Effect of AlN addition on spatial uniform distribution of Er^{3+} -doped CaF_2 nanocrystals in oxyfluoride glass-ceramics

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The morphology and spatial distribution state of CaF_2 nanocrystals in oxyfluoride glass-ceramics based on the ErF_3 – CaF_2 – Al_2O_3 – SiO_2 system with different ErF_3 contents of 1–3 mol % and the addition of AlN were examined from transmission electron microscope (TEM) observations. The content of 3 mol % ErF_3 induced the growth of CaF_2 nanocrystals with star-like morphologies and their assemblies with the size of ~ 70 nm. The addition of a small amount (2 mol %) of AlN has a remarkable effect on the spatial uniform distribution (i.e., disappearance of assembly) of CaF_2 nanocrystals. The present study proposes a new method for the design of composition in rare-earth doped oxyfluoride glass-ceramics.

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1. Introduction

Optically transparent oxyfluoride glass-ceramics containing rare-earth (RE^{3+})-doped fluoride nanocrystals such as Er^{3+} -doped CaF_2 have received much attention for use of optical devices such as laser and phosphor.^{1)–3)} In such materials, RE^{3+} ions are incorporated into fluoride nanocrystals having low phonon energies and consequently excellent photoluminescence (PL) properties of RE^{3+} ions are obtained. Furthermore, host oxide glassy matrices such as Al_2O_3 – SiO_2 having strong glass network structures guarantee mechanical and chemical stability in oxyfluoride glass-ceramics.^{4),5)} Usually, oxyfluoride glass-ceramics are fabricated through well-controlled heat treatments in an electric furnace and desired fluoride nanocrystals are formed in the interior of glasses.

Besides heat treatment condition, the design of glass system and chemical composition is also important for controlling the size and morphology of fluoride nanocrystals in oxyfluoride glass-ceramics. The most well-known and familiar system in oxyfluoride glass-ceramics is CaF_2 (or BaF_2 , SrF_2)– Al_2O_3 – SiO_2 , and the content of CaF_2 is around 15–30 mol %. The doping amount of RE^{3+} ions in oxyfluoride glass-ceramics showing strong PL intensities is usually limited to around 1–2 mol %, because more large RE^{3+} contents induce the so-called concentration quenching. From the point of view of practical device applications, however, a large amount doping of RE^{3+} into fluoride nanocrystals would be desirable, especially for luminescence of Er^{3+} in the infrared region or upconversion laser.^{6),7)} Furthermore, a deep understanding of the morphology and spatial distribution state of fluoride nanocrystals in oxyfluoride glass-ceramics with a large amount of RE^{3+} ions would be also important.^{4),5)} Although it has been reported that the formation behavior of fluoride nanocrystals in oxyfluoride glasses is largely affected by the addition of RE^{3+} ions,^{8)–10)} the morphology of fluoride nanocrystals has not been well understood.

The purpose of this study is to clarify the morphology and spatial distribution state of CaF_2 nanocrystals in oxyfluoride glass-ceramics based on the ErF_3 – CaF_2 – Al_2O_3 – SiO_2 system with different ErF_3 contents of 1–3 mol % from transmission electron microscope (TEM) observations. We found that the addition of a small amount (2 mol %) of AlN has a remarkable effect on the spatial uniform distribution (i.e., disappearance of assembly) of CaF_2 nanocrystals. The present study proposes a new method for the design of composition in rare-earth doped oxyfluoride glass-ceramics.

2. Experimental procedures

Glasses with the nominal compositions of $x\text{ErF}_3$ – $(30-x)$ – CaF_2 – $20\text{Al}_2\text{O}_3$ – 50SiO_2 ($x = 0, 1, 3$) and 2AlN – 3ErF_3 – 27CaF_2 – $19\text{Al}_2\text{O}_3$ – 50SiO_2 (mol %) were prepared using a conventional melt-quenching method. Commercial powders of reagent grade ErF_3 , CaF_2 , AlN, Al_2O_3 , and SiO_2 were used. The batch of 20 g was mixed and melted in a platinum crucible or an aluminum crucible with a cover at 1350°C for 1 h in an electric furnace. The melts were poured onto an iron plate and pressed by another iron plate. The glass transition (T_g) and crystallization peak (T_p) temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min in air. The glasses were annealed at the temperature of $T_g - 30^\circ\text{C}$ for 3 h to release internal stresses. The glasses were heat-treated at 700°C for 3 h in an electric furnace in air. The crystalline phase present in the heat-treated samples was examined by X-ray diffraction (XRD) analyses at room temperature using $\text{CuK}\alpha$ radiation. TEM and scanning transmission electron microscope (STEM) observations in the high angle annular dark-field (HAADF) imaging mode (STEM-HAADF) with an energy dispersive spectrometry (EDS) were conducted for pulverized particles on molybdenum mesh using JEOL JEM-2100F microscope (JEOL, Tokyo, Japan).

