

Nano-crystallized glass-ceramic of BaO-TiO₂-SiO₂ system containing ZrO₂

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Fresnoite (Ba₂TiSi₂O₈) materials, which exhibit piezoelectricity, ferroelectricity, and nonlinear optical properties, can be used as core materials for optical communication and optical information processing devices. In this study, glass-ceramics with nanometer size fresnoite crystal phase were prepared from BaO-TiO₂-SiO₂ (BTS) glass containing ZrO₂ as a nucleating agent and their microstructure, crystallization behavior, and photoluminescence properties were analyzed. The heat treatment process for glass-ceramics was designed based on data obtained by non-isothermal analysis using differential thermal analysis (DTA). The crystal morphology and microstructure of the prepared specimens were analyzed by X-ray diffraction analysis (XRD), optical microscopy (OM), and field emission scanning electron microscopy (FE-SEM), respectively. The luminescence properties of the specimens were analyzed by photoluminescence (PL) measurements. When the BTS glass with 15 wt% ZrO₂ (15Z) was heat treated at 1,015 °C, a dendritic structure by gathering very small spherical crystalline phases of 10-30 nm was formed. In addition, when the 15Z was excited by light of 309 nm wavelength, strong light of 469 nm wavelength was emitted, and this light appeared to be blue light close to white in the Commission International de l'Eclairage (CIE) diagram.

Keywords: Glass-ceramic, Fresnoite, Nano-crystal, Photoluminescence.

Introduction

Glass-ceramic is a composite material in which crystals are dispersed in a vitreous matrix. When the glass specimen is subjected to sufficient thermal energy required for nucleation and crystal growth, glass-ceramic is formed. Glass-ceramic has completely new electrical, optical, mechanical, and chemical properties due to the crystalline phase produced in the matrix as compared to the parent glass. In order to produce a glass-ceramic having high functionality, the target crystal phase should be precipitated in a vitreous state. For this purpose, the temperature and time of heat treatment in the nucleation and crystal growth process must be strictly controlled. Generally, it is known that nuclei generated in a glass-ceramic do not grow epitaxially during crystal growth [1].

There are some glass compositions capable of forming nuclei by themselves. However, in general, when a glass-ceramic is manufactured, a nucleating agent is added to the glass-ceramic or droplets induced by a liquid/liquid phase separation phenomenon in the glass serve as nuclei. When the nuclei thus produced are subjected to heat treatment at a high temperature, crystallization occurs to precipitate target crystals [2]. Typical nucleating agents used in the crystallization process include ZrO₂, TiO₂, P₂O₅, CaF₂, Cr₂O₃, Fe₂O₃, etc [3]. TiO₂ and ZrO₂ nucleating agents are predominantly used in silicate-

based glasses. However, it is known that the addition of TiO₂ decreases the crystallization temperature of the parent glass and the addition of ZrO₂ increases the crystallization temperature. Reben et al. also published an interesting result that the addition of TiO₂ to CRT (Cathode Ray Tube) glass powder induces surface crystallization behavior, not bulk crystallization [4]. Wondraczek et al. established optimal crystallization conditions by selecting TiO₂ and ZrO₂ to produce β-quartz crystal phases of 100 nm or less in LAS (Li₂O-Al₂O₃-SiO₂) glass [5]. In addition, by adding ZrO₂ to the glass composition, Duke et al. produced β-quartz crystals uniformly, thereby obtaining high transparency and low expansion rate. Therefore, ZrO₂ and TiO₂ has been widely conducted as nucleating agent [6].

On the other hand, it is known that fresnoite (Ba₂TiSi₂O₈) crystals exhibit piezoelectricity, ferroelectricity, and nonlinear optical characteristics. When fresnoite is irradiated with ultraviolet light, blue light is emitted due to Ti⁴⁺ ions present in the square-pyramidal TiO₅ structure. Recently, fresnoite-based glass-ceramics have been attracting interest. Fresnoite-based glass-ceramics can be applied to optical devices such as optical switches and optical waveguides [7-11]. Lee et al. studied the fluorescence properties of BaO-TiO₂-SiO₂ (BTS) as a function of the ratio of K₂O/BaO. Lee contended that the degree of crystallinity and the PL intensity of glass-ceramics without K₂O are high, but that the degree of crystallinity and the photoluminescence (PL) intensity decrease with an increasing K₂O/BaO ratio [12].

