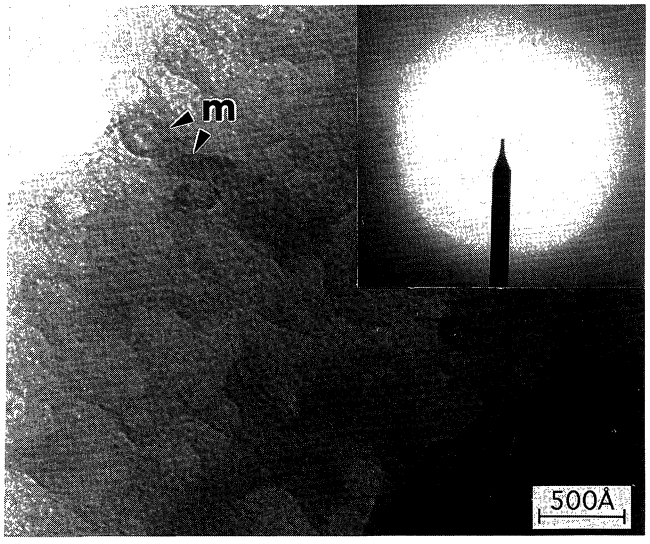
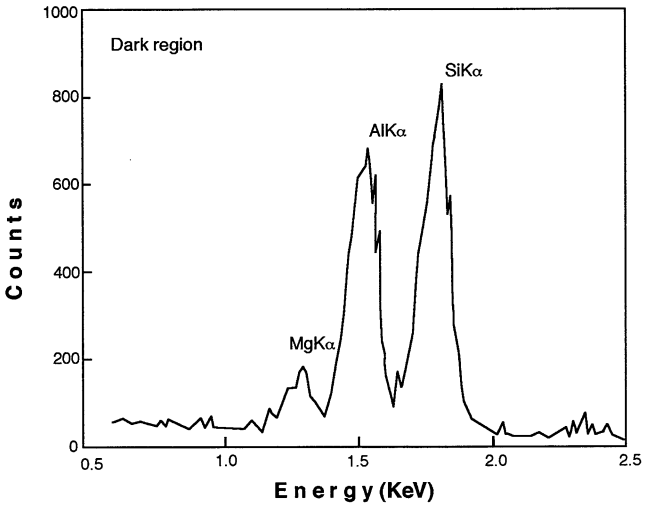


(b)



(d)

Fig. 5. TEM micrographs of CM glass sample sintered at 850°C/20 h. Phase-separated features appeared (a) in the amorphous region, in which the white region is Si-rich and the dark region is Al-rich according to EDS analyses. (b) Semi-continuous features developed. It is observed that mullite begins to nucleate in some dark regions. ESD spectra of (c) white region and (d) dark region are also shown.

White spots with irregular shape (200 Å), which are regarded as an Si-rich phase, form toward the matrix glass from the surface. The crystalline phase (grey region) begins to nucleate in the white spots. The big crystal was determined to be μ-cordierite with a zone axis orientation of $[\bar{3}123]$ by microdiffraction.

Glass-in-glass phase separation could be observed in the sample sintered at 850°C for 20 h (Fig. 5). White spots grew up to 300 Å. The ring pattern in this region indicates an almost amorphous phase, but several weak spots which indicate the crystalline phase could also be seen. These white spots developed to a semicontinuous feature as shown in Fig. 5(b). The white region was interpreted as an Si-rich amorphous phase, whereas the dark region was an Al-rich amorphous phase from EDS analyses (Figs. 5 (c) and 5 (d)).

It was observed that mullite began to nucleate in some parts of the dark region (Fig. 5 (b)). Coarsened phase separated features were expected to appear with heat treatment for a prolonged period of time, but a number of spherical μ-cordierite areas (200 Å) formed in the sample of 850°C/20 h instead of a coarsening the microstructure (Fig. 6).

