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A Study on the Transparent Glass-Ceramics on the MgO-Al_2O_3-SiO_2 System

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투명 결정화유리에 관한 연구 -MgO-Al_2O_3-SiO_2계에 대하여

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ABSTRACT

The composition of base glass was selected as MgO 8, Al_2O_3 24, SiO_2 68 in weight percent. TiO_2 and ZrO_2 were added to the base glass to investigate their effects as nucleating agents.

In the case of ZrO_2 addition, the optimum temperature for nucleation, which was related to the precipitation of tetragonal ZrO_2, was 800℃. The optimum growth condition for the crystal was 870℃ for 8 hrs, and the major crystal phases precipitated in the samples were β-quartz ss. and mullite. The light transmissivity turned out to be around 80 per cent.

On the other hand, when the TiO_2 was added, it was difficult to determine the nucleating temperature, because the samples turned easily into translucency during the heat treatment. Therefore, it was almost impossible to retain transparency in the samples. The light transmissivity was below 30 per cent.

요 약

유리의 조성을 MgO 8, Al_2O_3 24, SiO_2 68%(중량)로 하고, 핵 형성제로 TiO_2와 ZrO_2를 첨가하여, 그 효과를 검토하였다.

ZrO_2를 첨가한 경우, 최적 핵 형성온도는 800℃이었으며, 이는 tetragonal ZrO_2의 석출에 관련된 것이었다. 결정성장을 위한 최적 열처리 조건은 870℃에서 8시간 유지하는 것이었으며, 이때 나타난 주 결정상은 β-quartz ss.과 mullite 등이었다. 이렇게 얻어진 시료의 광 투과율은 약 80%이었다.

TiO_2를 첨가한 경우, 핵 생성온도를 결정하기가 어려웠으며, 열처리에서 쉽게 반투명체로 변하여, 투명성을 유지하기가 거의 불가능하였다. 이 경우 광 투과율은 30% 미만이었다.

1. Introduction

The glass-ceramics which was invented by Stookey[1], is the polycrystalline material in which the fine and homogeneous crystals are precipitated through appropriate heat treatment.

However, the glass-ceramics may lose transparency which is the important property of glass, due to the difference in refractive index between the dispersed crystal and the residual glass matrix. To keep the transparency as well as the properties of the crystal, the crystal size should be smaller than the wave length

of visible light (0.4~0.8 μm), or anisotropy and refractive index of two phases should be very close.

Many investigations on the transparent glass-ceramics have been made. Beall *et al.*[2] reported that the transparent glass-ceramics can be made of the precipitation of β-eucryptite from $Li_2O-MgO-ZnO-Al_2O_3-SiO_2$ glass system, mullite from $Al_2O_3-SiO_2$ system, and spinel from $ZnO-Al_2O_3-SiO_2$ system. By adding ZrO_2 as a nucleating agent to $ZnO-Al_2O_3-SiO_2$ glass system, Yokoishi *et al.*[4] studied the effect of ZrO_2 amount on the formation of β-quartz ss. and the effect on the transparency. Zdawuski[5] worked on the crystallization and the microstructure of transparent glass-ceramics made from $MgO-Al_2O_3-SiO_2$ glass with TiO_2, ZrO_2 or CeO_2 as nucleating agents. Park[6] studied the transparent glass-ceramics made from $Li_2O-Al_2O_3-SiO_2$ glass by changing the composition of Li_2O and SiO_2 with TiO_2 or ZrO_2 as nucleating additives. Park[7] also reported the effect of nucleating agents on the microstructure of transparent glass-ceramics of the same system.

In this study, we selected the $MgO-Al_2O_3-SiO_2$ system where the β-quartz ss. stuffed with Mg^{2+} was expected. The β-quartz ss. is known as a crystal of low optical anisotropy but high chemical stability. The amount of SiO_2 was 68% by weight based on the report [7], in which the minimum anisotropy of β-quartz ss. was obtained near 70 weight % of SiO_2 in the base glass. And the ratio of MgO to Al_2O_3 was 8 to 24. ZrO_2 and TiO_2 were chosen as nucleating angents for this experiments, because they are less than 5% difference in lattice parameters with β-quartz ss. and are effective in rearrangement of glass into β-quartz ss. during heat treatment. The appropriate heating schedule for the nucleation and growth was investigated for the transparent glass-ceramics with the above mentioned glass composition.

The crystal phases, microstructures and the other relevant properties of the samples prepared from the tested condition were anlayzed by XRD, SEM, DTA and thermal expansion.

2. Experimental

2.1. Preparation of base glass

The reagents used for the experiment were chemical pure grade except Kimcheon quartzite, and were dried well in a dryer.