Although various studies have been carried out on fresnoite-based glass-ceramics exhibiting PL characteristics,

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it is difficult to find any studies to induce bulk crystallization by adding the ZrO₂ nucleating agent. Therefore, in this study, ZrO₂ was added to BTS glass to induce bulk crystallization behavior, and also controlled to produce only nanometer-sized fresnoite crystal phase. Finally, the microstructure and the crystal phase of the prepared glass-ceramic were analyzed and the results were discussed in relation to the luminescence properties.

Experimental

The starting materials were BaCO₃ (Kojundo Chemical Co., 99%), TiO₂ (Kojundo Chemical Co., 99.9%), SiO₂ (Kojundo Chemical Co., 99.9%), and ZrO₂ (Junsei Chemical Co., 99%). The composition of the mother glass was fixed to BaO : TiO₂ : SiO₂ = 26 : 13 : 61 (mol%), which is higher in the amount of SiO₂ than the composition of the fresnoite (Ba₂TiSi₂O₈) phase, to generate fresnoite crystals on the glassy matrix in which SiO₂ is the main component. To prepare the glass-ceramic, ZrO₂ was added to the mother glass in the range of 0 to 15 wt%. The batch powder was pulverized and mixed with zirconia balls as milling media for 24 h and then melted in an alumina crucible at 1,450 °C for 1 h in an electric furnace. The melt obtained was quenched by pouring into a graphite mold. The obtained glass was pulverized to a size of 45 μm or less and then subjected to differential thermal analysis (DTA, STA S1500, Scinco Co., Korea) at a heating rate of 5 °C/min to analyze the crystallization mechanism. Table 1 shows the heat treatment process conditions for glass-ceramics manufacturing based on the data obtained from the DTA results. The crystalline phase of the glass-ceramic was confirmed by X-ray diffraction analysis (XRD, Pan'alytical, X'pertpro, Netherlands), and the crystallization behavior was confirmed by optical microscopy (OM, ME-33, Daemyoung Optical Co., Korea). The nanoscale microstructure was confirmed with a field emission scanning electron microscope (FE-SEM, S-4800, HITACHI Co., Korea). Before the observation, the fractured surface of the glass-ceramic was polished by SIC sandpaper and etched with 1 wt% hydrofluoric acid (HF) for 30 seconds.

Table I. One-step heat-treatment condition for fresnoite-based glass-ceramics.

Specimen I.D	Composition (wt.%)		Heat-treatment condition for crystallization	
	Mother glass*	ZrO ₂	Temperature (°C)	Time (hour)
0Z	100	-	900	
5Z	95	5	933	1
10Z	90	10	1,018	
15Z	85	15	1,015	

*Composition of mother glass is BaO : TiO₂ : SiO₂ = 26 : 13 : 61 (mol%)

Luminescence properties of glass-ceramics were observed by photoluminescence and photoluminescence excitation spectroscopies (PL and PLE, Darsa-5000, PSI Co., Korea) at room temperature. A 500 W xenon lamp was used as the excitation source and the emitted light was analyzed using the Commission International de l'Eclairage (CIE) diagram.

Results and Discussion

DTA analysis was performed on glass prepared by substituting 0, 5, 10, and 15 wt% of nucleating agent ZrO₂ in BTS glass powder. The results are shown in Fig. 1. The maximum crystal growth temperature (T_p) is found to be 940 °C for the mother glass (0Z), 973 °C for the 5Z specimen, 1,058 °C for the 10Z specimen, and 1,045 °C for the 15Z specimen. That is, when the ZrO₂ substitution amount is in the range of 0-15 wt%, the T_p value increases with the ZrO₂ substitution amount, showing the highest value at 10% ZrO₂, and decreases when the ZrO₂ substitution amount is over 10%. Reben reported that the addition of ZrO₂ as a nucleating agent to fresnoite glass-ceramic tends to increase the crystal growth temperature [4]. However, when ZrO₂ was replaced at more than 15wt% in this study, T_p decreased. An accurate interpretation of this tendency is expected to require additional research.