Mullite nuclei with rectangular shape formed along a line between amorphous regions in the 875°C/3 h sample (Fig. 7). From the EDS results, mullite nuclei tend to form in Al-rich amorphous regions (Figs. 8(a) and 8(b)). Two kinds of amorphous features developed in this sample. The larger feature is a grainlike structure of 0.2–0.5-μm-sized amorphous grains, whereas the

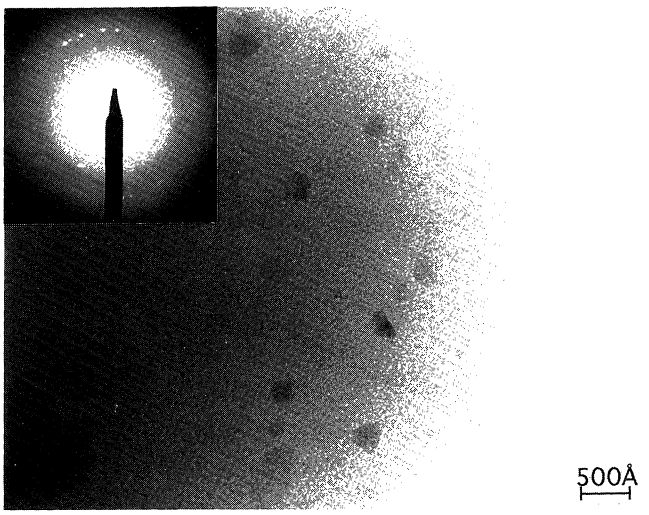


Fig. 6. Spherical μ-cordierite nuclei (200 Å) formed in matrix glass heat-treated at 850°C for 20 h. The density of nuclei was much higher than that of 850°C/10 h sample, and coarsening of features did not occur.

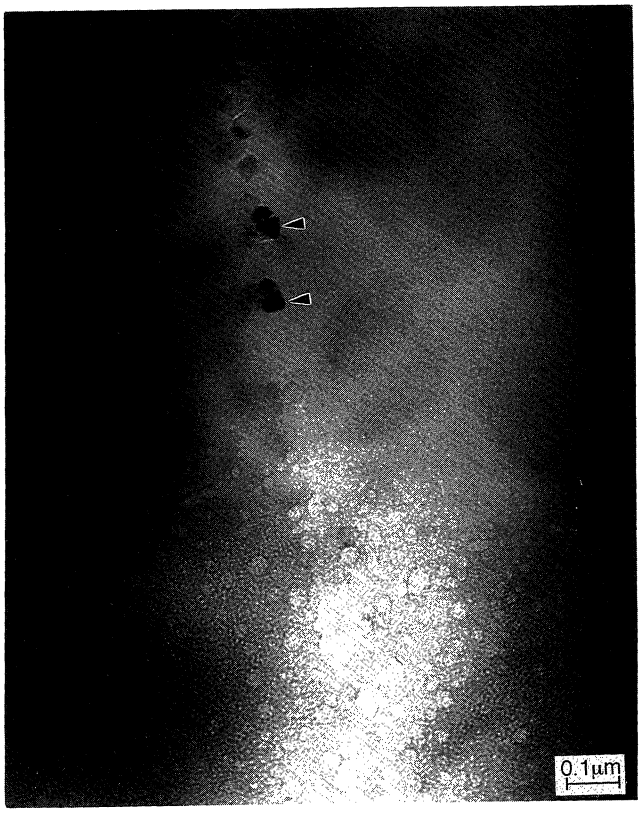


Fig. 7. Mullite nuclei (arrow) formed along the line between amorphous regions. Amorphous white spots which included primary and secondary (200–500 Å) phase-separated features began to form from the bottom (875°C/3 h).

