A Unique Approach to Characterization of Sol-Gel-Derived Rare-Earth-Doped Oxyfluoride Glass-Ceramics

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Using the sol-gel route Nd^{3+} -doped oxyfluoride glass-ceramics were prepared. LiYF₄ and YF₃ crystals were deposited in the glass-ceramics and their size, distribution, and amount ratio were varied by changing the compositions and heating temperatures. The incorporation of Nd^{3+} ions into both the fluoride crystals was confirmed by the high-resolution elemental mapping of the glass-ceramics. The incorporated Nd^{3+} ions showed up and down conversion photoluminescence whose properties were obviously different among the samples. The preliminary site analysis for Nd^{3+} ions was carried out using a unique approach associated with the Prony series approximation. Finally, the approach was found to be useful for the analysis of materials that are structurally complicating.

I. Introduction

T RANSPARENT glass-ceramics are materials containing nano-sized crystals inside amorphous matrices. Among various selections of nanocrystals and matrices, rare-earth ion-doped fluoride nanocrystals dispersed in oxide glass matrices have received attention due to the combined properties of low-phonon energy of fluorides and high chemical resistivity of oxides.^{1,2} In the past decade, the potentials of these materials toward the up-conversion photoluminescence (UC PL)³⁻⁶ and fiber amplification⁷ have been explored.

Since the pioneering work on UC PL of Er^{3+} and Yb^{3+} ions-co-doped oxyfluoride glass-ceramics was carried out,⁸ many researchers have focused on the investigation of PL properties, including UC PL, of rare earth ions-doped in oxyfluoride glass-ceramics.³⁻⁶ The results of researches state that the PL properties can be controlled by changing the local environment of the doped rare earth ions. However, the precise control of the local environment seems not to be achievable in oxyfluoride glass-ceramics. This is because, although the first-neighbor-coordinated atoms (FNCA) for rare earth ions should be fluorine in terms of reducing surrounding phonon energy, a not negligible amount of oxygen is detected as the FNCA using spectroscopic analyses even after prolonged heat treatment.^{7,9,10} Therefore, it is important that obtained rare-earth-doped glass-ceramics are rightly characterized by proper methods.

In this study, a unique approach is applied to reveal characteristics of sol-gel derived Nd³⁺-doped oxyfluoride

glass-ceramics. Various compositions and heating temperatures are selected to obtain glass-ceramics of aimed nanostructures. The distribution of Nd^{3+} ions in the glassceramics is investigated by elemental mappings associated with microscopic images. The UC PL, down conversion (DC) PL and PL lifetime are measured to discuss the local environment of doped Nd^{3+} ions. To analyze PL decay curves, the generalized Maxwell model (Prony series) approximation associated with the differential curve is used for the first time.

II. Experimental Procedure

Tetraethoxysilane (TEOS; Shin-Etsu, Tokyo, Japan), ethanol (EtOH; Wako, Osaka, Japan), H_2O and CH_3COOH (Sigma-Aldrich Japan, Tokyo, Japan) were mixed with a molar ratio for TEOS:EtOH: $H_2O:CH_3COOH$ of 1:10:4:0.5, and stirred for 1 h to obtain a silica source solution. Another mixture of Nd(CH_3COO)₃ (Wako), Y(CH_3COO)₃ (Wako), Li(CH_3COO) (Wako) and CF_3COOH (Wako) with the molar ratio for Nd:Y:Li:F of 1:20–60:20–60:369–729 was added to the silica source solution. The molar ratio for Nd: (Si+Y+Li) was fixed to be 1:200. After an additional stirring for 1 h, the mixed solution was aged at 60°C for 2 h in a sealed container. The gel powder was obtained, and heat treated at 500°C and 600°C to synthesize Nd³⁺-doped oxy-fluoride glass-ceramics. The list of samples used in this study is shown in Table I.