We often have found that when glass-ceramics are manufactured, the crystals grow beyond micrometer size due to too long heat treatment or excessively high temperature than maximum crystal growth temperature (T_p) obtained from DTA. Therefore, glass was heated at a temperature of 40 °C lower than T_p to produce a nano-sized fresnoite crystal phase. As shown in Fig. 1,

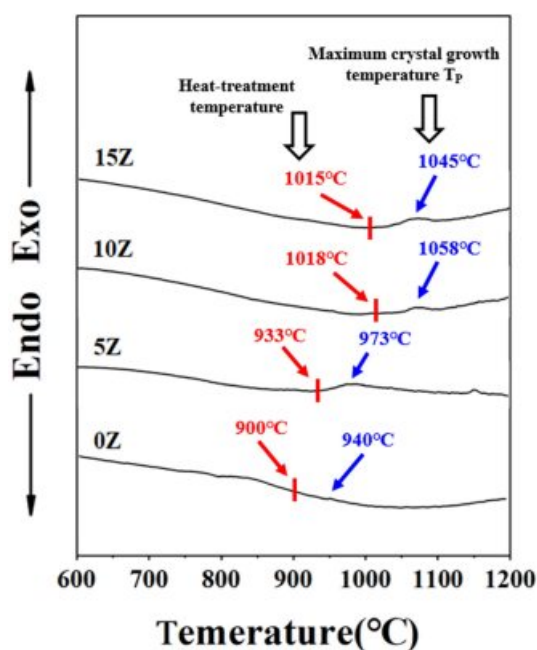


Fig. 1. DTA graph of glass according to amount of ZrO₂ added.

heat-treatment temperatures of the 0Z, 5Z, 10Z and 15Z specimens were 900 °C, 933 °C, 1,018 °C and 1,015 °C, respectively.

A graph of the XRD analysis results of the glass-ceramic prepared according to the ZrO₂ substitution amount is shown in Fig. 2. All glass-ceramics showed no or weak crystal peaks, whereas the strong peaks for fresnoite crystals were formed in the specimen containing 10% ZrO₂. The SiO₂ might involve in the formation of both the SiO₂-based crystal phase and the amorphous matrix due to the excessive amount of SiO₂ added compared to the stoichiometric fresnoite (Ba₂TiSi₂O₈) composition. Liu argued that when excess ZrO₂ was added to the glass-ceramic, it would no longer function as a nucleating agent but as a network former to strengthen the glass network, and thus inhibits crystal growth [13]. Thus, the decrease in crystal peak intensity of the 15Z specimen in the XRD graph is believed to be due to the excess ZrO₂ amount, acting as a glass former rather than as a nucleating agent, as claimed by Liu.

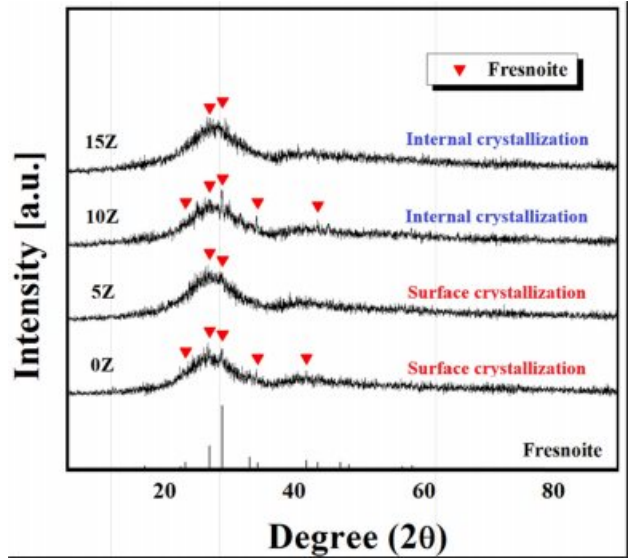


Fig. 2. XRD graph of glass-ceramics according to amount of ZrO₂ added.

