Green Color Purity Control of Dual-Excitation Upconversion Display by Using Polymer/ $\text{NaYF}_4\text{:Er}^{3+}$ Crystal Transparent Composite

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Invisible near-infrared (NIR) to visible (VIS) upconversion (UC) emission of rare-earth doped ceramics is receiving much attention for transparent display applications. In this study, a new dual-wavelength (DW) NIR excitation scheme for the VIS-UC emission of Er^{3+} doped NaYF_4 ($\text{NaYF}_4\text{:Er}^{3+}$) was proposed to achieve a high green color purity and was applied to non-projection-type transparent displays. For the optimization of green color purity, various rare-earth ions (RE^{3+}) were co-doped into $\text{NaYF}_4\text{:Er}^{3+}$ ($\text{NaYF}_4\text{:Er}^{3+}, \text{RE}^{3+}$). Among those, NaYF_4 co-doped with Er^{3+} and Ce^{3+} ($\text{NaYF}_4\text{:Er}^{3+}, \text{Ce}^{3+}$) showed the highest green color purity under DW-NIR excitation. Furthermore, the excitation wavelengths of DW-UC were also investigated. Moreover, a $\text{NaYF}_4\text{:Er}^{3+}, \text{Ce}^{3+}$ embedded transparent and flexible polymer composite was prepared, which emitted a strong “point emission” at the cross point of the DW-NIR excitation lights that were introduced from the side surface of the composite sheet. Therefore, the obtained polymer/ $\text{NaYF}_4\text{:Er}^{3+}, \text{Ce}^{3+}$ composite is an attractive candidate material for non-projection-type transparent and flexible displays.

Keywords: Upconversion, Rare-earth, Transparent display, Dual-wavelength Excitation, Near-infrared

1. Introduction

Rare-earth ion-doped ceramics are known to show upconversion (UC) luminescence (UCL) in the visible (VIS) wavelength region under invisible near-infrared (NIR) excitations [1]. The UCL materials have attracted attention for various applications such as solid-state lasers [2], solar cells [3], and biophotonics [4-6]. Additionally, many researchers have reported the application of UCL materials for transparent and/or flexible displays [7-9]. In these studies, the UCL crystals were embedded in transparent matrices and emitted VIS-UCL under invisible-NIR excitation, and could thus be used as projection-type transparent displays. Our group also reported a projection-type flexible and transparent UCL display based on

erbium (Er^{3+}) and ytterbium (Yb^{3+}) doped yttrium fluoride crystals and a transparent polymer film [10]. However, most of these projection-type displays require high-power laser exposure on the external surface, in open space, for excitation. Thus, their practical usage is hindered due to the safety issues related to the strong laser exposure on the external surface of the displays.

To address this, recently, our group has developed a non-projection-type transparent UCL display using dual-wavelength UCL (DW-UCL) [11]. In DW-UCL, excitation is carried out by two different NIR sources (excitation light 1: Ex.1 and excitation light 2: Ex.2). The DW-UCL display can show “point emission” at the cross point of two invisible

NIR excitation light beams by introducing the beams from the side surface of the display (Fig. 1). Therefore, a DW-UCL display can show a “point sign” without the exposure of an excitation light on the external surface of the display, and is thus much safer than the projection-type UCL display. One of the most commonly used rare-earth doped ceramics, Er^{3+} doped NaYF_4 ($\text{NaYF}_4:\text{Er}^{3+}$), is known to show green (550 nm) emission under DW-NIR (Ex.1: 1550 nm and Ex.2: 850 nm) excitation [12,13], and is thus one of the promising candidate materials for DW-UCL display for green sign. However, $\text{NaYF}_4:\text{Er}^{3+}$ also emits single-wavelength UCL (SW-UCL: 660 nm) under a single NIR light (1550 nm) excitation. Therefore, the “line emission” of red (660 nm) emission under a single 1550 nm excitation can be observed by naked eyes. Additionally, red (660 nm) emission causes the degradation of green color purity of the displays.

To solve this problem, NaYF_4 co-doped with Er^{3+} and various rare-earth ions were synthesized and evaluated for an optimum monochromatic UC green emission in this study. The rare-earth doped ceramics emitted UCL through multistep excitation of the electrons of the rare-earth ions, supported by the energy transfer (ET) processes among the rare earth ions. Due to the ET processes, the UCL is strongly dependent on the rare-earth ion concentrations [14]. Previous studies reported that the UCL process and its wavelength for $\text{NaYF}_4:\text{Er}^{3+}$ can be controlled by co-doping with different rare-earth ions such as cerium (Ce^{3+}) or praseodymium (Pr^{3+}) [15,16]. Therefore, rare-earth ions such as Ce^{3+} , Pr^{3+} , neodymium (Nd^{3+}), and holmium (Ho^{3+}) were co-doped into the $\text{NaYF}_4:\text{Er}^{3+}$ NPs for improving the color purity of the UC green emission.