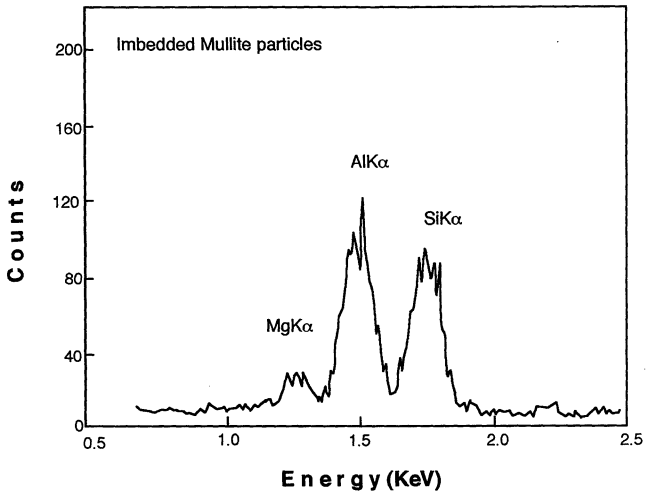
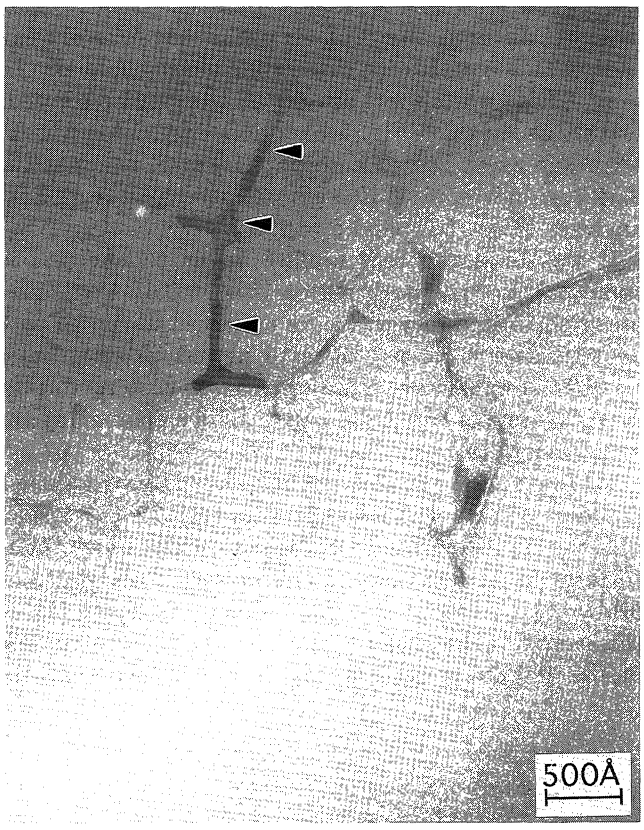
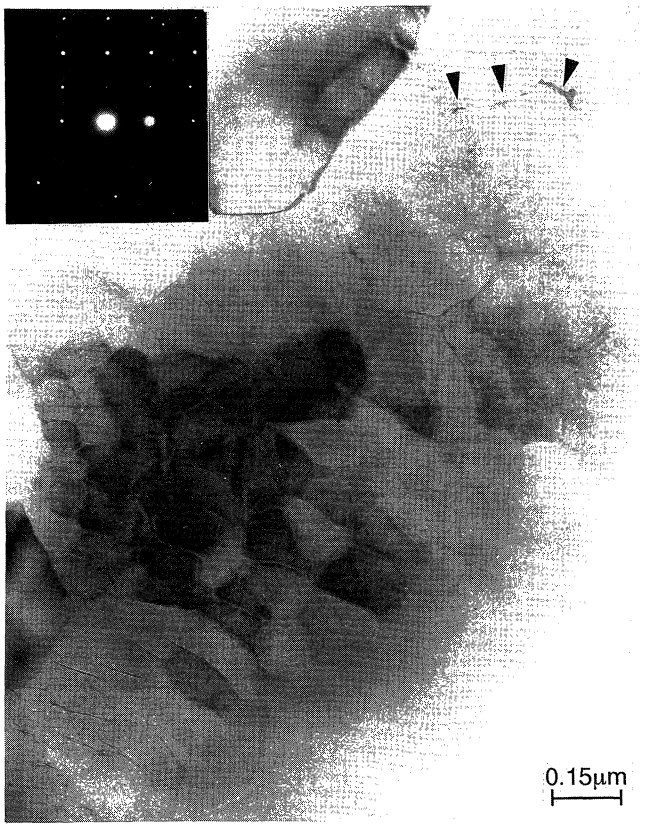


Fig. 8. EDS spectra of (a) mullite particles, and (b) glass region around mullite crystallites (A spot in Fig. 7).