3. Results and discussion

All of the samples obtained by a melt-quenching were optically transparent and their amorphous state was confirmed from XRD analyses. The glass with the addition of 2 mol % AlN and

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Fig. 1. XRD patterns at room temperature for the heat-treated (700°C, 3 h) samples in $x\text{ErF}_3-(30-x)\text{CaF}_2-20\text{Al}_2\text{O}_3-50\text{SiO}_2$ ($x=0-3$) and $2\text{AlN}-3\text{ErF}_3-27\text{CaF}_2-19\text{Al}_2\text{O}_3-50\text{SiO}_2$ glasses (mol %). All XRD peaks are assigned to the fluorite-type CaF_2 crystalline phase (ICDD: 035-0816).

3 mol % of ErF_3 keeps a good optical transparency, but some bubbles are present in the inside of the glass. The formation of bubbles suggests that the following reaction is taking place during melting at 1350°C in air:

All the melt-quenched samples showed similar DTA patterns with endothermic peaks due to the glass transition and exothermic peaks due to the crystallization. The glass with no ErF_3 has the values of $T_g = 576^\circ\text{C}$ and $T_p = 647^\circ\text{C}$. Other glasses showed the following values: $T_g = 603^\circ\text{C}$ and $T_p = 701^\circ\text{C}$ for the glass with 1 mol % ErF_3 , $T_g = 600^\circ\text{C}$ and $T_p = 717^\circ\text{C}$ for 3 mol % ErF_3 , and $T_g = 601^\circ\text{C}$ and $T_p = 647^\circ\text{C}$ for 2 mol % AlN. It is found that the crystallization temperature increases slightly with the addition of ErF_3 .

The XRD patterns for the samples obtained by heat-treatments at 700°C for 3 h are shown in Fig. 1. All peaks are assigned to the fluorite-type CaF_2 crystalline phase (ICDD: 00-035-0816). The peak positions of CaF_2 crystal shifted to a lower angle with the addition of ErF_3 , indicating the increase in the lattice constant. This result suggests that Er^{3+} ions are incorporated into Ca^{2+} sites in CaF_2 crystals. In the glass with the addition of 2 mol % AlN and 3 mol % of ErF_3 , the formation of CaF_2 crystals are clearly confirmed, indicating that the small addition of AlN does not depress the crystallization of CaF_2 crystals in aluminosilicate-based oxyfluoride glasses.

The optical photographs for the crystallized samples are also shown in Fig. 1. It is seen that the crystallized glass with no ErF_3 , i.e., $30\text{CaF}_2-20\text{Al}_2\text{O}_3-50\text{SiO}_2$, is colorless, suggesting that nano-scaled CaF_2 crystals are formed. The crystallized glass with 1 mol % ErF_3 still keeps a good optical transparency. The crystallized glass with 3 mol % ErF_3 , however, loses an optical transparency and is becoming a translucent sample. The crystal-

Fig. 2. TEM image (bright field) for the heat-treated (700°C, 3 h) samples in $x\text{ErF}_3-(30-x)\text{CaF}_2-20\text{Al}_2\text{O}_3-50\text{SiO}_2$ ($x=0-3$) and $2\text{AlN}-3\text{ErF}_3-27\text{CaF}_2-19\text{Al}_2\text{O}_3-50\text{SiO}_2$ glasses (mol %).

Fig. 3. STEM-HAADF image for the heat-treated (700°C, 3 h) sample in $3\text{ErF}_3-27\text{CaF}_2-20\text{Al}_2\text{O}_3-50\text{SiO}_2$ glass.

lized glass with the addition of 2 mol % AlN and 3 mol % of ErF_3 keeps a good optical transparency, although some bubbles are still present in the inside of the sample.

The TEM images for the crystallized (700°C, 3 h) samples containing CaF_2 crystals are shown in Fig. 2. The samples with no ErF_3 and 1 mol % ErF_3 show the formation of sphere particles with the size of $\sim 30\text{ nm}$ for no ErF_3 and $\sim 40\text{ nm}$ for 3 mol % ErF_3 and the particles are distributed homogeneously. In the sample with 3 mol % ErF_3 , however, star-like particles with a size of $\sim 50\text{ nm}$ or assembly of particles are formed. The HAADF image for the crystallized (700°C, 3 h) samples with 3 mol % ErF_3 is shown in Fig. 3. Many particles with a size of $\sim 50\text{ nm}$ and with a square morphology are observed, and some of them are assembled. The HAADF image shown in Fig. 3 means that the white color particles contain heavy elements such as Ca and Er. The EDS spectra for a white color particle and a grey color region are shown in Fig. 4. It is seen that elements of Ca, Er, and F are enriched in the white color particle compared with the grey color

Fig. 4. EDS spectra in the crystal (bright) region and glass matrix (dark) region measured by STEM-EDS for the heat-treated (700°C, 3 h) sample in $3\text{ErF}_3\text{-}27\text{CaF}_2\text{-}20\text{Al}_2\text{O}_3\text{-}50\text{SiO}_2$ glass.

region enriching Al, Si, and O. These results indicate that the white color particle is a CaF_2 crystal containing Er^{3+} ions.

