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The correlation between the crystalline phases and optical reflectance in glass-ceramics for IR reflector

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In this study, glass-ceramics containing cordierite ($2MgO{\cdot}2Al_2O_3 \cdot 5SiO_2$) as a major crystalline phase were prepared from the MgO-Al_2O_3-SiO_2 (MAS) glass system for application as IR reflectors. Glasses prepared with the addition of TiO_2 as a nucleating agent were crystallized by a two-step heat treatment of nucleation and crystal growth. The nucleation and crystal growth behavior, the influence of heat treatment schedule on the nature of the crystalline phases, and the diffuse reflectance spectra were investigated. Cordierite and rutile were precipitated as major crystalline phases in the glass-ceramics with nucleation at 750ºC for 3 hours and crystal growth at 1100ºC for 5 hours. This glass-ceramics showed over 90% reflectance in spectral range 570 to 2500 nm.

Key words : IR reflector, Glass-ceramics, Cordierite, MAS

Introduction

Recently, high-efficiency IR reflectors have been investigated in various material systems for a variety of industrial and home applications such as heating, drying, lighting and medical equipment. For successful application, IR reflectors should exhibit high reflectance in the IR spectral region without long-term deterioration of performance. The IR reflectance of reflector materials should be maintained at high temperature with high mechanical strength and thermal shock resistance also required.

At present, direct reflection metals and diffuse reflection glass-ceramics are used for IR reflectors. The metal reflector has high reflectance in the IR spectral region, but it has low thermal shock resistance. Although a glass-ceramic reflector has some advantages such as high mechanical strength and high thermal shock resistance, its relatively low reflectance prevents this material from competing successfully in the market. The main advantage of glass-ceramics is high mechanical strength and durability because it is made by a glass forming process that can avoid mechanical deformation [1]. These properties do not change over long operation times. It was not realized until recently that reflectors with high reflectance can be made by control of the heat treatment for nucleation and crystal growth.

Glass-ceramics with cordierite ($2MgO$-$2Al_2O_3$-$5SiO_2$) as a major crystalline phase, made by crystallization of glass in the MgO-Al_2O_3-SiO_2 (MAS) system, have many advantages: high mechanical strength and hardness, high chemical durability and high thermal shock resistance owing to their low thermal expansion coefficient [2, 3]. Therefore, this material system is a major candidate for IR reflectors.

In a preliminary study of nucleation and crystal growth in the MAS system, Yamane investigated the nucleation of MgO-Al_2O_3-TiO_2 (MAT) crystals. The nucleation rate of MAT is maximum at low temperature below glass transition temperature (T_g) where T_g was kept low by TiO_2 addition [4]. Barry investigated crystalline phases in glass-ceramics by changing the heat treat- ment temperature and the amount of nucleation agents, such as TiO_2 and ZrO_2, added to stoichiometric cordie- rite ($2MgO$-$2Al_2O_3$-$5SiO_2$). Crystalline phases of β-quartz solid solution, MAT, spinel, sapphirine, Mg-petalite, cristobalite, rutile and cordierite were found, and the amounts of these crystalline phases were a function of the heat treatment temperature and proportional to the amount of TiO_2 and ZrO_2 [5].

In this study, glass-ceramics were prepared in the MAS system. The nucleation and crystal growth behavior and resulting IR reflectance were investigated under various heat treatment conditions in the hope of improving the reflectance by control of the crystalline phases and their size.

Experiments

Batches of glass in the MAS system were prepared from SiO_2 (2N, Cerac, USA), Al_2O_3 (Extra Pure, Junsei Chemical Co., Japan), and MgO (Extra Pure, Yakuri Pure Chemicals Co., Japan). As_2O_3 (Extra Pure, Junsei Chemical Co., Japan) was used as a fining agent and

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TiO_2 (GR, Junsei Chemical Co., Japan) was used as a nucleation agent. The glass composition was 11MgO-27.9Al_2O_3-49.3SiO_2 in wt% corresponding to stoichiometric cordierite. As_2O_3 at 0.8 wt% was added as a fining agent and 11 wt% TiO_2 was added as a nucleation agent. Glass-ceramics were then fabricated containing cordierite and rutile as major crystalline phases [5, 6]. Small amounts of TiO_2 cause inhomogeneous crystallization, and large amounts make it hard to get a smooth surface on cooling due to phase separation. Therefore, the nucleation agent was added within the range for homogeneous nucleation.