The crystalline phases of the samples were identified using X-ray diffraction (XRD) measurement (Ultima IV; Rigaku, Tokyo, Japan) with CuK α radiation source ($\lambda = 1.5418$ Å). The elemental distributions and microstructures of the samples were observed using an energy-dispersive X-ray detector (EDX, 2300T; JEOL, Tokyo, Japan) equipped with a transmission electron microscope (TEM, JEM-2100F; JEOL). The PL properties were measured under a pulsed 800 nm diode laser (SDL-2362-P1; JDS Uniphase, CA) for UC PL using a monochromator (HR-320; Jobin Yvon, Longjumeau, France) equipped with an optical double chopper and a photomultiplier (R955; Hamamatsu Photonics, Shizuoka, Japan). The DC PL spectra and PL decay curves were measured under a pulsed 355 nm diode laser (FTSS 355-50; CryLaS, Berlin, Germany) using a monochromator (HR-320; Jobin Yvon) equipped with a time-resolved fluorescence system (Insta-SpecTM V & DG535; Oriel Instruments, CA).

III. Results and Discussion

Heat treatment of the dried gels is expected to convert them to fluoride nanocrystals dispersed in an amorphous silica matrix.^{1,2} As seen in Fig. 1(a), 11A showed only a halo pattern at $\sim 23^{\circ}$, which was attributed to the short-range order

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 Table I.
 Names, Molar Ratios, and Heating Temperatures

 (°C) of the Prepared Samples

Sample name	Nd	Li	Y	Si	Heating temperature (°C)
11A	0.5	10	10	79.5	_
115	0.5	10	10	79.5	500
116	0.5	10	10	79.5	600
3L6	0.5	30	10	59.5	600
3Y6	0.5	10	30	59.5	600



Fig. 1. XRD patterns of 11A, 115 and 116 (a), and of 3L6 and 3Y6 (b). The data of JCPDS files of $\rm LiYF_4$, and $\rm YF_3$ are also embedded.

of amorphous silica that was the main component of the sample. On the other hand, peaks of tetragonal LiYF₄ (JCPDS file 17-0874) and orthorhombic YF₃ (JCPDS file 70-1935) expectedly appeared in the XRD patterns of 115 and 116, where the peaks were sharpened by heat treatment at higher temperature, indicating the formation of bigger crystals. Glass-ceramics with various compositions and heating temperatures were also prepared for comparison. Among them, 3L6 showed only the XRD peaks of LiYF₄; the predominant formation of YF₃ was observed in 3Y6 [Fig. 1(b)]. These results showed that crystal-phase-selected oxyfluoride glass-ceramics were successfully prepared by choosing the specific compositions and heating temperatures. The crystal structures of obtained LiYF₄ and YF₃ were drawn using VESTA and are shown in Fig. 2 for reference.¹¹ In the fluoride crystals, Nd³⁺ ions, the ionic radii (IR) of

In the fluoride crystals, Nd^{3+} ions, the ionic radii (IR) of which for coordination numbers (CN) of 8 and 9 are 110.9 and 116.3 pm, respectively, would substitute for Y^{3+} ions, the IR of which for CN 8 (LiYF₄) and 9 (YF₃) are 101.9 and 107.5 pm, respectively, due to the similarity of their ionic radii (see Fig. 2 for checking the Y^{3+} sites visually).^{12–14}



Fig. 2. Crystal structures of tetragonal $LiYF_4$ (a) and orthorhombic YF_3 (b) drawn using VESTA.