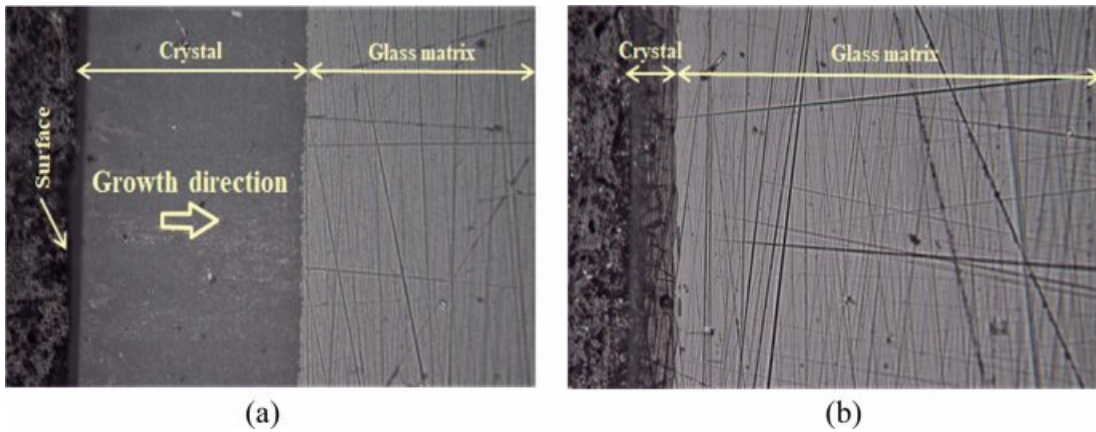


Fig. 3. The cross-section of glass-ceramics observed magnified 200 times with an optical microscope; (a) 0Z and (b) 5Z.

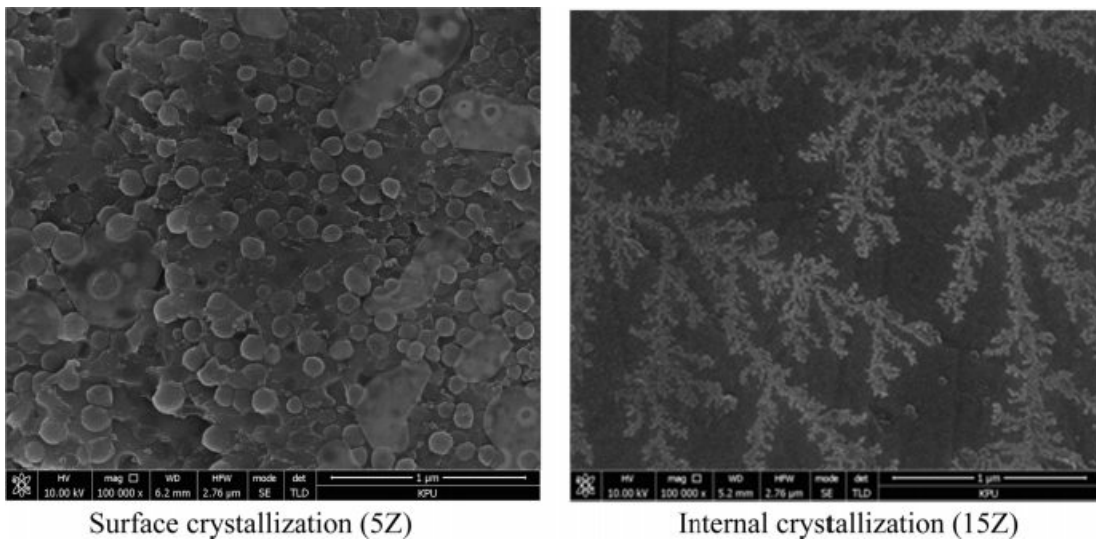


Fig. 4. Microstructure of glass-ceramics according to amount of ZrO₂ added observed by SEM.