Batches were well-mixed in the dry condition and milled for 10 hours. They were then melted at 1550°C for 3 hours in a Pt-10%Rd crucible in an electric furnace. After fusion, the melt was stirred by a Pt-10%Rd stirrer for 90 minutes (60 rpm for 30 minutes, 30 rpm for 30 minutes, 10 rpm for 30 minutes) to improve the homogeneity of the melt. It was then stabilized for one hour. The melt was poured into graphite molds preheated at 650°C and the internal stress was removed by annealing. The glass samples were cut into plates of 20×20×2 mm^3 for additional heat treatment and measurement of various properties.

The glass samples were heat treated through the two-step crystallization process of nucleation and crystal growth. In the nucleation step, the glass samples were heat treated near the glass transition temperature (T_g) for 3 hours. Nucleation temperatures used in this study were 700, 750 and 800°C. In the crystal growth step, the glass samples were heat treated at various temper-

Table 1. Heat treatment condition to fabricate the MAS glass-ceramics

	Heat treatment condition (Temperature/Time)	
	Step 1	Step 2
S1	750°C/3h	900°C/5h
S2	750°C/3h	950°C/5h
S3	750°C/3h	1000°C/5h
S4	750°C/3h	1050°C/5h
S5	750°C/3h	1100°C/5h
S6	750°C/3h	1150°C/5h
S7	750°C/3h	1200°C/5h
S8	750°C/3h	1250°C/5h
S9	750°C/3h	1300°C/5h
S10	750°C/3h	1050°C/1h
S11	750°C/3h	1050°C/2h
S12	750°C/3h	1050°C/3h
S13	750°C/3h	1050°C/4h
S14	750°C/3h	1050°C/7h
S15	750°C/3h	1050°C/10h
S16	750°C/3h	1050°C/20h

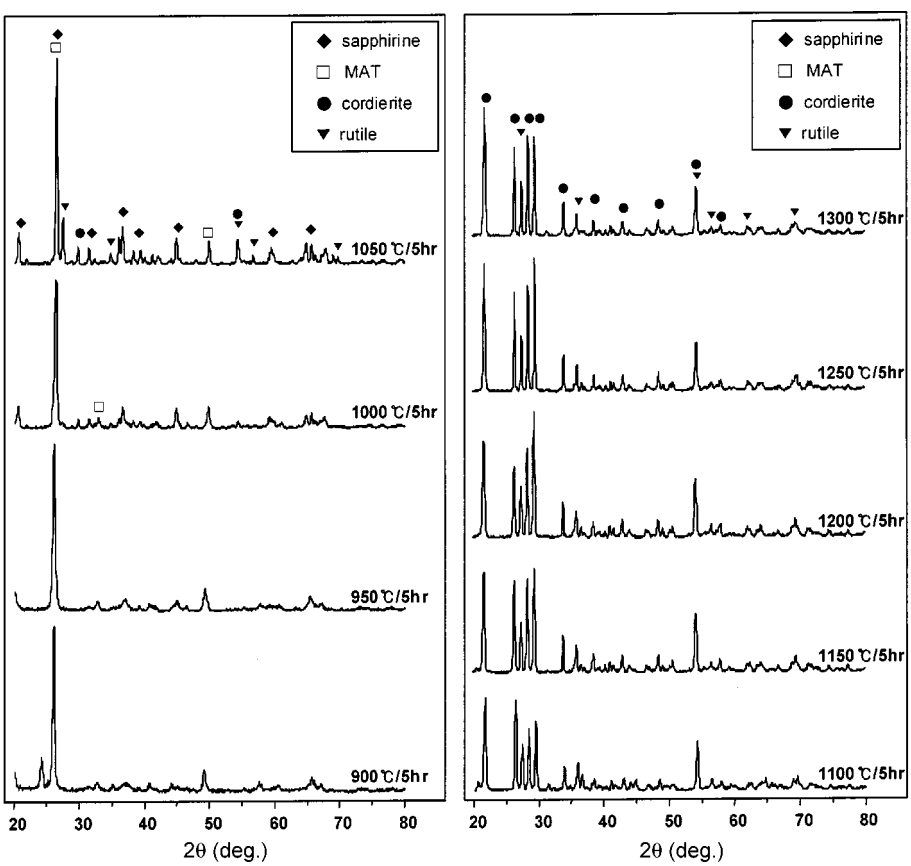

Fig. 1. X-ray diffraction patterns of MAS glass-ceramics nucleated at 750°C/3h and heat treated for 5 hours at various crystal growth temperature.

atures in the range 900 to 1300ºC for 1 to 20 hours. In the crystallization process, the heating rate was kept low (5ºC/min and 2ºC/min) to prevent sample cracking after heat treatment. Table 1 summarizes heat treatment temperatures and times used in the experiment.