Table 1. Compositons of the base glass.

Sample	Additives		Base glass			
	ZrO_2	TiO_2	SiO_2	Al_2O_3	MgO	
Zr-10	10					
Zr- 5	5		68	24	8	wt%
			(72.29	15.03	12.68	mol%)
Ti-10		10				
Ti- 5		5				

The compositions of each sample are listed in Table 1. The batches were loaded in alumina crucibles of more than 90% purity, and were melted at 1,600℃ for 1 hr. The melts were then formed into 5 mm diameter rods and plates.

2.2. Crystallization

The nucleating temperature was expected between 870 to 920℃, which is typically determined from the softening point and 50℃ higher than this point. However, the devitrification due to crystallization was always observed from all the samples heat-treated at 920℃. Therefore the nucleation was done at lower temperatures such as 780, 800, 820, 840℃ for 3 hrs, then XRD analysis and SEM observation were done to find out the optimum nucleating temperature. From the result of analysis, the nucleating temperature was around 800 ℃ for the case of ZrO_2 addition. In the case of TiO_2 addition, however, it was difficult to determine the optimum nucleating temperature by the same analysis. So 780℃ was decided as the nucleating temperature referred to the other report[12] in the TiO_2 addition.

To determine the appropriate temperarture of crystal growth, the nucleated samples were heated at different temperatures of 870, 900, 930, 960℃ for 3 hrs, and various properties were examined.

2.3. Property measurement

2.3.1. Thermal expansion

The thermal expansions were measured to determine softening points, nucleating temperatures and thermal expansion coefficients after heat-treatment.

The coefficients of thermal expansion were measured in the range from 30℃ to 600℃ by the dilatometer (Rigaku Co.). The heating rate was 10℃/min.

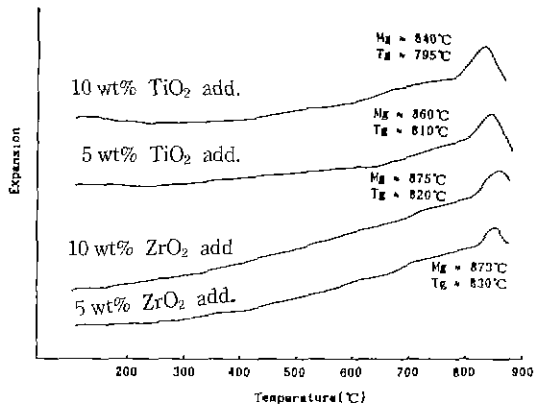


Fig. 1. Thermal expansion curves of the base glasses.

2.3.2. Differential thermal analysis

DTA were carried out to study the thermal phenomena, to investigate the crystal growth, and to find out the exothermic peak of phase transformation.

Differential Thermal Analyzer (model 910) from Dupont Co. was used.

2.3.3. X-ray diffraction analysis

The XRD were carried out to define the glassy phase of the base glass, and to determine the crystal phases.

The apparatus was X-ray Diffractometer (Geigerflex of Rigaku Co.).

2.3.4. Microstructure

Samples for the microstructure analysis were ground and polished with #8000 SiC and 0.05 μm Al_2O_3 powders. The ZrO_2 added samples were etched in 2% HF solution for 20 seconds and the TiO_2 added samples were etched in 48% HF solution for 10 seconds. Afterwards the samples were coated with gold.

2.3.5. Transmissivity of light

The samples prepared from the optimum condition were cut and polished to 4.3 mm thick to measure transmissivity of light. The range of measurement was from 300 nm to 800 nm and the characterization was completed by Spectrophotometer (λ 9 type) from Perkin Elmer Co..

3. Results and Discussion

3.1. Thermal expansion and DTA

The thermal expansion curves of base glasses are shown in Fig. 1. The softening points (M_g) and transformation points (T_g) of the TiO_2 added samples were lower than those of the ZrO_2 added.

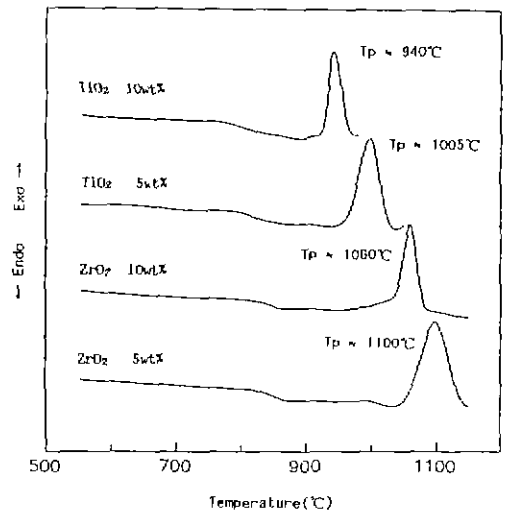


Fig. 2. DTA curves of the base glasses.

