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Rare earth doped silicate-oxyfluoride glass ceramics incorporating LaF_3 nano-crystals for UV-LED color conversion

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ABSTRACT

Rare earth doped oxyfluoride glass ceramics with LaF_3 nano-crystals formed inside were fabricated for color converter of UV-LED. Among various rare earth ions, Dy^{3+} and Eu^{3+} showed practically utilizable visible emissions under UV-LED excitation of 365 nm. The visible emission has been improved by the formation of LaF_3 brought by heat treatment. X-ray diffraction and transmission electron microscopy along with its energy dispersive spectra confirmed the formation of LaF_3 nano-crystals. Compositional dependence and the effects of heat treatment conditions on the visible emissions have been investigated. The CIE chromaticity coordinates of the glasses were also examined for Dy^{3+} singly doped and co-doped samples. The effect of LaF_3 nano-crystals and co-dopants on the visible emission properties of Dy^{3+} was discussed.

1. Introduction

Oxyfluoride glass consists of oxide and fluoride components, and can be controlled to have nano-sized fluoride crystals inside via heat treatment. Rare earth (RE) doped oxyfluoride glass–ceramics (GC) are quite attractive for photonics applications since these host materials can provide the doped RE ions to feel low phonon energy environments of fluoride components compared to other oxide glasses, and at the same time the oxide components largely preserve the enhanced chemical and mechanical stability of oxide glasses. Reduced local phonon energy can improve quantum efficiency of the doped RE ions, thus enhancing emission properties. This characteristic contribution of quantum efficiency enhancement as a result of the formation of fluoride nano-crystals (NCs) has been recently exemplified from the remarkable improvement of mid-IR emission out of Dy^{3+}-doped oxyfluoride glasses via the formation of β-PbF_2 NCs [1]. Changes in visible and near IR emissions have also been observed from the same glasses with β-PbF_2 NCs [2–4]. In addition, other applications such as optical waveguide [5] and magnetic field detection [6] have been proposed based on NCs formed in oxyfluoride GCs.

NCs other than PbF_2 such as CaF_2 [7,8], BaF_2 [9,10] and LaF_3 [11–13] have been widely studied recently and also showed high potential for photonic applications. Among various potential applications for which they would be available, there is inorganic color converter for white LED that is likely to replace the conventional phosphor materials embedded within silicone resins which suffers from long-term stability problems [14]. Both BaF_2 and LaF_3 GCs doped with Dy^{3+}, Eu^{2+} or Ce^{3+} have been investigated [10,12,13] to study their luminescence characteristics. However, most of the studies used either intense laser sources or excitation wavelengths in the UV region at which high-power LED is hardly available commercially. Moreover, systematic study on the effects of NCs for visible emissions has not been properly addressed. Based on these considerations, in this study, we prepared oxyfluoride glasses doped with different kinds of REs, and observed their visible emissions when pumped with 365 nm commercial high power LED source. RE ions have been searched for their use in the 365 nm UV-LED color conversion, and the effects of LaF_3 NC formation as well as co-dopant on the visible emission spectra were also investigated.

2. Experimental

The parent oxyfluoride glass has compositions of $45SiO_2$–$15Na_2O$–$25Al_2O_3$–$15LaF_3$ in mol% to which 3 mol% of REF_3 (RE = Ce, Pr, Eu, Dy, Ho, Er or Tm) is additionally introduced. Highly pure (>99.99%) raw materials were weighed and mixed thoroughly. Glasses were prepared following the conventional melt-quenching route at 1450 °C for 1 h under ambient atmosphere. Glasses thus

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obtained were all annealed at 400 °C for 2 h to eliminate thermal stress. Heat treatment at various temperatures and durations was subsequently performed to invoke formation of NCs. An X-ray diffractometer (XRD; Rigaku, D/MAX-2500U) and a field-emission transmission electron microscope (FE-TEM; JEOL, JEM-2100F) were used to observe the formation of NCs within oxyfluoride glasses. A UV-LED peaking its emission intensity at around 365 nm (Thorlabs, M365L2) was served as the pump source for optical excitation of the glasses and GCs. Emission spectra have been collected by using 0.25 m monochromator (Thermo Oriel, MS257) equipped with lock-in amplifier (Thermo Oriel, Merlin™) and detected with a photomultiplier tube. Note that a 475 nm cut-off filter has been applied in order to completely eliminate the unnecessary photons coming from the UV-LED source.

3. Results and discussions

In an effort to properly specify activator RE ion(s) suitable for the 365 nm UV-LED excitation source, various RE ions such as Ce^{3+}, Pr^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} were examined after they were all incorporated into the oxyfluoride glasses. As shown in Fig. 1, when excited with 365 nm LED, a noticeable emission has been observed from Eu^{3+} and Dy^{3+} ions due to their characteristic 4f-4f transitions. Little emission, however, has been monitored from other RE ions. Almost no emission could be expected from Ce^{3+} and Pr^{3+} ions as they have no practical absorption bands near the excitation wavelength. Ho^{3+} has absorption in fluoride glasses [15], but has very narrow energy gap to the lower-lying energy states which resulted in no apparent emissions due to prevailing non-radiative transitions. Tm^{3+} also has an absorption band near 365 nm corresponding to $^3H_6 \rightarrow {}^1D_2$ transition but showed little emission. Relatively low absorption coefficient of $^1D_2$ and small branching ratio [15] to the $^1G_4$ state which gives the visible emission are believed to be responsible for the result. Er^{3+} ion has strong absorption from $^2G_{9/2}$ and $^2G_{11/2}$ states near 365 nm but showed not strong green emission, which is most likely due to non-radiative transitions such as multi-phonon relaxation or cross relaxation in addition to the small population feeding to the $^4S_{3/2}$ state. Although the absorption coefficient of Dy^{3+} and Eu^{3+} ions near 365 nm is small compared to Er^{3+}-ion [15], Both of them have energy states which give visible emissions with high radiative transition rates owing to large energy gap to the lower-lying energy states such as Dy^{3+}: $^4F_{9/2}$ and Eu^{3+}: $^5D_0$. Moreover, Dy^{3+} produces the characteristic blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and orange ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions, while Eu^{3+} gives red ($^5D_0 \rightarrow {}^7F_{1,2}$) which can effectively be used for LED color conversion. We, thus concentrate upon Dy^{3+} and Eu^{3+} doped oxyfluoride glasses for further investigations in this study.