(a)



(b)

Fig. 9. Polycrystalline structure of crystallized glass: (a) diffracted condition of grain boundary phase between amorphous grains (875 °C/3 h) and (b) diffracted condition of μ-cordierite grains after soaking time of 7 h. Diffraction pattern shows the $[1\bar{1}04]$ zone axis orientation of μ-cordierite.

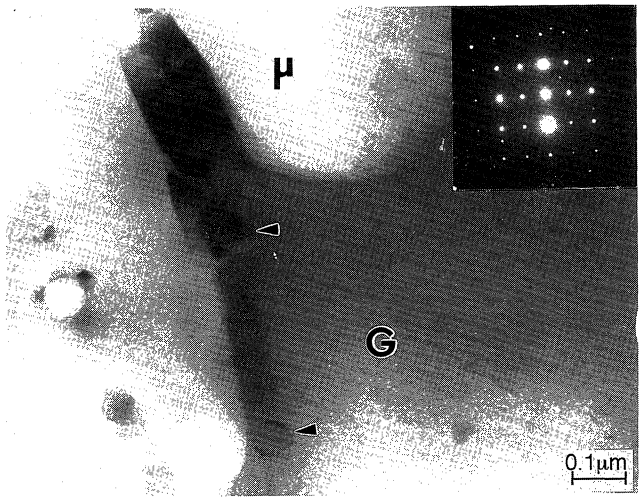


Fig. 10. Mullite particles (arrow; 700 Å) formed a line and μ-cordierite (diffraction pattern $Z=[10\bar{1}2]$) grew along the mullite boundary in the sample sintered at 875 °C for 7 h. Phase-separated residual glass (G) could be observed.

other feature is 300-Å-sized white spheres with small dots (30 Å), which are believed to be due to two kinds of phase separation.

Polycrystalline structures formed at the crystalline grain boundary between amorphous grains (Fig. 9(a)). The thickness of the grain boundary was 60–100 Å. The amorphous phase crystallized over a longer duration (Fig. 9(b)). μ-Cordierite growing with the grain boundary could be observed in the sample sintered at 875 °C for 7 h. The diffraction pattern shows the $[1\bar{1}04]$ zone axis orientation of μ-cordierite. Part of the grain boundary phase (arrow) revealed a diffraction condition during tilting of the sample which indicates a crystalline phase. A large amount of μ-cordierite with a zone axis of $[10\bar{1}2]$ grew along the mullite boundary in the sample sintered at 875 °C for 7 h (Fig. 10). Phase-separated residual glass with spheroidal droplets (G) could be seen in this sample.

4. Discussion

Glass-ceramic materials can be fabricated by strictly controlled heat treatment of glass since crystallization is dependent upon thermal history. It is well known that glass powder crystallizes on the powder surface because the surfaces of the grain act as nucleating sites. The same phenomena were observed in this study. A dense and fully crystallized body could be developed by sintering at 900 °C for 10 h (Fig. 3(b)). At this temperature, the sintering and crystallization of glass powder occurred at the same time.

The glass powder of a cordierite-based composition is hard to sinter due to its narrow sintering range and its crystallization which impedes further sintering. Glass in the glass-forming region of MgO–Al_2O_3–SiO_2 ternary system, restricted by a composition in the range of 40–70 mol% SiO_2 and a MgO/Al_2O_3 ratio <1, is characterized by a high tendency to separate in the glass phase.[15]

Glass can easily separate during heating after quenching or during cooling from the melts because glass in this region has a high immiscibility temperature. Prior phase separation leads to a reduction of the crystal growth rate, possibly by a "mechanical interference effect." Prior glass-in-glass phase separation has a significant effect on the microstructure developed during crystallization. Higher nucleation density and reduction of crystal growth rate are important factors for the production of fine-grained glass ceramics. No phase-separated feature was observed in as-quenched glass powder in this system, but some glass cullets were opaque, since mullite precipitates in quenched glass.