Fig 2 shows the DTA curves of the base glasses. The exothermic peaks relevant to crystal growth temperatures appeared to be in 940~1,100℃. According to XRDA, the crystals precipitated at each temperature were identified as mullite, cristobalite or spinel. The exothermic peaks of the TiO_2 added samples appeared at lower temperatures compared to those of the ZrO_2 added samples. The crystal growth temperatures shifted to lower temperatures as the amount of nucleating agent increased. We expected the exothermic peaks of the ZrO_2 nucleation, which were reported for Li_2O-Al_2O_3-SiO_2[6,7] and ZnO-Al_2O_3-SiO_2[1] system glasses. But any peaks regarded as ZrO_2 nucleation were not seen in our DTA curves. This should be from the difference in compositions of base glasses.

3.2. Nucleation and crystal growth

The crystal size must be controlled smaller than 0.1 μm for the transparent glass-ceramics. Therefore, we designed that the nucleating temperature to be as high as possible and the crystal growth temperature to be as low as possible

3.2.1. Nucleation

According to McMillan's report[8], the nucleating temperature in our study is believed to be between softening point 810℃ and 920℃ for the ZrO_2 added samples, and between 840℃ and 890℃ for the TiO_2 added sam-

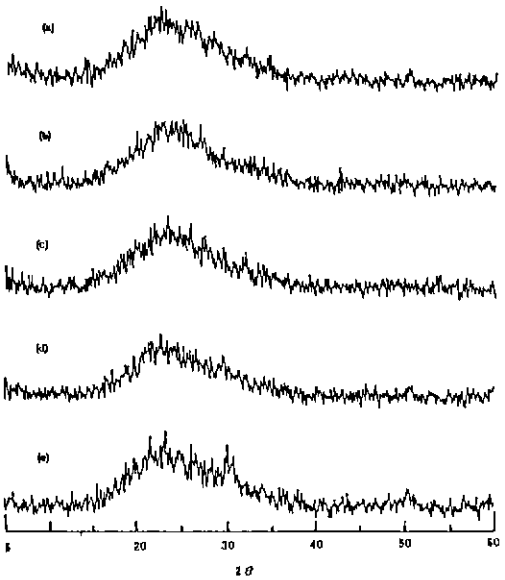


Fig. 3. XRD paterns of heat-treated glasses containing 10 wt% ZrO_2 with various nucleating temperatures.
(a) base glass, (b) 780℃, (c) 800, (d) 820℃, (e) 840℃.

ples. In the ZrO_2 added samples. however, devitrification occured at 920℃, and the TiO_2 added samples had the same tendency.

From the results of preliminary experiments, the ZrO_2 added samples were heat-treated at considerably low temperatures as 780, 800, 820, 840℃. The specific temperatures were selected based on the other reports[4,6,7], in which ZrO_2 crystals were formed at 800± 50℃ in $Li_2O-Al_2O_3-SiO_2$ and $ZnO-Al_2O_3-SiO_2$ system glass with the nucleating agent of ZrO_2. Other experimental results[12] suggested that the optimum nucleating temperature was around the transformation temperature in the TiO_2 added glass.

By DTA, the precipitation of ZrO_2 crystal could not be observed even in the sample with 10% ZrO_2. Therefore XRDA was applied to confirm the ZrO_2 precipitation in the nucleated sample. The results are shown in Fig. 3. As we can see in Fig. 3, the X-ray pattern of the sample nucleated at 780℃ shows only glassy phase, and the same pattern is seen from the sample at 800℃. In the samples heat-treated at 820℃, the weak