The precipitated crystalline phases were identified by X-ray diffraction (XRD), (PW1830, Philips, Netherlands). The microstructure and the morphology of the crystal- line phases were observed by a scanning electron microscope (SEM), (S-2700, Hitachi, Japan).

The glass-ceramics specimens were not polished for the reflectance measurement in order to maximize the diffuse reflectance. The measurement was carried in a spectrophotometer (Lamda 19, Perkin-Elmer, USA) in the spectral range from 400 to 2500 nm with intervals of 10 nm.

Results and discussion

Figure 1 shows the XRD patterns of glass-ceramics heated for 5 hours at various crystal growth temperatures. MAT containing a relatively large amount of TiO_2 contained sapphirine ($4MgO{\cdot}5Al_2O_3 \cdot 2SiO_2$) as a major crystalline phase, and the amount of this phase increased up to 1050ºC. TiO_2 began to crystallize to rutile, and cordierite also began to precipitate above the growth temperature of 1000ºC. The amounts of these two phases increased rapidly as the growth temperature increased over 1100ºC. Based on the results of XRD analysis, one can conclude that MAT and sapphirine precipitate as major crystalline phases at growth temperatures between 900ºC and 1050ºC, and that cordierite and rutile precipitate as a major crystalline phases over 1100ºC.

Barry observed the precipitation of crystalline phases by adding various amounts of TiO_2 and ZrO_2 and changing the growth temperature. He reported that only β-quartz and MAT precipitated in the range 850 to 1050ºC in the MAS system with stoichiometric cordierite composition and 11.5 wt% (TiO_2+ZrO_2) as added nucleation agents [5]. Around 1050ºC, the major crystalline phase changed from β-quartz to spinel. Around 1100 ºC, the amount of spinel phase began to decrease with increasing growth temperature, and sapphirine, rutile and cordierite began to appear at the same time. The major phase change occurred around 1150ºC again from sapphirine and MAT to rutile and cordierite. The results shown in Fig. 1 suggest that the major crystalline phases changed from MAT and sapphirine to rutile and cordierite with increasing growth temperature. This result is similar to Barry's result [5],

