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Visible spectroscopic properties of SiO_2–Na_2O–Al_2O_3–LaF_3 glass ceramics doped with Dy^{3+} and Ho^{3+} under blue LED excitation

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ABSTRACT

SiO_2–Na_2O–Al_2O_3–LaF_3 glasses were doped with various rare earth ions to find the proper active ions for blue LED (λ = 455 nm) color conversion. Based on photo-luminescence (PL) spectra, a combination of Dy^{3+} and Ho^{3+} was selected and their visible spectroscopic properties were investigated for possible candidate of white color conversion of a blue LED. Concentrations of Dy^{3+} and Ho^{3+} were varied to find the proper combination, and 2 mol% DyF_3 and 1 mol% HoF_3 co-doped glass showed reasonable visible emissions. When the glasses were heat treated, emission intensities from both ions were clearly increased by the formation of LaF_3 nano-crystals, which were identified by X-ray diffraction and TEM analyses. Emission peak at ~525 nm newly appeared due to nano-crystal formation and the related local phonon energy change nearby Dy^{3+} ion. Energy transfer between Dy^{3+} and Ho^{3+} was also observed and discussed. Photo-luminescence excitation (PLE) spectra were measured and also discussed.

1. Introduction

Inorganic color converters can overcome the poor chemical and thermal stability of the organic resins used for conventional white LEDs (WLEDs), provide highly reliable and high powered WLEDs, and thus have been recently studied and applied [1–4]. Glasses containing active elements such as rare earth (RE) and transition metal ions can also be reasonable candidates for inorganic color converters since they can be easily fabricated in various shapes without additional processes to make phosphor ceramic plates [1,2] or to embed ceramic phosphors [3,4]. For example, Rocha et al. [5] reported visible emissions from $Eu^{2+,3+}$ and Ce^{3+} doped alumino-silicate glasses under 405 nm excitation and showed their potential as inorganic color converters. However, the relatively high phonon energy of oxide glasses restricts the quantum efficiency of the doped RE ions as well as their actual feasibility. Oxyfluoride glasses are composed of oxides and fluorides and contain fluoride nano-crystals within the glass matrix when they are properly heat treated. This makes the high quantum efficiency of the doped RE ions possible and provides high chemical and thermal stability at the same time, prompting extensive studies of RE-doped oxyfluoride glasses [6–13].

White emission was reported out of oxyfluoride glass with LaF_3 nano-crystals [7] when it was co-doped with Dy^{3+} and Ce^{3+} ions. However, the excitation wavelength was 320 nm, a wavelength at which practical application is hard to achieve, due to the lack of commercial high power LEDs. Dy^{3+} and Eu^{3+} co-doped oxyfluoride glasses with LaF_3 nano-crystals were also suggested for 365 nm LED color conversion [8] but white emission has not been achieved. For the color conversion of 450 nm, which is the commercially used wavelength for WLEDs, Babu et al. [6] suggested Dy^{3+}-doped oxyfluoride glasses and showed white emission, but they used PbF_2 nano-crystals, which cannot be used commercially for environmental reasons. It should be noted that most of the previous reports on oxyfluoride glasses for color conversion used inappropriate excitation sources such as UV wavelengths or lasers, restricting their practical feasibility.

In this study, we synthesized Dy^{3+} and Ho^{3+} co-doped oxyfluoride glass ceramics with LaF_3 nano-crystals and investigated their visible spectroscopic properties under blue LED excitation for possible white color converter. Visible emissions out of Dy^{3+} and Ho^{3+} ions were adjusted by varying the content of the rare earth ions and heat treatment conditions. The effect of nano-crystal formation on the PL spectra and energy transfer between rare earth ions was also observed and discussed.