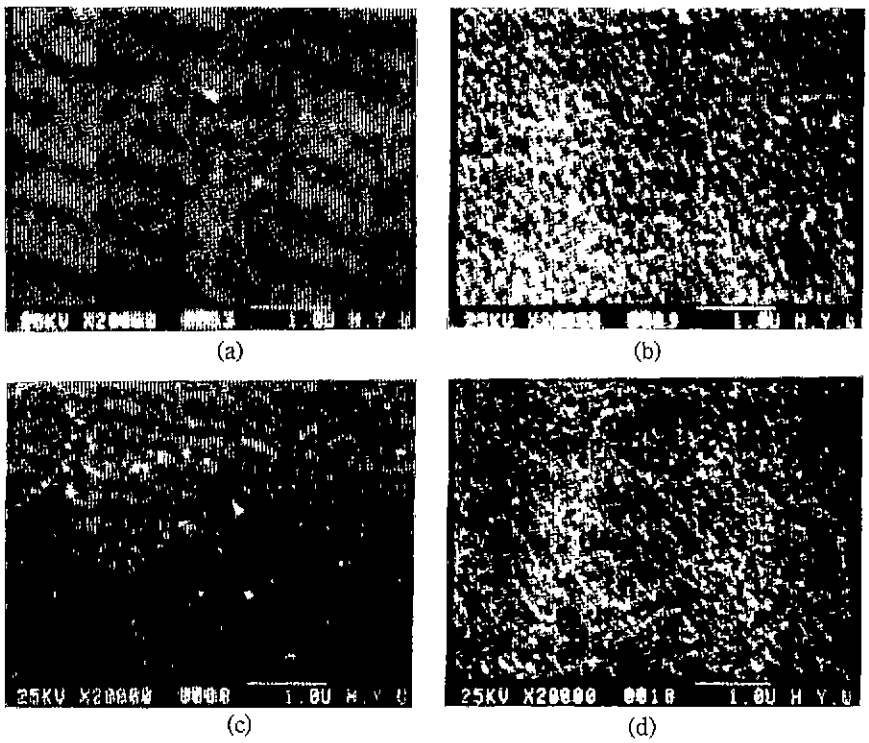
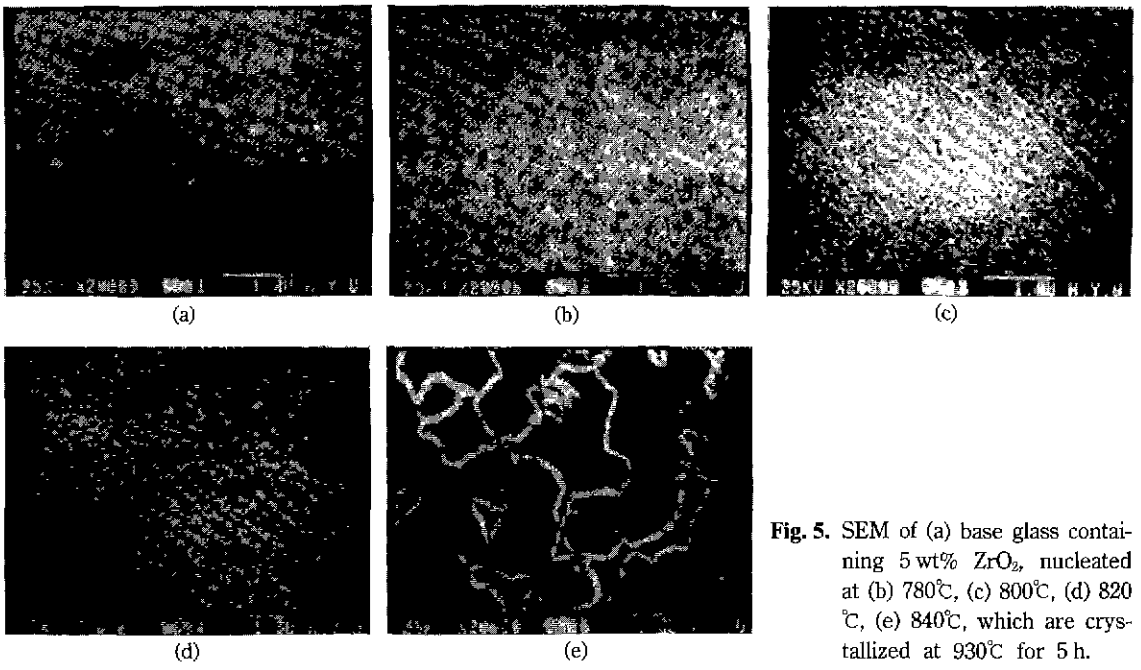


Fig. 4. SEM of (a) base glass containing 10 wt% ZrO_2, nucleated at (b) 780℃, (c) 800℃, (d) 820℃, which are crystallized at 870℃ for 5 h.



(a) (b) (c)

(d) (e)

Fig. 5. SEM of (a) base glass containing 5 wt% ZrO_2, nucleated at (b) 780℃, (c) 800℃, (d) 820 ℃, (e) 840℃, which are crystallized at 930℃ for 5 h.

liffraction pattern from tetragonal ZrO_2 starts to appear at $2\theta=30°$ after halo curve of galss, and that peak becomes even clear in the sample treated at 840 ℃.

800℃, at which any crystal pattern was not recognized, was decided as the nucleating temperature in this temperature, because we considered that there must be tiny crystals in the sample treated at 820℃.