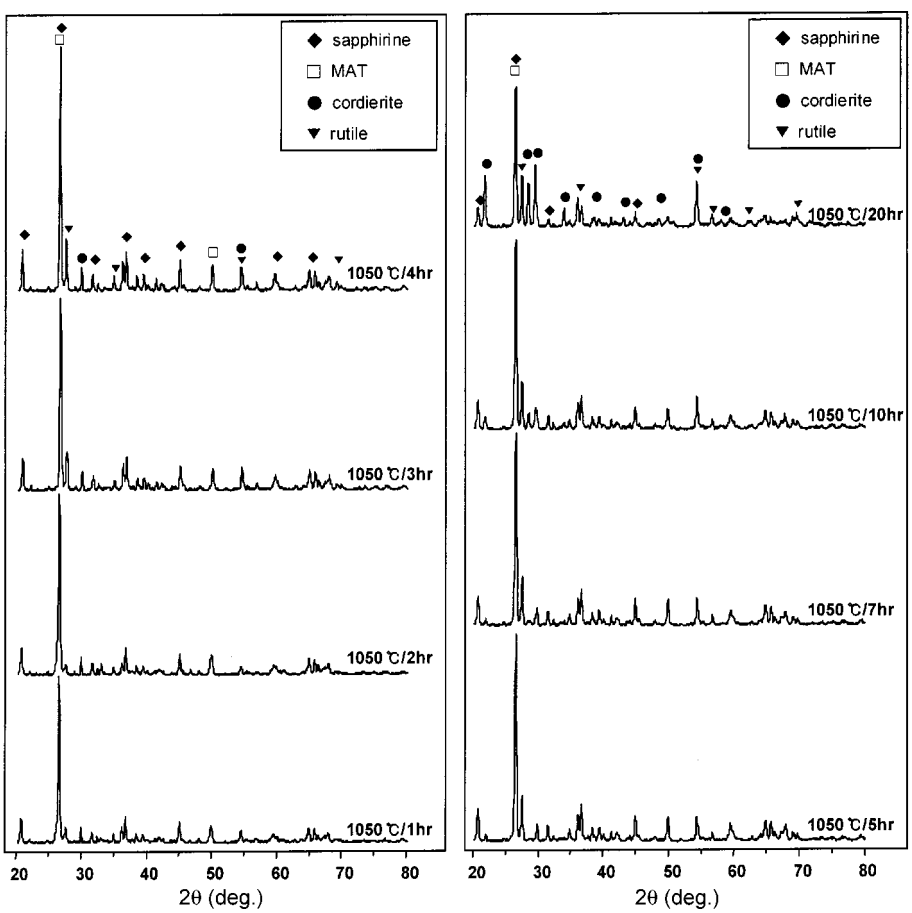

Fig. 2. X-ray diffraction patterns of MAS glass-ceramics nucleated at 750ºC/3h and heat treated at 1050 ºC for various crystal growth time.

even though the exact temperatures for the change of major phases were a bit different.

Figure 2 shows the XRD patterns of crystalline phases observed in the glass-ceramics specimen heated at 1050ºC for various growth times. One can see that around 1150ºC, the major crystalline phases changed from MAT and sapphirine to cordierite and rutile. A similar change of major phases could be observed by keeping the specimen at a constant temperature for a long time, even though the change was not as dramatic as that observed in the experiments with different growth temperatures. From the results in Figs. 1 and 2, it is concluded that, at the beginning of crystallization, sapphirine and MAT precipitate first and then cordierite and rutile precipitate later.

Since the heat treatment for nucleation in glass is performed near T_g, either T_g or the energy barrier of crystallization must be lowered to promote nucleation. A nucleation agent promotes nucleation by accelerating phase separation or by lowering the energy barrier of nucleation [7, 8]. In the case of TiO_2 addition, the glass separated into two phases by phase separation in the nucleation step of the heat treatment. One phase contains more TiO_2, the other phase contains more MAS. The glass transition temperature (T_g) of the phase containing more TiO_2 is lower and the nucleation in this phase is accelerated [9, 10]. Therefore, crystal growth proceeds faster during the growth-step heat treatment and the major crystalline phases at this stage are sapphirine and MAT.

Figure 3 shows the SEM images of MAS glass-ceramics that were crystallized under the following conditions: 1100ºC/5h, 1150ºC/5h and 1200ºC/5h. The size of the crystalline phase increased with increasing heat treatment temperature for crystal growth as shown in the XRD result of Fig. 1.

Figure 4 shows SEM images of MAS glass-ceramics that were heat-treated at growth conditions of 1050ºC/7h, 1050ºC/10h and 1050ºC/20h. The size of the crystalline phase increased with increasing heat treatment time as analyzed in the XRD pattern shown in Fig. 2, although the change was not as large as the change with heat treatment temperature.

For the glass-ceramics specimen, the diffuse reflectance in a spectral range from 400 to 2500 nm was measured. The change of reflectance for various heat treatment conditions is shown in Figs. 5 and 6.

Figure 5 shows the reflectance of glass-ceramics specimens nucleated at 750ºC/3h heat treated for crystal growth at various temperatures. One can see that the measured reflectance increased with increasing growth temperature in the wavelength range from 400 to 2500 nm. The increase of reflectance was especially remarkable in the growth temperature range from 1000 to 1100ºC where the crystalline phases cordierite and rutile begin to precipitate and the major crystalline phases change from MAT and sapphirine to cordierite and rutile.