To confirm if the substitution occurs, the distributions of the fluoride crystals and Nd³⁺ ions in the glass-ceramics were investigated. Fig. 3 shows the bright field (BF) TEM images and the corresponding EDX mappings (for Si, Y, and Nd elements) of 115 (a), 3L6 (b), and 3Y6 (c). From this figure, it was found that the dark regions in the BF TEM images contained higher concentration of Y, where the amount of Si in the regions was low. This result revealed that the dark regions in the BF TEM images signified the deposited fluoride crystals. The BF TEM image and Y-element mapping of 115 clearly showed that the fluoride crystals with a diameter of less than 10 nm were predominantly formed. On the other hand, fluoride crystals of 10-100 nm were obtained in 3L6 and 3Y6. These results are consistent with the XRD patterns of Fig. 1, where sharper and stronger peaks appeared in the patterns of 3L6 and 3Y6 than 115. The size of fluoride crystals in each sample was roughly the same. This is because the mobility of atoms is restricted when fluoride crystals form in the amorphous SiO₂ matrix. Regarding the distribution of Nd³⁺ ions, the concentration of Nd was obviously high where the fluoride crystals were located, even though the contrast in Nd mapping was weak due to the small amount of Nd element. This tendency that Nd is incorporated into the fluoride crystals was equally observed in all the samples. As only quite small crystals, LiYF₄, and a large quantity of YF₃ formed in 115, 3L6, and 3Y6, respectively, it can be said that Nd³⁺ ions are preferentially located in the sites of Y³⁺ ions in the fluoride crystals regardless of the crystal sizes and phases. An area analysis of EDX was further performed to investigate the detailed distribution state of Nd³⁺ ions in 3L6 and 115 (Fig. 4). The areas 1 and 2 are the dark and bright regions in the BF TEM image of 3L6. The relative amounts of F, Y, and Nd in the area 1 were apparently larger than those in the area 2. In contrast, the amounts of Si and O in the area 1 were smaller than those in the area 2. A similar tendency was observed in the results of 115, where areas 3 and 4 were the dark and bright regions, respectively. The differences in the elemental amounts between areas 3 and 4, however, were relatively small because the size of fluoride crystals dispersed in the glass was too small to separately obtain the EDX signals from dark and bright regions. On the other hand, unexpectedly large amounts of F and Y were also detected from area 2, which contained no detectable fluoride crystals (this amorphousness in area 2 was confirmed by high-resolution TEM and selected-area electron diffraction). The results suggest that the small, but observable amounts of F, Y, and probably Nd remain in the glass region, although these elements basically gather and form fluoride crystals in the sample. The remaining Nd in the glass region would affect the optical properties of the prepared glass-ceramics, and this is described in detail later.

Due to the unique UC function of Nd³⁺ ions, the characterization of UC PL of the samples is important. The UC PL spectra of the samples excited using an 800 nm diode laser Journal of the American Ceramic Society—Kawamura et al.



Fig. 3. Bright field TEM images (BF) and elemental mappings for Si, Y, and Nd of 115 (a), 3L6 (b), and 3Y6 (c).



Fig. 4. Bright field TEM images of 3L6 and 115, and the corresponding EDX spectra at the squared regions shown in the TEM images. The EDX probe diameter was 1 nm.

are shown in Fig. 5. 11A which contained no fluoride crystals showed no UC PL peak, whereas all the other samples exhibited distinct UC PL peaks at ~ 525, 590, and 660 nm. The appearance of these peaks in the samples heat-treated indicates that the formation of fluoride crystals and incorporation of Nd³⁺ ions into them are indispensable for the UC PL. Furthermore, each spectrum showed a different shape from the others. The shape of PL spectrum is known to strongly depend on the surrounding conditions of Nd³⁺ ions, i.e., the crystal field, ligand positions, covalence, etc. The UC PL peaks are, for example, broadened when the inhomogeneous width is widened by the effects of disordered amorphous matrix or defects on the crystal surfaces. These kinds of effects in 115 must be the strongest in the samples because the observable amount of Nd^{3+} ions is located outside or near the surface of the crystals due to the fluoride crystals of small size. Similar spectra were seen in the UC PL of 116 and 3L6. This is because LiYF₄ is the main phase of fluoride crystal in these samples, thus the Nd^{3+} ions are presumably located in the same site. On the other hand, a unique spectrum was observed in 3Y6 in which YF₃ was the main phase of fluoride crystal and thus the site of Nd^{3+} ions must be different to those in 116 and 3L6.

The DC PL spectra of the samples excited using 355 nm diode laser are shown in Fig. 6. It was unveiled that they were in different shapes among the samples. This is due to the same reason as the UC PL spectra, where the sites of Nd^{3+} ions were different among the samples. The site analysis



Fig. 5. UC PL spectra of samples.