According to the results from XRDA, the samples were nucleated at 780, 800 and 820℃ respectively for 3 hrs and then crystallized at 870℃ for 5 hrs. These samples were inspected by SEM and the results are shown in Fig. 4. Fairly big crystallites appeared in the samples nucleated at 780℃ and 820℃. On the other hand, small crowded crystallites were observed in the sample nucleated at 800℃.

The observation was not surprising from the fact that the samples which were not subjected to the maximum nucleating temperature would end up with smaller number of nuclei and the crystal would grew bigger. As a consequence, through the investigations we figured out was that the most optimum nucleating temperature was 800℃ for the sample Zr-10.

To find out the optimum temperature of nucleation in the sample Zr-5, XRDA was applied to the samples heat-treated in the range of 780~840℃. However the XRD patterns were same as the base glass. Therefore the samples were treated at 930℃ for crystal growth, and the SEM observation was carried out. As we can see in Fig. 5, the sample nucleated at 840℃ shows enormous crystal growth, and the phase separation occured for the sample at 820℃. Almost identical microstructures were observed samples treated from the 780℃ and 800℃. With the observation by SEM and the result of XRDA from the sample ZR-10, 800℃ was chosen as the optimum nucleating temperature.

The nucleating temperature for the TiO_2 added sample could not be determined either by XRD or SEM. However, 780℃ was chosen as the nucleating temperature in this case, according to Yamane's report[12] which claimed that the optimum nucleating temperature existed around the transformation point.

3.2.2. Crystal growth

(1) Crystal phases with heating temperature

Fig. 6 shows XRD patterns of the samples containing 5% ZrO_2. These samples were nucleated at 800℃ and then heated at various temperature 870~1,000℃ for crystal growth for 3 hrs. No crystal peak was seen below 900℃, but tet.-ZrO_2, mullite and β-quartz ss. phases started to appear above 960℃. Besides these phases

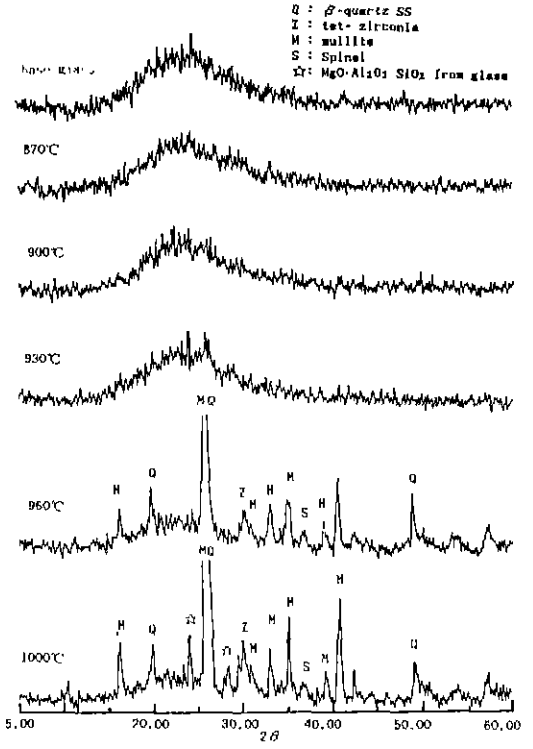


Fig. 6. XRD patterns of the sample containing 5 wt% ZrO_2 with the different heating temperatures after nucleated at 800℃ for 3 h.

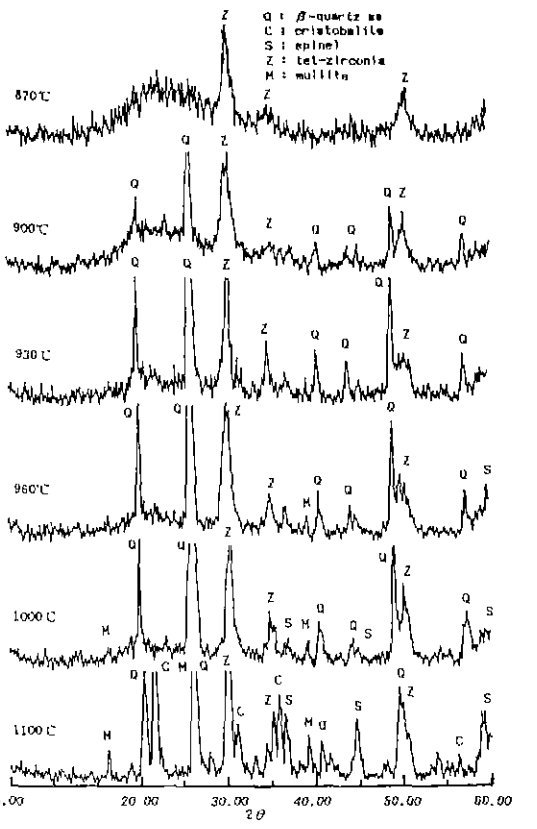


Fig. 7. XRD patterns of the sample containing 10 wt% ZrO_2 with the different heating temperatures after nucleated at 800℃ for 3 h.

magnesium aluminosilicate phases existed in the sample heated at 1,000℃.

