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A STUDY ON THE NANOMETER SCALE CRYSTALLIZATION MECHANISM AND PHOTOLUMINESCENCE CHARACTERISTICS OF B_2O_3-Al_2O_3-CaF_2 : Eu GLASS

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Abstract - In this study, crystallization glass containing CaF_2-Al_2O_3-B_2O_3: Eu_2O_3 (hereinafter referred to as CAB: Eu) glass was controlled to produce calcium difluoride crystal phase. The crystal structure and optical properties of the sample were evaluated by DTA, XRD, SEM, and photoluminescence(PL) spectrometer. CAB mother glass had a glass transition temperature (T_g) of 557.1℃, a glass softening point (T_s) of 638.5℃, and a crystallization maximum ratetemperature (T_p) of 831.4℃. In this study, heat treatment was performed at 680 ~ 820℃, which is lower than T_p, in order to induce nano-scale crystallization and to inhibit excessive crystal growth. Eu-doped parent glass produced CaF_2 crystal at a higher temperature than Eu-free glass and a PL-independent Al_5BO_9 phase was formed at 800 ℃ or higher. The CAB crystal glass samples showed a high value of PL intensity at 613 nm when given a wavelength of 395 nm. In addition, the maximum PL strength was appeared at the heat treatment condition of 780° C and 4 hours within a range of 760 to 820°C and 0 to 16 hours. In this study, we confirmed the relationship between the crystal structure, microstructure, and photoluminescence properties of crystallized glass with CaF_2 crystal phase and confirmed that it can be applied to transparent ceramic materials requiring red color in the future.

Keywords - Oxy Fluoride Glass, CaF_2, Nanometer Crystal, Photoluminescence, Eu-Doping, Crystallization

I. INTRODUCTION

Glass-ceramic products have been widely used in daily life for decades as well as in special applications due to their high transparency, chemical durability, and formability. In recent years, glass-ceramics have been extensively used in environment, energy, optical, and semiconductor applications. In particular, optical glass has attracted a great deal of attention because it can be applied to sensors, lasers, and LED luminescence. [1], [2] Boron oxide (B_2O_3) is used as an important glass former and flux material in the glass industry. Although the B_2O_3-rich melt has a disadvantage of high viscosity, the crystalline form has linear and nonlinear optical properties and is used in optoelectronic sensors, lasers for optical and electronic devices, and phosphorescent devices. On the other hand, fluorine-containing glass is characterized by excellent photoluminescence characteristics when rare-earth ions are doped due to its lowered phonon energy. [3] However, in the case of fluorine glass, there is a problem that the thermal stability and the water resistance are low and the fluorine component can be volatilized through the melting process. To resolve this problem, Al_2O_3 has been added to fluoride glass, producing oxy fluoride glass, which reduces fluoride loss. [4] Oxy fluoride-based glass gained recognition after Wang and Ohwaki successfully manufactured transparent glass ceramics containing (Pd, Cd)F_2 crystals,[5] which exhibited improved luminescence properties such as low phonon energy and high rare earth ion solubility and long fluorescence lifetime. The types of rare earth ions doped on the oxy fluoride system glass include Eu^{3+}[6][7], Tb^{3+}[8], Er^{3+}[9][10], Dy^{3+}[1], and Sm^{3+}[11]. Recently, K. Shinozaki and others reported 97% high-lightness (PL) quantum yield (QY) in Eu-doped 50 BaF_2-25Al_2O_3-25B_2O_3 glass. [12] In addition, Takumi Kato et al studied the optical, acidification and characteristics of Ce-doped 30CaF_2-20Al_2O_3-50B_2O_3 glass and reported changes due to the substitution quantity of CeO_3.[13] Xin-yuan Sun et al reported that the crystallized glass had excellent photoluminescence properties depending on the heat treatment of the oxy fluoride glass substituted with Tb^{3+}. [14] Despite the foregoing studies, relatively little research has been carried out on the photo-luminescence properties of boric oxide-fluoride mixed glass doped with Eu_2O_3. In response, in this study, the mechanism of crystal growth of nano-sized crystals and its photoluminescence properties were investigated by doping Eu_2O_3 for CaF_2-Al_2O_3-B_2O_3 glass.