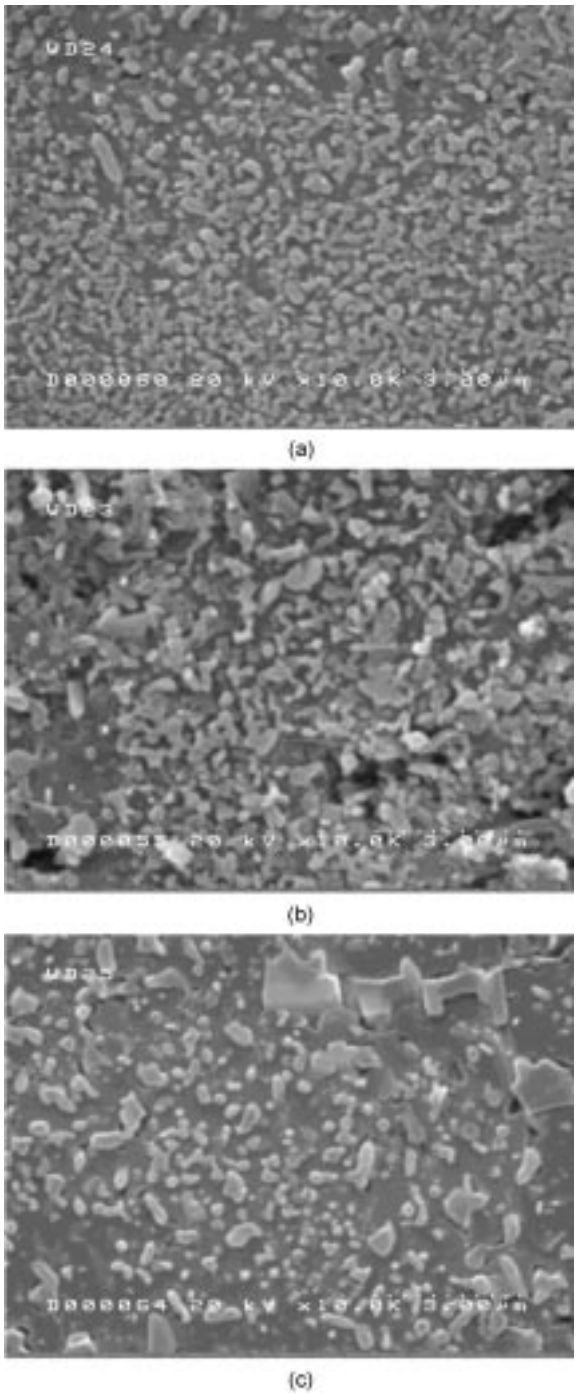

Fig. 3. Scanning electron microscopy image of MAS glass-ceramics prepared at crystal growth conditions of (a) 1100ºC/5h, (b) 1150ºC/5h, (c) 1200ºC/5h. (Nucleation at 750ºC/3h)

It is thought that MAT and sapphirine did not grow to a large enough size to be effective scattering centers. On the other hand, cordierite and rutile grew rapidly during the heat treatment to a size comparable to the wavelengths of the reflectance measurements. This speculation is supported by an observation that the reflectance measured in a sample heat treated at a growth temperature of 1000ºC increased first in the visible

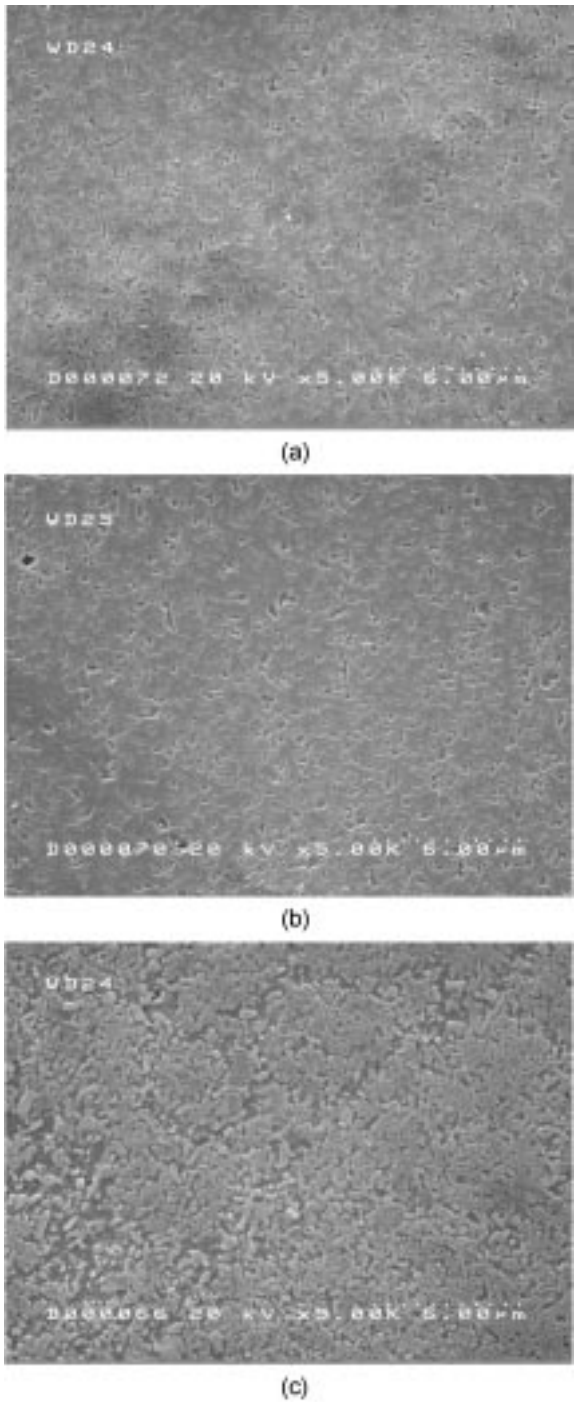

Fig. 4. Scanning Electron Microscopy image of MAS glass-ceramics prepared at crystal growth conditions of (a) 1050°C/7h, (b) 1050°C/10h, (c) 1050°C/20h (Nucleation at 750°C/3h).