Fig. 7 shows XRD patterns of the samples containing 10% ZrO_2, which were heated in a same way as the previous samples.

Only ZrO_2 crystal appeared in the sample heated at 870℃. As the temperature of treatment increased β-quartz ss. started to appear. In the sample heated at 1,100℃, phase transformation from β-quartz ss. to mullite or cristobalite was observed. This transformation is also confirmed from DTA data, where the exothermic peak appeared at 1,060℃. In addition, spinel peaks which were belived to be formed from Mg^{2+} and Al^{3+} ions from β-quarts ss., were detected. This result corresponds to that from Barry *et al.*[9] who studied the coridierite glass system.

Fig. 8 shows XRD patterns of the samples containing 5% TiO_2, which were nucleated at 780℃ and heat-treated at various temperatures of 870~1,000℃ for the crystal growth. Major phases are mullite and spinel regardless of heating temperatures. Almost same XRD patterns were obtained in the samples containing 10% TiO_2.

(2) Crystal phases with heating time

XRDA of the samples containing 5% ZrO_2, which were heat-treated for various periods at 900℃, are shown in Fig. 9. There was no indication of crystal phase up to 7 hr heating, but mullite and β-quartz ss. appeared after 8 hrs.

The sample Zr-10 devitrified by heat treatment at 900℃ for3 hrs, therefore 870℃ was selected as the crystal growth temperature.

XRD patterns of the samples treated at 870℃ for 4 to 8 hrs are as shown in Fig. 10. From the patterns of the samples heated for 4 and 5 hrs, only ZrO_2 phase was observed. Whereas in the samples heat-treated

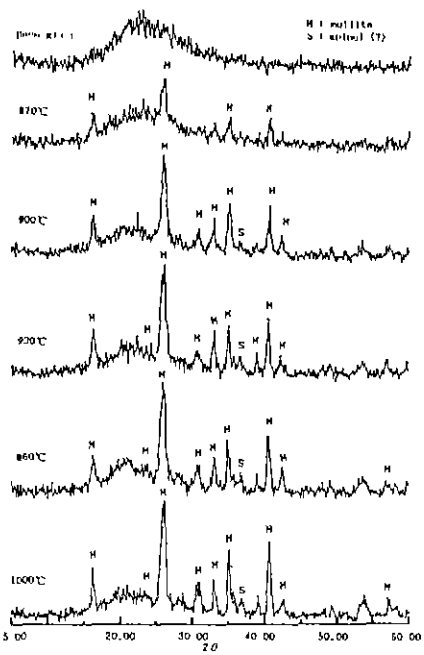


Fig. 8. XRD patterns of the sample containing 5 wt% TiO_2 with the different heating temperatures after nucleated at 780℃ for 3 h.

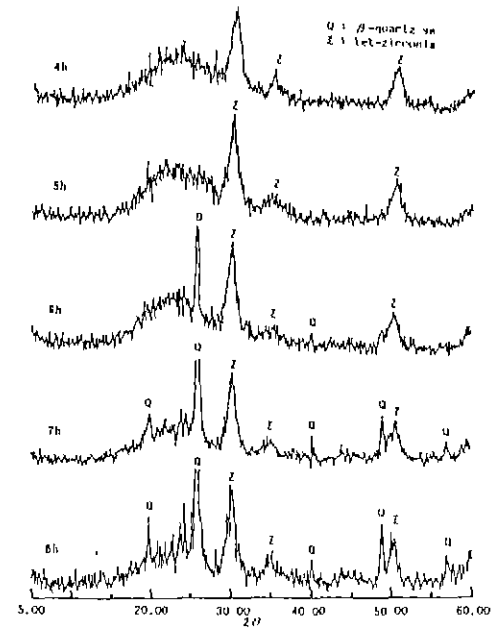


Fig. 10. XRD patterns of glass-ceramics containing 10 wt% ZrO_2 on isothemal treatment with the various heating times (heated at 870℃ after nucleated at 800℃).