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

CaF_2 (KOJUNDO Chemical Co., 99.9%), Al_2O_3(KO-JUNDO Chemical Co., 99.9%),B_2O_3(SAMCHUN PURE Chemical Co., 99.9%), and Eu_2O_3(KO-JUNDO Chemical Co., 99.9%) were used as raw materials for the preparation of the calcium difluoride crystal phase. The batch composition of the mother glass was set at 3:2:5 for CaF_2, Al_2O_3, and B_2O_3. In the case of Eu_2O_3, 0.4 mol% was substituted. The batched powder was pulverized and mixed with zirconia balls for 24 hours and then placed in an alumina crucible. The powder was melted in an electric furnace at 1100°C for 1 hour, and then quenched by pouring it into a graphite mold. The quenching mother glass was kept at the glass transition temperature for 30 minutes to cool it down to room temperature to remove the internal stress. The obtained CAB glass was pulverized to a size smaller than 45 µm, and the temperature of the glass transition temperature (T_g), the temperature of the glass softening temperature (Ts), and the temperature of crystallization (T_p) were found by DTA (Differential Thermals Analysis, Seiko Exstar 6000) with a temperature of 10°C/min. The crystal phase analysis of the parent glass and crystallized glass samples was confirmed using XRD (X-Ray Diffractometer, Pan'alytical, X'pertpro, Ne-therlands). In addition, the microstructure of the CAB glass was observed through FE-SEM (Field Emission Scanning Electron Microscope, NanoSEM 450, Nova Co.). Before observation, the surface of the sample was etched with 3wt% hydrofluoric acid (HF) for 20 seconds. For the emission analysis of the prepared glass-ceramics, the luminescence charac-teristics in the region of 400-780 nm were observed with a PL apparatus (Photo-luminescence, PSI, Darsa-5000). A 500 W xenon lamp was used as the excitation source.

III. RESULTS AND DISCUSSION

3.1. DTA analysis of CAB system glass

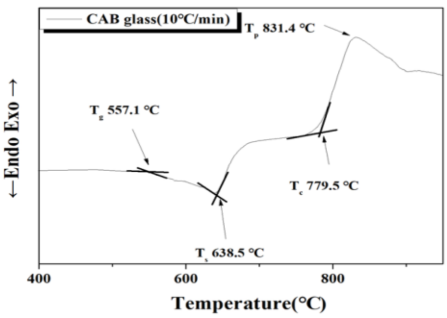


Fig. 1. DTA curve of CaF_2-Al_2O_3-B_2O_3 glass system measured at heating rate of 10℃/min

Fig. 1 shows the DTA analysis results of the mother glass. The glass transition temperature (T_g) was 557.1°C, the glass softening point (T_s) 638.5°C, the crystal growth starting temperature (T_c) 779.5°C, and the crystal growth maximum temperature (T_p) 831.4°C. For CaF_2 crystal growth, the heat treatment temperature interval was selected from 680°C to 820°C below T_p in this study.

3.2. XRD analysis of CAB system glass

The results of the XRD analysis of CAB glasses heat treated at 680~760°C for 8h are shown in Fig. 2. The mother glass was found to be completely amorphous, and the samples heat-treated at 760°C for two to four hours also had an amorphous structure. However, eight hours of heat treatment revealed the target crystal CaF_2 (calcium difluoride) peak. On the other hand, XRD analysis results of the CAB glasses heat-treated at 760^0 for 0~8h are shown in Fig. 3. The samples heat-treated at 760 for 2~4h showed an amorphous structure similar to that of CAB glass. However, the CaF_2 crystal phase was formed in the sample heat-treated at 760^0 for 8h. Fig. 4 shows the XRD analysis results of samples doped with 0.4mol% Eu_2O_3 and heat-treated at 760~820^0 for 8 hours. The Eu-doped parent glass showed an amorphous structure and the 760^0 annealed sample also showed an amorphous form. Calcium difluoride was formed in the sample heat-treated at 780^0 higher and the CaF_2 crystal peak intensity became stronger as the heat treatment temperature was increased. In particular, from the heat treatment temperature above 800^0, not only CaF_2 but also aluminum borate (Al_5BO_9) was formed. The XRD analysis results of the samples heat-treated at 820^0 for 4 ~ 16h are shown in Fig. 5 Calcium difluoride was formed from more than 4 hours of heat treatment time and the peak intensity increased with heat treatment temperature. As can be seen from the XRD results of Fig. 2 and 3, when CAB glass was heat treated, Eu-doping was shown to inhibit crystalline growth. Eu^{3+} is present in the glass as a network modifier instead of a network former due to its large ion radius and high atomic number. Eu^{3+} enters the crystallization network under the influence of the heat treatment, and the amount of heat energy required for crystallization is increased, and the T_c value is increased, thereby suppressing crystalli-zation.[1][16]

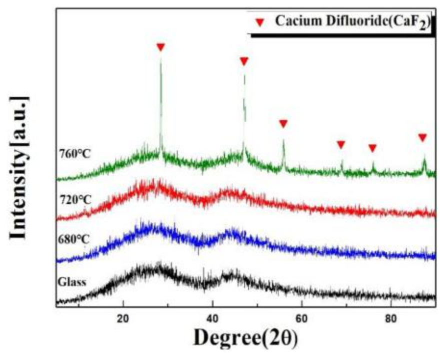


Fig. 2. XRD results of CaF_2-Al_2O_3-B_2O_3 glass-ceramics heat treated at 680~760℃ for 8h.