2. Experimental

$45SiO_2$–$15Na_2O$–$15Al_2O_3$–$25LaF_3$ in mol% was used for the nominal composition of the glasses; this was modified from the previous studies [8,12,13]. Various RE fluorides (REF_3; RE = Eu, Dy, Ho, Er, Pr or Tm) were additionally doped to find the proper color converting ions under 450 nm excitation. Raw materials with high purity (>99.99%) were weighed and thoroughly mixed. Glasses were melted at 1450 °C

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for 1 h under ambient atmosphere using an alumina crucible and quenched on a brass mold followed by annealing at 400 °C for 2 h. Heat treatment was performed to induce LaF_3 nano-crystal formation within the glass matrix, varying the duration time at 750 °C. X-ray diffractometer (XRD; Rigaku, D/MAX-2500U) and a field-emission transmission electron microscope (FE-TEM; JEOL, JEM-2100F) examined the formation of nano-crystals. Glasses and glass ceramics were pumped with a 455 nm blue LED source (Thorlabs, M405L2) to obtain PL spectra which were recorded by a 0.25 m monochromator (Thermo Oriel, MS257), a lock-in amplifier (Thermo Oriel, Merlin™) and a photomultiplier tube. A blue-LED chip with 3528 package (λ_{center} ~ 450 nm) was used to mount the glass and glass ceramics and to examine their practical feasibility.

3. Results and discussions

In order to find the proper RE-ions to give visible emissions under blue LED excitation, various rare earth ions such as Dy^{3+}, Er^{3+}, Eu^{3+}, Eu^{2+}, Ho^{3+}, Pr^{3+} and Tm^{3+} were inspected by fabricating oxyfluoride glasses doped with 3 mol% of REF_3. When glasses were excited by 455 nm LED source and a cut-off filter at 475 nm was applied, as shown in Fig. 1, the Dy^{3+} and Ho^{3+}-doped glasses presented noticeable emissions compared to other RE-ions. Dy^{3+} showed strong blue (~487 nm) and orange (~576 nm) emissions out of $^4F_{9/2}$ state while Ho^{3+} gave green (~550 nm) emission out of ($^5S_2$, $^5F_4$) state as illustrated in Fig. 2. The absorption bands of Dy^{3+}:$^4I_{15/2}$ and Ho^{3+}:$^5F_1$ located near 455 nm are responsible for the emission spectra [14]. Eu^{3+} and other RE ions also showed some visible emissions but their intensities were relatively very weak, mostly due to their weak absorption bands near 455 nm and non-radiative transitions. Pr^{3+} showed blue emission thanks to its absorption bands of ($^1I_6$, $^3P_1$) states. However, in order to adjust the chromaticity of the converted lights under a blue excitation source, Dy^{3+} and Ho^{3+} were selected and used to co-dope the oxyfluoride glass for further study.

The concentrations of Dy^{3+} and Ho^{3+} in the co-doped oxyfluoride glasses were varied to control the visible emission spectra, which were monitored under blue LED excitation with a 475 nm cut-off filter, and are represented in Fig. 2. Combination of blue, green, orange and red emissions out of Dy^{3+} and Ho^{3+}-ions could be achieved. It is interesting to find that the strong orange emission due to Dy^{3+}:$^4F_{9/2} \rightarrow {}^6H_{13/2}$ was significantly reduced while green emission due to Ho^{3+}:($^5S_2$, $^5F_4$) → $^5I_8$ increased as Ho^{3+} content was increased at the expense of Dy^{3+} concentration. Considering the excited energy states of Dy^{3+} and Ho^{3+} ions, which are closely located, the spectral

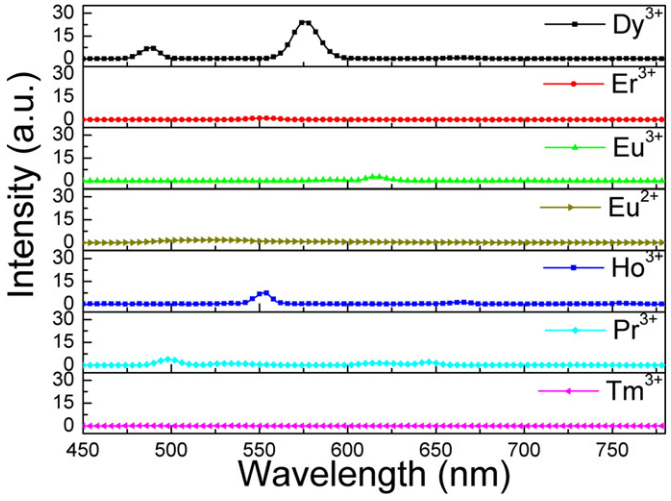

Fig. 1. Emission spectra of RE-doped oxyfluoride glasses (RE = Dy^{3+}, Er^{3+}, Eu^{3+}, Eu^{2+}, Ho^{3+}, Pr^{3+} and Tm^{3+}) pumped by 455 nm LED with 475 nm cut-off filter.