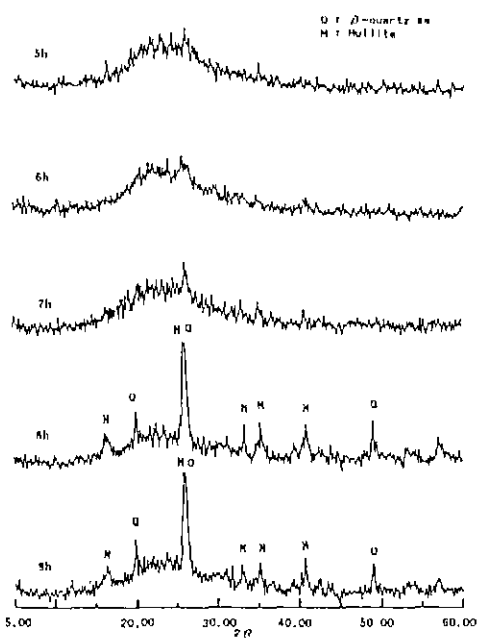


Fig. 9. XRD patterns of glass-ceramics containing 5 wt% ZrO_2 on isothermal treatment with the various heating times (heating at 900℃ after nucleated at 800℃).

for 6 to 8 hrs, β-quartz ss. phase was detected and all the samples were transparent.

The microphotographs of SEM of the above samples are shown in Fig. 11. The crystallites smaller than 0.1 μm, which might be ZrO_2 phase, were observed. In the samples heated longer than 3 hrs, much more crystals were observed as we can see in Fig. 11. Comparing with the XRD patterns, the crystal phases were identified as the mixtures of ZrO_2 and β-quartz ss.. The crystal sizes in these samples were smaller than 0.1 μm, therefore the transparency of these glass-ceramics could be maintained.

The sample Ti-5 was easily devitrified after the heat treatment at 900℃ for 3 hrs. The sample also lost the transparency after the heat treatment at 870℃ for 4 hrs.

The sample Ti-10 changed to bluish-brown opaque at either 870℃ or 900℃.

3.3. Thermal expansion

The thermal expansion characteristics from 30℃ to 600℃ for the crystallized samples are shown in Fig. 12.

The thermal expansion coefficient of the base glass

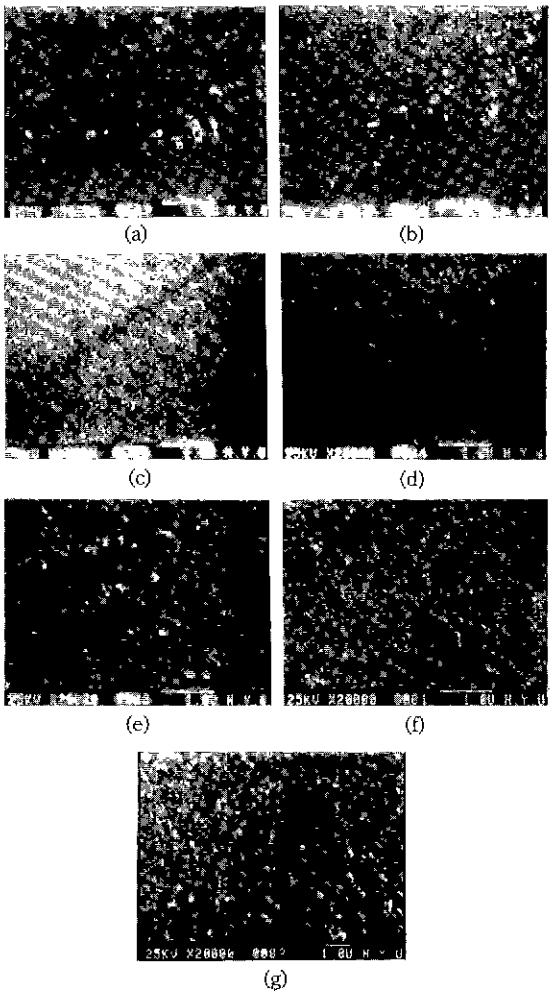


Fig. 11. SEM of glass-ceramics containing 10 wt% ZrO_2 on isothermal treatment with the various heating times. (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, (e) 5 h, (f) 6 h, (g) 7 h (heated at 870℃ after nucleated at 800℃).

containing 10% ZrO_2 is fairly low as 2.3×10^{-6}. The thermal expansion coefficient increased with the crystallization period up to 6 hrs then started to decrease after 7 hrs. The increase of the coefficient might be due to ZrO_2 precipitation ($8\sim12\times10^{-6}℃^{-1}$), while the decrease might be explained by -β-quartz ss. foramtion. Yokoishi[4] reported the similar results from the transparent glass-ceramics of $ZnO-Al_2O_3-SiO_2$ system.