Also, as can be seen from the vertical section image shown in Fig. 3, surface crystallization phenomenon occurred in 0Z and 5Z specimens. Both specimens produced thick crystals on the surface, the thicknesses of surface crystal of 217 μm and 46 μm , respectively. Due to the low hardness of the glass matrix, the crystal layer was polished cleanly, whereas the glass matrix had many polishing marks. On the other hand, in 10Z and 15Z specimens, no crystal layer was observed on the surface, indicating that internal crystallization occurred.

The microstructure of glass-ceramics prepared according to the amount of ZrO₂ substitution was observed by FE-SEM and the results are shown in Fig. 4. The microstructure of the surface crystal part of the 5Z specimen, magnified 50,000 times by SEM, was filled with spherical crystals of 80-120 nm in size. On the other hand, the 15Z specimen showed a dendrite-shaped crystal phase composed of very small spherical particles of 10-30 nm in size.

Wisniewski et al. reported that several mechanisms are involved in the growth of fresnoite crystals. Relatively slow growing crystals form spherical or polygonal crystals, and relatively fast growing crystals form dendrites [14-16]. In this study, the amount of ZrO₂ added determines the internal or surface crystallization, indicating that the crystallization rate varies depending on the amount of ZrO₂ added, and eventually the crystal phase changes.

Photoluminescence excitation (PLE) and photoluminescence (PL) analyses were performed to analyze the light emission characteristics of the glass-ceramics prepared according to the amount of ZrO₂ added, and the results are shown in Figs. 5 and 6, respectively. When the light of 309 nm wavelength is irradiated to the glass ceramic specimen, the light of 469 nm wavelength is emitted most as shown in Fig. 5. Therefore, when analyzing the luminescence characteristics of the specimen prepared in this study, 309 nm light was used as excitation light.

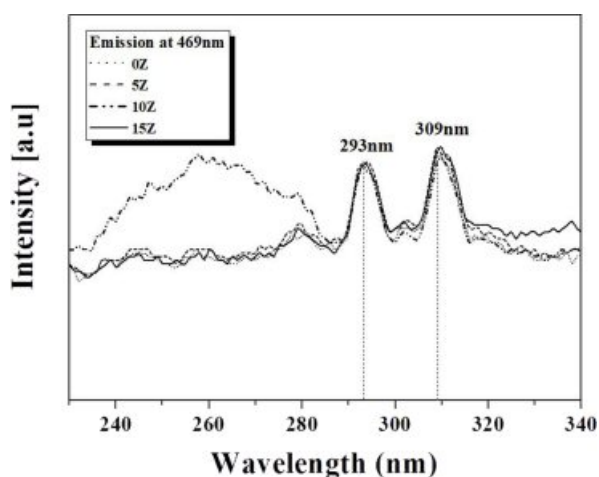


Fig. 5. PLE spectra of fresnoite-based glass-ceramics.

The PL spectra emitted from the glass-ceramics were shown in Fig. 6 as a function of amount of ZrO₂ added. The PL characteristics of the fresnoite crystal phase are due to the crystal structure, and when UV light is excited, blue-white light is emitted in the 400-600 nm wavelength range due to the structure of the pyrosilicate groups (Si₂O₇) and the square pyramidal groups (TiO₂) [17]. The PL intensities at 469 nm of the 0Z, 5Z and 10Z samples were similar, but the intensity of the 15Z specimens was the highest among the specimens prepared in this study. It can be seen that as the amount of the nucleating agent added increased, the PL intensity increased overall, and the 15Z specimen showed the