Fig. 6. DC PL spectra of samples.

for doped rare earth ions is normally carried out using the Judd-Ofelt theory,^{15–17} fluorescent line narrowing spectra,¹⁸ and the Rietveld analysis,^{19,20} and each method is very useful, but chooses its own materials. In this study, a unique method different from these conventional ones was employed to preliminarily analyze the sites for Nd³⁺ ions. The method can be applied to any material systems and facilitate comparison of the PL lifetimes among the samples. Fig. 7(a) shows the DC PL decay curves (monitored at 384 nm) and their fitting curves drawn using the Prony series approximation. The used equation (Eq.) of Prony series is as follows,

$$\mathbf{R}(t) = \mathbf{E}_0 = \Sigma_{i=1}^{N} \mathbf{E}_i \exp\left(\frac{-t}{\tau_i}\right) \tag{1}$$

where, R(t) is the relaxation function, t is the time, and E_0 , E_i , and τ_i are constants (but $0 \le \tau_i \le 7$). Equation (1) is generally used for the representation of the relaxation function of viscoelasticity of materials,^{21,22} and the similar Eq. is sometimes applied to the analysis of PL decay.²³ The equation is simplified and it makes a precise site analysis for rare earth ions possible, when the effects of multiphonon relaxation and clustering of the ions on the PL can be ignored.²³ However, the PL of the glass-ceramics prepared in this study must be influenced by such effects. Thus, the lifetime decay curves of Nd³⁺ ions in our samples were fitted by Eq. (1) using N = 4 without any simplification [Fig. 7(a)]. The number of N has no special meaning here, hence the number, 4 which was appropriate to fit the experimental data was used. The differential curves of R(t) are shown in Fig. 7(b). With the differential, R(t) becomes the amount of relaxed component at the time, i.e., in our case, R(t) represents the amount of radiated Nd³⁺ ions at the moment. The vertical axis of Fig. 7(b) was normalized to compare the amount ratio of



Fig. 7. Experimental and fitted PL decay curves of samples (a). The fitted curves are drawn using Prony series approximation. (b) is the corresponding differential curves of the fitted PL decay shown in panel A.

radiated Nd³⁺ ions at the moment among the samples. The peak positions of 115, 3Y6, and 3L6 were 0.30, 0.37, and 0.55 µs, respectively. The result means that the majority of Nd^{3+} ions in 115, and 3L6 emit at the earliest and latest moments in the samples, respectively. Besides, a relatively large amount of ${\rm Nd}^{3+}$ ions in 115 was emitted at the time later than 2 µs compared with the other samples. These results suggest that the lifetime of Nd³⁺ ions in 115 is basically shortened due to the effects of defects on crystal surface and amorphous silica matrix, which can be the electron trap centers and stimulate the nonradiative transitions by the high phonon energy, respectively. Such effects in 115 should be the strongest in the samples because the size of fluoride crystals is a single nanometer range. On the other hand, as the phases of $LiYF_4$, YF_3 , and amorphous silica are intricate in 115, the sites of Nd³⁺ ions should be diverse, leading to the wide distribution of the lifetime of Nd³⁺ ions even longer than 2 µs. The longer lifetime of 3L6 than 3Y6 suggests that Nd³⁺ ions should be incorporated into not YF₃ but LiYF₄ for prolonging the PL emission. These results and discussion reveal that the application of the Prony series approximation to the lifetime decay curve and the following differential is quite useful, and it makes the preliminary site analysis for Nd³⁺ ions possible. Moreover, because the application of this approach is not limited for the kind of rare earth ion and/or matrix and the degree of crystallization, it is worth using for the analysis of the complicating systems like sol-gel derived glass-ceramics used in this study.

IV. Conclusion

In the prepared sol-gel-derived oxyfluoride glass-ceramics, Nd^{3+} ions were located only in the fluoride crystals dispersed in the amorphous silica matrix. The predominant incorporation of Nd^{3+} ions into fluoride crystals seemed to greatly enhance UC PL intensity. The unique approach using Prony series approximation and the differential to analyze the lifetime of Nd^{3+} ions in the oxyfluoride glass-ceramics was

performed for the first time. The approach revealed that 115 consisting of complicating nanometric fluoride crystal mixture and amorphous silica possessed many Nd3+ ions radiating quicker than those in the other glass-ceramics. On the other hand, some of Nd³⁺ ions in 115 radiated very slowly, indicating that the sites of Nd³⁺ ions were diverse in the complex structure. This approach seemed to be appropriate to use for materials with complicating structures because it requires no special conditions, whereas the conventional approaches require some.

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