For the sample Zr-5, the thermal expansion coefficient of the base glass was $1.9\times10^{-6}℃^{-1}$, and the similar expansion coefficient resulted from the sample

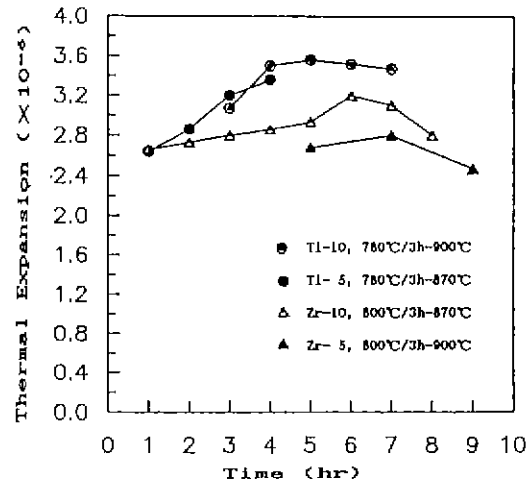


Fig. 12. Variations of thermal expansion coefficents with the various heating times.

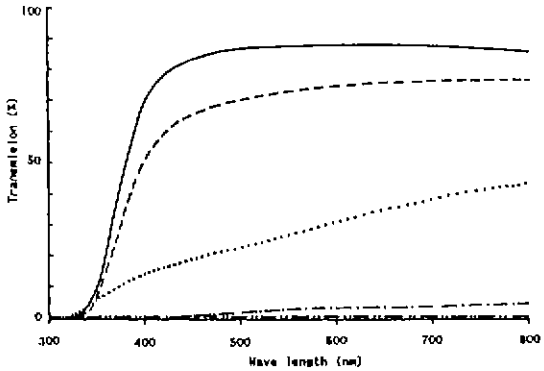


Fig. 13. Transmission spectrum of samples with various heat-treatment.
(——): 10 wt% ZrO_2, 800℃/3 h-870℃/7 h
(- - - - - - -): 10 wt% ZrO_2, 800℃/3 h-930℃/3 h
(·····): 5 wt% ZrO_2, 800℃/3 hr-900℃/7 h
(— · —): 10 wt% TiO_2, 780℃/3 h-900℃/7 hr
(— · · —): 5 wt% TiO_2, 780℃/3 h-900℃/7 h

Zr-10.

In the sample Ti-10, the thermal expansion coefficient of the base glass was $1.0\times10^{-6}℃^{-1}$, and the coefficient was almost constant for 1 hr heating. The formation of mullite is responsible for the constant expansion coefficient.

The expansion coefficient of the base glass in the sample Ti-5 was $1.3\times10^{-6}℃^{-1}$, and the coefficient slope became gentle from the sample heat-treated more than 3 hrs.

3.4. Transmissivity of light

The transmissivites of light measured in the range of visible light are shown in Fig. 13.

In the sample Zr-10, the transmissivity was more than 85% for the sample nucleated at 800℃ and heat-treated for crystal growth at 870℃ for 7 hrs. The transmissivity droped to 70% when the sample was treated at 930℃ for 3 hrs.

The sample Zr-5 after nucleated at 800℃ and heat-treated at 900℃ for 7 hrs showed the transmissivity around 30%.

Regardless of the contents TiO_2, all the TiO_2 added sample showed very low transmissivities as shown in Fig. 13.

4. Conclusions

This study was explored to prepare the transparent glass-ceramics from $MgO-Al_2O_3-SiO_2$ glass by adding ZrO_2 or TiO_2 as nucleating agents.

The optimum temperature for nucleation was 800℃ in the case of ZrO_2 addition. Despite of the difficulty in determining the nucleating temperature of the TiO_2 added glass-ceramics through the experiment, the temperature was presumed to be around the transformation temperature.

The preferable treatment condition for the crystal growth was at 870℃ for 8 hrs for the sample Zr-10, and 900℃ for 6 hrs for Zr-5. Unfortunately TiO_2 containing glass lost transparency fairly easily.

Major crystal phases were β-quartz ss. and zirconia in the sample Zr-10, whereas β-quartz ss and mullite in Zr-5. When TiO_2 was added, the crystallized phases in the samples Ti-5 and Ti-10 were mullite and spinel.

The transmissivity of light was measured to be more than 80% in Zr-10 prepared with the optimum condition. That was reduced to 30% in Zr-5. The transmissivity of TiO_2 containing glass-ceramics were even lower.

감사의 글

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