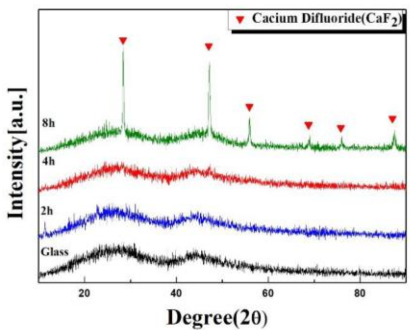


Fig. 3. XRD results of CaF_2-Al_2O_3-B_2O_3 glass-ceramics heat treated at 760℃ for 0~8h

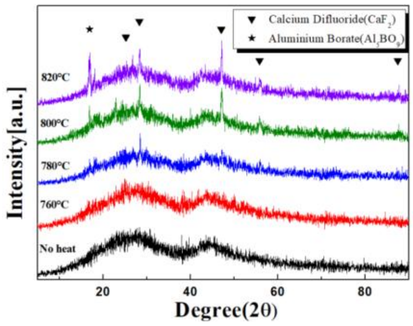


Fig. 4. XRD results of CaF_2-Al_2O_3-B_2O_3 : Eu glass-ceramics heat treated at 760~820℃ for 8h

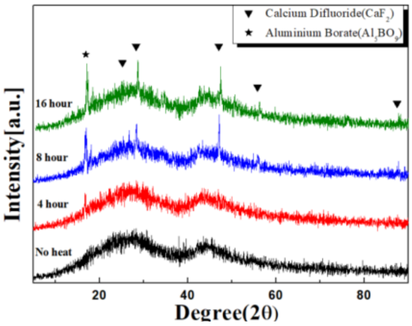
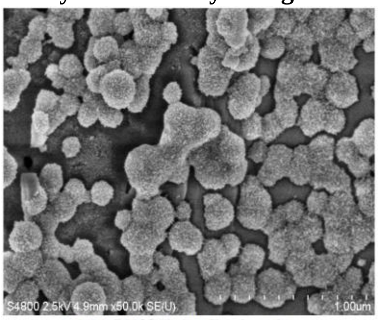
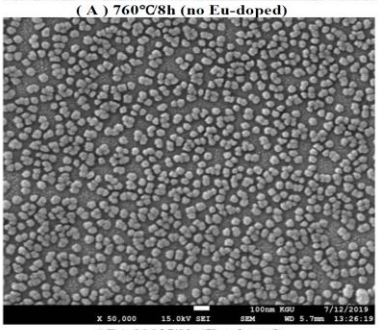


Fig. 5. XRD results of CaF_2-Al_2O_3-B_2O_3 : Eu glass-ceramics heat treated at 820℃ for 0~16h

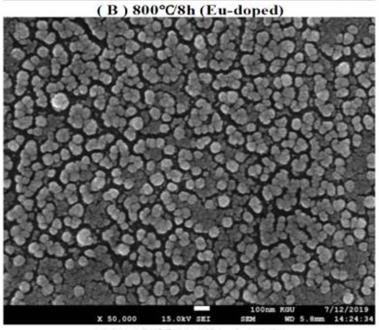
3.2. SEM analysis of CAB system glass



(A) 760°C/8h (no Eu-doped)



(B) 800°C/8h (Eu-doped)



(C) 820°C/8h (Eu-doped)

Fig. 6. Microstructure of glass-ceramic of CAB system according to Eu-doping and heat treatment temperature.

The microstructure of CAB glass-ceramic samples according to the Eu_2O_3-doping and the heat treatment conditions is shown in Fig. 6. In the case of the Eu-undoped samples (a), crystals of 100-200 nm size were produced, whereas the Eu-doped glass-ceramic samples (b and c) had much finer in size at 40-50 nm. From observation of the microstructure of the samples, it was found that Eu-doping inhibits the growth of crystals generated in the CAB glass.