spectral region. Namely, the size of cordierite and rutile, which are effective scattering centers, began to increase and became comparable to the wavelength of visible light with heat treatment at 1000°C for 5 hours.

Figure 6 shows the reflectance with varying growth times at a fixed growth temperature of 1050°C. As mentioned above, major crystalline phases change at this temperature. The measured reflectance showed a rapid increase as growth time increased from 1 to

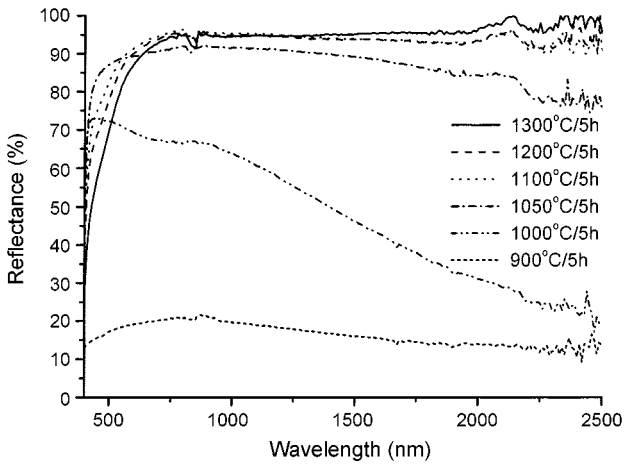

Fig. 5. Reflectance spectra of MAS glass-ceramics heat treated at 750°C/3h and heat treated for growth 5 hours at various temperatures.

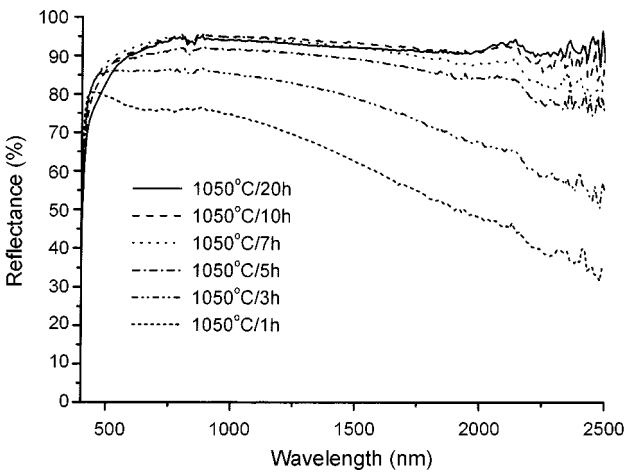

Fig. 6. Reflectance spectra of MAS glass-ceramics heat treated at 750°C/3h and heat treated for growth at 1050°C for various times.

5 hours in all spectral ranges studied. The increase of reflectance was almost saturated at 7 hours heat treatment, which means that most of the glass phase changed to crystalline phases.

Conclusions

Glass-ceramics for IR reflectors were fabricated from MAS glass by a two-step nucleation and crystal growth heat treatment. Glass of composition $11MgO$-$27.9Al_2O_3$-$49.3SiO_2$-$11TiO_2$-$0.8As_2O_3$ (wt%) precipitated cordierite and rutile as major crystalline phases at crystal growth temperatures over 1100°C. The glass-ceramics with nucleation at 750°C for 3 hours and crystal growth at 1100°C for 5 hours showed reflectance over 90% for the widest spectral range, from 570 to 2500 nm. Also, the glass-ceramics with crystal growth at 1300°C for 5 hours showed the highest reflectance. From these results, one can conclude that reflectance of glass-ceramics can be controlled by manipulating the type, size, and volume fraction of crystalline phases without surface

coating or other special processes. A glass-ceramic reflector with high reflectance in the IR spectrum can be fabricated by controlling the heat treatment temperature and time for nucleation and crystal growth.

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