The present study indicates the following three features in the crystallization of CaF_2 nanocrystals in a ErF_3 added aluminosilicate-based oxyfluoride glass: 1) the addition of an amount (~ 3 mol %) of ErF_3 induces the increase in the size of CaF_2 crystals and also their assembly, 2) Er elements are incorporated into CaF_2 nanocrystals, 3) the addition of an amount (2 mol %) of AlN depresses the increase in the size of CaF_2 crystals and also their assembly.

Barros et al.⁸⁾ studied the effect of ErF_3 addition on the crystallization behavior of BaF_2 nanocrystals in aluminosilicate-based oxyfluoride glasses and reported that small amount of ErF_3 addition promotes droplet-type phase separations. It has been also suggested that Er^{3+} ions act as nucleating agents in the formation of fluoride nanocrystals in oxyfluoride glasses.⁹⁾ Hu et al.⁸⁾ studied the effect of ErF_3 content on the crystallization behavior of $41.2\text{SiO}_2\text{-}29.4\text{Al}_2\text{O}_3\text{-}17.6\text{Na}_2\text{O}\text{-}11.8\text{LaF}_3\text{-}x\text{ErF}_3$ glasses ($x = 0\text{--}6$) (mol %) and reported that the size of LaF_3 nanocrystals increases with increasing ErF_3 content. These studies^{8)–10)} suggest that the increase in Er^{3+} content in oxyfluoride glasses induces the increase in the size and the assembly of fluoride nanocrystals, and thus the maximum concentration of ErF_3 in oxyfluoride glasses is generally limited to ~ 2 mol % in order to keep a good optical transparency and also to avoid the concentration quenching.

The results obtained in this study, i.e., the addition of an amount (2 mol %) of AlN depresses the increase in the size of CaF_2 crystals and also their assembly. This is a new finding in rare-earth doped oxyfluoride glass-ceramics. At this moment, the amount of nitrogen remained in the oxyfluoride glass prepared in this study is unclear. If all AlN added are converted to Al_2O_3 and N_2 gas followed by the reaction (1), the composition of $2\text{AlN}\text{-}3\text{ErF}_3\text{-}27\text{CaF}_2\text{-}19\text{Al}_2\text{O}_3\text{-}50\text{SiO}_2$ (mol %) corresponds to $3\text{ErF}_3\text{-}27\text{CaF}_2\text{-}20\text{Al}_2\text{O}_3\text{-}50\text{SiO}_2$. That is, the content of Al_2O_3 in both glasses, i.e., the ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$, is the same. It is, however, noted that the glass with 3 mol % ErF_3 has the values of $T_g = 600^\circ\text{C}$ and $T_p = 717^\circ\text{C}$ and the glass with 2 mol % AlN shows the values of $T_g = 601^\circ\text{C}$ and $T_p = 647^\circ\text{C}$. The results, therefore, suggest that the addition of AlN as a source of Al_2O_3 has a

significant effect on the phase separation (e.g., more small size), crystal nucleation (e.g., promotion), or crystals growth (e.g., suppression).

It is recognized that the rigid network structure constructed by Al_2O_3 and SiO_2 has a key role for the formation of fluoride nanocrystals in aluminosilicate-based oxyfluoride glasses. Recently, Raghuwanshi et al.¹¹⁾ studied that the crystallization of the oxyfluoride glass-ceramics having narrow crystallite size distribution with the composition of $69.6\text{SiO}_2\text{-}7.5\text{Al}_2\text{O}_3\text{-}15.0\text{K}_2\text{O}\text{-}1.9\text{Na}_2\text{O}\text{-}6\text{BaF}_2$. They proposed that the BaF_2 nanocrystals having narrow size distribution are formed due to the SiO_2 -enriched high viscosity barrier formed around the BaF_2 nanocrystals and it prevents crystal growth and Ostwald ripening. It indicates that the viscosity around the nanocrystals affects largely for the crystal size. It is required to clarify the coordination state of Al in oxyfluoride glasses prepared by using AlN.

4. Conclusion

The morphology and spatial distribution state of CaF_2 nanocrystals in oxyfluoride glass-ceramics in the system of $x\text{ErF}_3\text{-(}30-x\text{)CaF}_2\text{-}20\text{Al}_2\text{O}_3\text{-}50\text{SiO}_2$ ($x = 0\text{--}3$) and $2\text{AlN}\text{-}3\text{ErF}_3\text{-}27\text{CaF}_2\text{-}19\text{Al}_2\text{O}_3\text{-}50\text{SiO}_2$ (mol %) with different ErF_3 contents of 1–3 mol % and the addition of AlN were examined from TEM and STEM-HAADF observations. The content of 3 mol % ErF_3 induced the growth of CaF_2 nanocrystals with star-like morphologies and their assemblies with the size of ~ 70 nm. The addition of a small amount (2 mol %) of AlN has a remarkable effect on the spatial uniform distribution (i.e., disappearance of assembly) of CaF_2 nanocrystals. The present study proposes a new method for the design of rare-earth doped oxyfluoride glass-ceramics.

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