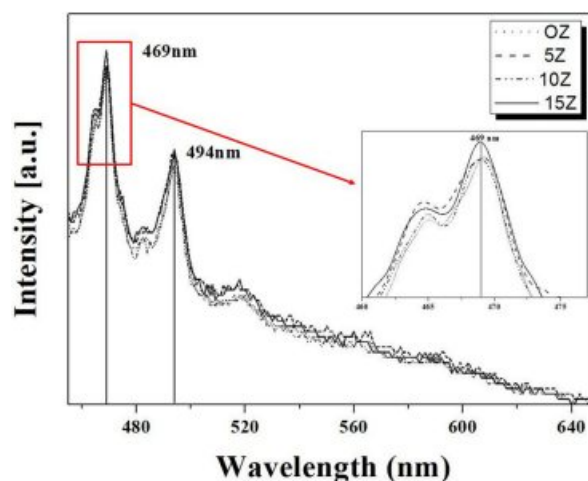


Fig. 6. PL spectra of fresnoite-based glass-ceramics according to amount of ZrO₂ added. The excitation light used has wavelength of 309 nm.

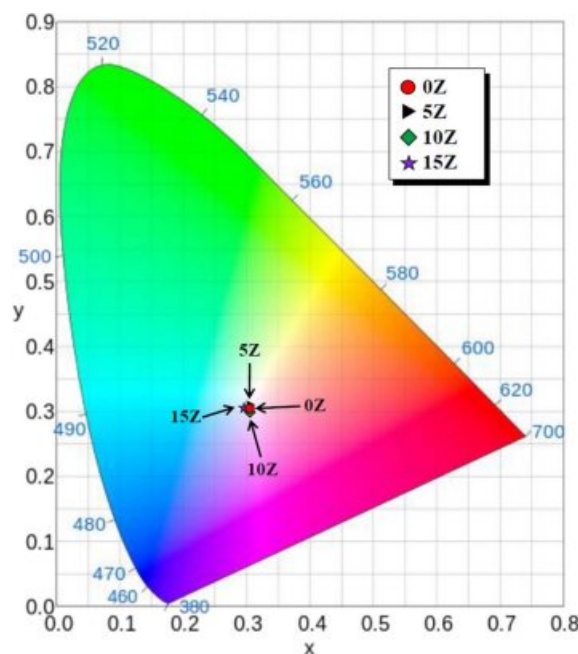


Fig. 7. CIE diagram of light emitted from glass-ceramics with varying amounts of ZrO₂ added.

best PL properties. As a result, it can be seen that ZrO₂, which acts as a nucleating agent, has a direct effect on the crystallization of Fresnoite crystals exhibiting PL properties and has been a factor in improving PL properties.

The color of PL spectra of the prepared specimen is indicated in the CIE color coordinates, as shown in Fig. 7. The PLs of all the specimens had similar color coordinates, appearing in blue light close to white.

Conclusions

In this paper, glass-ceramics of BaO : TiO₂ : SiO₂ = 26 : 13 : 61 (mol%) composition containing 0-15 wt% of ZrO₂ as nucleating agent were prepared and its phase identification, microstructure observation and PL analysis were performed. All glass-ceramics showed no or weak crystal peaks, whereas the strong peaks for fresnoite crystals were formed in the specimen containing 10% ZrO₂. The surface crystallization phenomenon occurred in 0Z and 5Z specimens, meanwhile, in 10Z and 15Z specimens, an internal crystallization occurred. The microstructure of the surface crystal part of the 5Z specimen was filled with spherical crystals of 80~120 nm in size. On the other hand, the 15Z specimen showed a dendrite-shaped crystal phase composed of very small spherical particles of 10~30 nm in size, indicating that the amount of ZrO₂ added determines the internal or surface crystallization and the crystallization rate.

When the specimens were excited with 309 nm light, all the glass-ceramic specimens emitted 469 nm wavelength light. The light emission intensity was highest in the 15Z specimen, and the emitted light showed blue color light close to white in the Commission International de l'Eclairage (CIE) diagram. It was possible to produce nano-sized fresnoite-based glass-ceramics by substituting the nucleating agent ZrO₂ into BaO-TiO₂-SiO₂ glass having an excellent PL property.

Acknowledgments

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