3.3. PhotoLuminescenceanalysis of CAB system glass

A photoluminescence analysis was per-formed on the glass-ceramic specimens prepared according to the heat treatment conditions. At first, a wavelength of 365 nm generated in the mercury lamp was used. All specimens emitted the strongest light at 613 nm regardless of the fabrication conditions. Based on this, when light of several wavelengths was examined on glass-ceramics within a range of 200-450 nm to find the suitable excite light, the wavelength of 395 nm was appeared to cause the specimens to emit the light of 613 nm wavelength with the greatest intensity. In this study, therefore, the excitation wavelength for emitting the glass-ceramics was eventually set to 395 nm. The CaF_2: Eu system is luminous because Eu ions are dissolved in CaF_2 crystals to help the energy transfer due to lowered phonon energy of F ions present in the crystal phase of calcium difluoride. The Eu ions are easily dissolved in CaF_2 crystals due to the electric field strength and ion size. The electric field strength of Eu^{3+} ions is higher than that of Ca^{2+} ions, and thus F^- ions are preferred over Eu^{3+}. Furthermore, since the ion radius of the Eu^{3+} ions (94.7 pm) is smaller than the ion radius of the Ca^{2+} ions (197 pm), the Eu^{3+} ions can replace the Ca^+ ions and can be dissolved in the CaF^2 crystal lattice. [1] The photoluminescence spectra for CAB:Eu glasses heat-treated at 760~820^0 for 8h are shown in Fig. 7. The energy transformation of the overall oxy fluoride glass matrix showed a pattern of improved energy transmission with a transition of $^5D_0 \rightarrow {}^7F_2$. The PL strength of the crystallized glass was higher than that of the mother glass, and the sample, which was heat treated at 780°C, showed the highest value. However, when the glass was heat-treated at 800^0 or higher, the photoluminescence peak tended to decrease. The photoluminescence spectra for CAB: Eu glasses heat-treated at 820□ for 0~16h are shown in Fig. 8. When the heat treatment time is increased from 0 hours to 8 hours, the light emission intensity is increased, but when the heat treatment is performed at a higher temperature higher, the light emission intensity rather decreased. The existence of the maximum value of the PL intensity at the heat treatment temperature and time can be interpreted from the XRD analysis results. Fig. 4 shows that an Al5BO9 phase, which is irrelevant to PL excitation, is formed in addition to

CaF_2 by heat treatment above 780^0. As the crystallized Al_5BO_9 phase grows, crystal agglomeration occurs and surface defects increase to decrease photoluminescence efficiency. This phenomenon may be interpreted as the aggregation of Eu^{3+} ions at high temperature. For-mation of uniformly distributed CaF_2 nanocrystals is uniformly distributed together while suppressing aggregation of Eu3 ions in the glass matrix, thereby enhancing photoluminescence properties. However, continuous heat treatment at high temperatures leads to excessive aggregation of calcium difluoride crystal phases, leading to Eu^{3+} ion clusters, reducing the photoluminescence intensity.

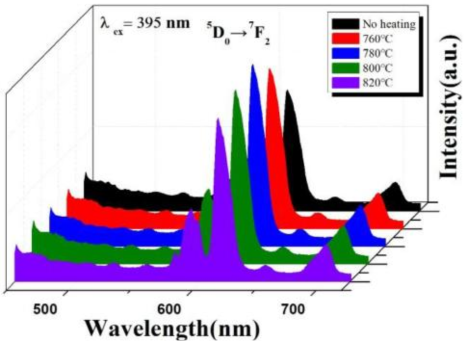


Fig. 7. PL spectrum results of CaF_2-Al_2O_3-B_2O_3 : Eu glass-ceramics heat treated at 760~820^0 for 8h

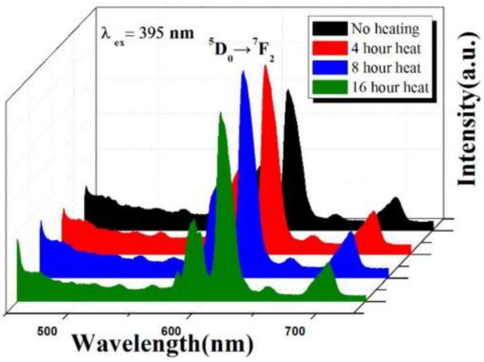


Fig. 8. PL spectrum results of CaF_2-Al_2O_3-B_2O_3 : Eu glass-ceramics heat treated at 820℃ for 0~16h

IV. CONCLUSION

In this study, glass-ceramic with a calcium difluoride phase, which has low phonon energy characteristics in the CaF2-Al2O3-B2O3 system and amplifies the photoluminescence, was prepared, and the crystallization behavior, microstructure, and luminescence characteristics were analyzed. The main conclusions are as follows.

1. Calcium Difluoride was produced in 760 ℃ heat treatment without Eu^{3+} doping, but Calcium Difluoride was produced in 780 ℃ heat treatment higher than 760 ℃ when Eu^{3+} was doped..
2. CAB:Eu glass-ceramics containing CaF_2hibited a red PL spectrum in which the peak at 613 nm was largest when excited at 395 nm. The PL intensity of CAB:Eu glass-ceramics increased with heat treatment temperature and time, but tended to decrease from a certain point
3. In this study, CAB glass doped with 0.4 mol% of Eu_2O_3 exhibited the highest photo-luminescence characteristics under conditions of heat treatment at 780 ℃ for 8 hours
4. The CAB:Eu glass-ceramics produced in this study showed applicability as transparent ceramic materials exhibiting optical properties. However, in order to achieve higher luminous intensity, further growth and luminous studies should be carried out in the future so that only a pure CaF_2 phase can be produced while increasing the PL intensity.

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