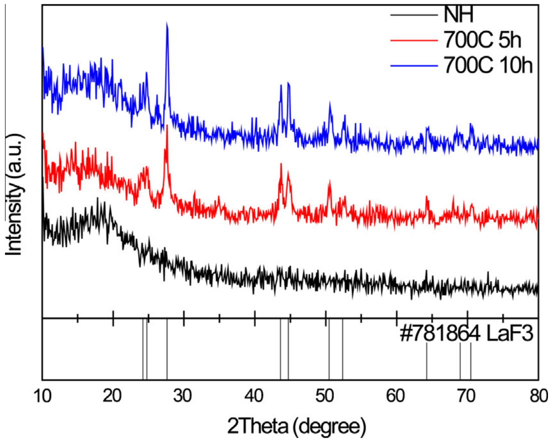

Fig. 1. XRD patterns of oxyfluoride glass ceramics for different duration times of heat treatment performed at 700 °C.

As was reported previously [1], formation of fluoride NCs that are able to effectively surround RE ions and change the local phonon energy, thus enhancing quantum efficiency and corresponding emission intensity. In this study, LaF_3 NCs incorporating RE ions inside have been considered as the material of choice that we want to form with the present glass system. In Fig. 2, XRD patterns obtained from the oxyfluoride glasses heat treated at 700 °C are displayed as a function of varying heat treatment time. Diffuse characteristic patterns of the precursor glass can be found before the heat treatment, and diffraction peaks corresponding to the LaF_3 crystalline phase have been observed after the heat treatment, of which intensity is increased as the heat treatment time increases. This suggests the successful formation of LaF_3 crystals within the glass matrix of which morphology has further been examined via FE-TEM. Fig. 3 exhibits the FE-TEM images of the heat treated oxyfluoride GCs by which the formation of nano-sized LaF_3 crystals are visualized more clearly. The LaF_3 NC was estimated to be ~10 nm in size and agglomerated in the form of clusters in the case of a sample heat treated at 700 °C for 5 h. The agglomeration turned to be kept, eventually resulting in size of ~100 nm when the duration time increased up to 10 h. The compositions of the NCs examined by using energy dispersive analysis (EDS) were confirmed to be LaF_3 NCs as shown in Fig. 3b.

Changes of the RE emission spectra accompanying with the advent of the NCs have been studied with Dy^{3+}-doped oxyfluoride GCs. When heat treatment temperature was allowed to vary but duration time and Dy^{3+} concentration fixed to be 5 h and 3 mol%, respectively, the emission intensity increased as heat treatment temperature increased up to 675 °C which started to decrease for further increase of temperature (Fig. 4a). It was recently found that RE ions are preferentially located within fluoride NCs actually being agglomerated [16]. It is also known that the concentration quenching increases as the inter-ionic distance between RE ions decreases also reducing the emission intensity [17]. Thus, a proper compromise should be made in consideration of the local phonon energy and the distance between RE ions when fluoride NCs form and surround RE ions. As shown in Fig. 4a, formation of LaF_3 brought the improved visible emission intensity of Dy^{3+} via local environment change, whereas further growth of NCs induced by heat treatment at beyond 675 °C reduced emission intensity due to concentration quenching of Dy^{3+}-ions that were presumed to be effective agglomeration within LaF_3 NCs. Thus, in the present system, it seems reasonable to choose 675 °C as the optimal heat treatment temperature. The concentration of RE-ions can also affect the emission intensity by way of varying number of activators and distance between RE-ions. Fig. 4b displays the changes of visible emission intensity, plotted as a function of Dy^{3+} concentration, for oxyfluoride GCs heat-treated at 675 °C for 5 h. As can be seen from the emission spectra, a maximum intensity of the visible emission appears at 3 mol% of Dy^{3+}. Increased clustering of Dy^{3+}-ions beyond 3 mol% may be responsible for the decrease of the emission intensity.

As Dy^{3+} can emit blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$), orange ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and red ($^4F_{9/2} \rightarrow {}^6H_{11/2}$) emissions when excited to its $^4F_{9/2}$ state, the white color conversion can be realized by careful adjustment of these emissions. Babu et al. observed white emission from Dy^{3+}-singly doped PbF_2 NC embedded in oxyfluoride GCs [4]. White light emission from Dy^{3+} also could be achieved via co-doping with Ce^{3+}-ions in oxyfluoride GCs [12], or Eu^{2+} co-doped borosilicate glasses [18]. In order to control the color coordinate of the present system, we co-doped Eu^{3+}-ions with varying Dy^{3+}:Eu^{3+} concentration at 1:2 and 2:1 (in mol%). As shown in Fig. 5a and b, red emission centered at 615 nm due to Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$ transition has appeared and increased as Eu^{3+} concentration increased.