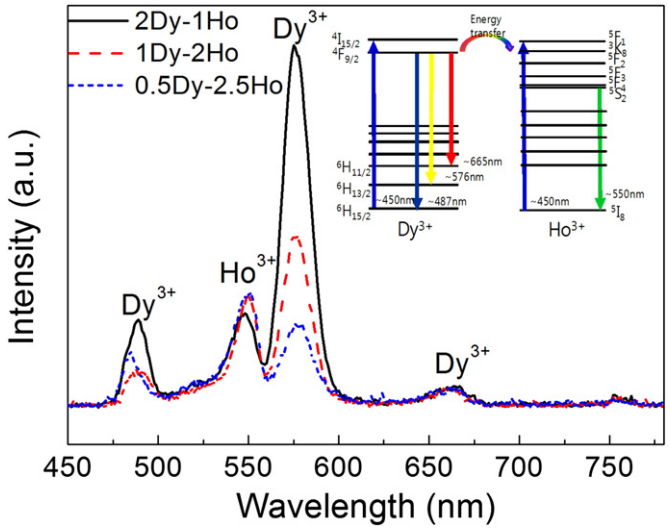

Fig. 2. Emission spectra of oxyfluoride glasses co-doped with DyF_3 and HoF_3 varying their concentration as 2 mol% DyF_3/1 mol% HoF_3, 1 mol% DyF_3/2 mol% HoF_3 and 0.5 mol% DyF_3/2.5 mol% HoF_3 when excited by 455 nm LED with 475 nm cut-off filter. The inset figure illustrates the schematic energy diagram and transitions of rare earth ions.

change upon RE concentration seems mostly due to the efficient energy transfer from Dy^{3+}:$^4F_{9/2}$ to Ho^{3+} states as depicted in the inset figure. Such effective energy transfer can reduce the emission intensity of Dy^{3+} and thus restrict the conversion efficiency. The weak development of the green emission from Ho^{3+} ion compared to the remarkable decrease of the Dy^{3+} orange emission suggests the contribution of non-radiative transitions within Ho^{3+} ions which can further restrict the conversion efficiency.

Enhancement of the emission intensity due to fluoride nano-crystal formation within the glass matrix was investigated by heat treatment. A glass with 2 mol% of DyF_3 and 1 mol% of HoF_3 which showed a reasonable combination of visible emissions was heat treated at 750 °C for varying time durations. As shown in Fig. 3, all of the emission intensities were considerably improved when the glass was heat-treated for 20 h, and decreased when it was heat-treated for 40 h.

Using electron energy loss spectroscopy (EELS), Liu et al. [15] clearly showed the preferential incorporation of RE ions when PbF_2 nano-

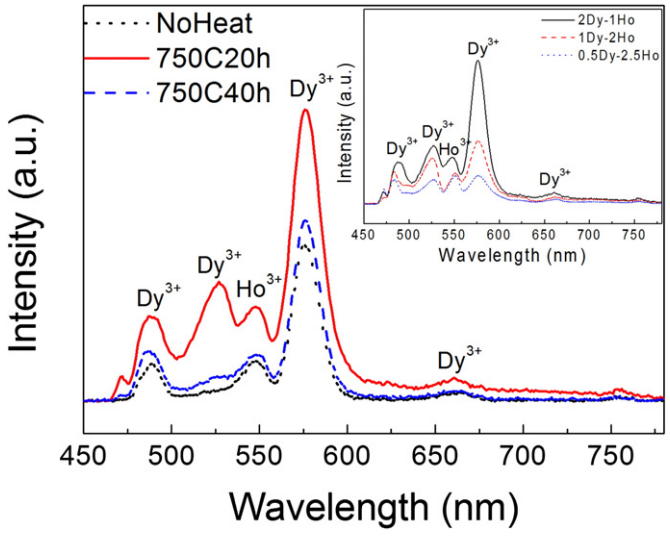

Fig. 3. Emission spectra of oxyfluoride glasses co-doped with 2 mol% DyF_3 and 1 mol% HoF_3 before (no heat) and after heat treatment at 750 °C for 20 and 40 h, respectively. The inset figure shows the emission spectra of the glasses for varying RE contents when they were heat treated at 750 °C for 20 h.