The opaque glass powder could not densify although the sintering temperature was high enough (1000 °C). Rigid inclusion can dramatically reduce the densification rate of glass powder compacts because there are changes in the path length from sources to sinks and development of anisotropy in the sintering driving force.[16]

Glass-in-glass separation arises from the competition between cations surrounded by oxygen ions with minimum energy configurations, which is characterized by the ionic potential of the cations, Z/R_{Me} (Z: atomic number, R_{Me}: atomic radius). The greater the ionic potential, the stronger the tendency toward immiscibility.[17] First glass-in-glass phase separation could be observed in the sample sintered at 850 °C for 10 h. The two kinds of phase separation features included a 30-Å-sized "interconnected structure" and irregular white regions with 300 Å size.

The "interconnected structure" was reported in previous works.[18–20] MacDowell and Beall[22] discussed the morphology of the crystalline phases in quenched melt in relation to the glass-in-glass separation. Glass containing 20 mol% Al_2O_3 which was subjected to rapid quenching had an "interconnected structure," whereas glass with the same composition but slower quenching had a structure of typically spheroidal droplets.

Isolated white spots and the interconnected structure were visible in the sample sintered at 850 °C for 20 h (Figs. 5(a) and 5(b)). These results indicate the secondary phase separation[23] which can occur during reheating of the phase-separated glass at two different temperatures within the metastable immiscibility cupola. Figure 11 shows the schematic diagram of two-stage immiscibility in a binary system. Small phase-separated features (30 Å) developed with secondary heat treatment at a lower temperature, since the interdiffusion rate drastically decreased with the fall in temperature. Although small separated features could not be analyzed due to the limit of probe size, larger features (300 Å) were clearly determined to have a different chemical composition in white (Si-rich phase) and dark (Al-rich phase) regions. In the sample heated at 850 °C for 20 h, small spherical μ-cordierite (stuffed β-quartz solid solution) nuclei were embedded throughout the matrix glass (Fig. 6). It should be noticed that the glass-in-glass phase-separated features did not enlarge without causing crystallization in this region.[22]

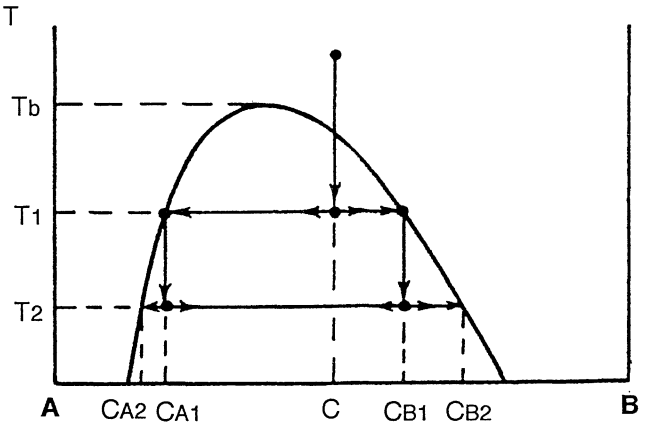


Fig. 11. Schematic diagram of two-stage immiscibility in a binary system.[23]

The TEM micrograph shown in Fig. 7 illustrates the significant feature which represents phase separation of this glass system. It was observed that an interconnected structure (30 Å) as well as a spheroidal structure (300 Å) began to develop from the bottom in this micrograph.

4.1 *Crystallization of mullite*

Mullite could be detected in the sample heated to 850 °C at the heating rate of 10 °C/min without soaking. The growth rate of mullite was extremely slow after initial formation. This indicates that the nucleation rate of the mullite phase should be very fast at the initial stage. The peak for the formation of mullite does not appear in DTA analysis below 950 °C. This implies that the initial nucleation energy of mullite is very low.

Mullite readily forms in the Al-rich region after glass phase separation. Morikawa *et al.*[24] reported from X-ray scattering intensity data that the short-range structure of Al-rich glass is similar to that of mullite. In the Al-rich region, the concentration of non-bridging oxygen ions will be high, weakening the network structure so that in some cases a coherent silicate network may no longer exist. Thus the Al-rich phase may tend to crystallize more easily than the Si-rich phase.

The partial crystallization of mullite in quenched glass cullets reflects the fact that mullite can readily crystallize in a short time. Mullite crystallized at the grain boundary between amorphous grains (Fig. 9(a)). The mechanism of formation of the crystalline grain boundary with 60–100 Å thickness may be different from that of aligned mullite (500 Å) shown in Fig. 7. The large number of dark lines (50 Å thick) randomly distributed in the matrix glass are believed to be in the formation process of grain boundary crystalline phase (Fig. 9(b)).

Fine-grained cordierite-mullite composite with a polycrystalline structure could be obtained by heating at 875 °C for 7 h (Fig. 9). The size of the grains is about 500–1000 Å. It was observed that some of the glass still remained in the process of grain structure formation. The observation of aligned mullite crystallites between large μ-cordierite grains (>0.2 μm) can be explained as

the effect of secondary phase separation on the microstructure of glass ceramics (Fig. 10).

4.2 *Crystallization of μ-cordierite*

From the XRD results, we see that although μ-cordierite formed at a higher temperature than mullite, it grew and transformed into α-cordierite very quickly. Schreyer and Schairer[25,26] found that metastable μ-cordierite corresponded to stuffed β-quartz, using a distortion index. The composition of a solid solution of β-quartz lies on the SiO_2–$MgO \cdot Al_2O_3$ tie line; the structure is a stuffed β-quartz-type formed by substitution for Si^{4+} ions by Al^{3+} ions. For the charge neutrality of modified structures by the substitution of the Al^{3+} ions, alkali or alkali earth ions are introduced into the interstices of quartz structure. The lattice parameters of a metastable solid solution of β-quartz are dependent on the SiO_2 content.

The initial nucleation procedure of μ-cordierite is clearly shown in Fig. 4 (850°C/10 h). Small dark spots (30–50 Å) with the same dimensions of primary phase separation grow and coagulate into large crystals. White spots with irregular shape (200 Å) which are regarded as an Si-rich phase form toward the matrix glass. The crystalline phase (grey region) begins to nucleate in the white spots.

It should be noted from this observation that phase separation occurred prior to nucleation, and that the size of the crystalline phase was dependent upon those of the phase-separated features. After a longer soaking time at 850°C, a number of μ-cordierite nuclei (200 Å), formed in the matrix glass (Fig. 6). A fine-grained polycrystalline structure of μ-cordierite-mullite composite could be obtained in the sample sintered at 875°C for 7 h. The grain size of the polycrystalline structure is 250–600 Å, which is similar to the dimensions of secondary phase separation in this glass system. The thickness of the grain boundary phase (30 Å) is also comparable to that of primary phase separation. The observation that mullite crystallites formed a line between large μ-cordierite crystals supports the theory of glass phase separation prior to crystallization (Fig. 10).

5. Conclusions

The main results in this study are summarized as follows.

(1) Fine-grained cordierite-mullite composite ceramics with mullite as the grain boundary phase could be formed by sintering glass powder with the composition of cordierite-mullite (75 wt%:25 wt%) below 1000°C.

(2) Primary phase separation can occur during sintering above 850°C after a duration of 10 h in the order of 30 Å, and secondary phase separation (larger-scale phase separation: 200–300 Å) also begins from the surface at the same time. Phase separation in glass can significantly affect the resultant microstructure of cordierite-mullite composite ceramics.

(3) Mullite first crystallized rapidly below 850°C in the CM glass in an amount small enough to allow further viscous glass sintering. The amount of mullite formed in the glass increased very slowly with crystallization temperature and time. Mullite crystallites (700 Å) formed a line along the Al-rich region associated with secondary phase separation.

(4) The μ-cordierite phase (stuffed β-quartz) appeared after sintering for 10 h at 850°C in Si-rich white spots. Polycrystalline structures of the μ-cordierite-mullite composite with grain size of 300–500 Å could be developed with sintering at 875°C for 7 h.

Acknowledgments

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