Furthermore, recently, H. Xia *et al.* reported that the DW-UCL wavelength and the emission intensity of $\text{NaYF}_4:\text{Er}^{3+}$ can be effectively changed by changing the excitation wavelengths of the two excitation lights [17]. Therefore, optimization of two excitation wavelengths of the rare-earth ion co-doped NaYF_4 samples is required for ideal DW-UCL for bright displays. Thus, in this study, the excitation wavelengths of DW-UCL were also investigated under a combination of two NIR excitation sources, ranging from 1470-1500

nm as Ex.1 and 790-860 nm as Ex. 2. Additionally, as a proof of concept, rare-earth co-doped NaYF_4 were embedded into a transparent and flexible polymer to form a composite, and the DW-UCL of the prepared composite was observed (Fig. 1).

Fig. 1. Illustration of a dual-wavelength upconversion display.

2. Materials and methods

2.1. Materials

Yttrium(III) nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and sodium fluoride (NaF) were purchased from Kanto Chemicals (Tokyo, Japan). Erbium(III) nitrate pentahydrate ($\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma-Aldrich (St Luis, MO, USA). Holmium(III) nitrate pentahydrate ($\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was purchased from Kojundo Chemical Laboratory (Saitama, Japan). Praseodymium(III) nitrate hexahydrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ammonium fluoride, decahydronaphthalene, oleic acid, benzophenone, and pentaerythritol tetrakis-3-mercaptopropionate (PEMP) were purchased from Wako Pure Chemicals Industries (Osaka, Japan). Ethoxylated bisphenol A diacrylate (FA-321A) was purchased from Hitachi Chemical (Tokyo, Japan). All the reagents were used without further purification.

2.2. Synthesis of rare earth doped NaYF_4

$\text{NaYF}_4:\text{Er}^{3+}$ and NaYF_4 co-doped with Er^{3+} and various rare-earth ions ($\text{NaYF}_4:\text{Er}^{3+}, \text{RE}^{3+}$) ($\text{RE}^{3+} = \text{Ho}^{3+}, \text{Nd}^{3+}, \text{Pr}^{3+}$, and Ce^{3+}) were synthesized by a standard co-precipitation method [18]. In a typical procedure for the preparation of NaYF_4 : 1% Er^{3+} , 1% RE^{3+} (mol%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (9.8 mmol), $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1 mmol), and

$\text{RE}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.1 mmol) were dissolved in 10 mL of distilled water. The mixture solution was dropped into 40 mL of an aqueous solution of NaF (60 mmol) and stirred for 1 h at 75 °C. After stirring, the precipitation in the solution was collected by centrifugation (20,000 g, 10 min, $\times 3$). The sample was then dried at 80 °C for 24 h. Subsequently, the samples were treated with NH_4F (800 mg) for 1 h at 550 °C to yield NaYF_4 : 1% Er^{3+} , 1% RE^{3+} . Samples with different concentrations of RE^{3+} were prepared using a similar process.

2.3. UCL measurement

VIS-UCL spectra of the synthesized NaYF_4 : Er^{3+} , RE^{3+} were measured in immersion liquids (a mixture of decahydronaphthalene and oleic acid, 3:1 vol/vol) to avoid scattering effects. The refractive index of the immersion liquids corresponded to that of NaYF_4 (1.471). 10 vol% of NaYF_4 : Er^{3+} , RE^{3+} was dispersed in an immersion liquid and poured into a quartz cuvette. The UCL of NaYF_4 : Er^{3+} , RE^{3+} was measured by using a spectrometer (USB2000, Ocean Optics, Dunedin, FL, USA) equipped with two fiber laser line (Ex.1: 1470-1550 nm and Ex.2: 790-860 nm) excitation sources, wherein the excitation lights were coupled by a dichroic mirror. The emission intensities of the particles were evaluated from the integrated emission intensities of the spectra. The ratio of the intensity of the green emission to that of the red emission (I_G/I_R) was evaluated from the integrated emission intensities in the green range (510-560 nm) and in the red range (640-680 nm). The DW-UCL image of NaYF_4 : Er^{3+} , RE^{3+} was observed through a normal digital CCD camera under right-angled irradiation with two NIR excitation beams (Ex.1: 1470-1550 nm and Ex.2: 790-860 nm).

2.4. Preparation and evaluation of transparent and flexible DW-UCL composites

Polymer composites containing NaYF_4 : Er^{3+} , RE^{3+} were prepared according to a previously reported procedure [10]. Briefly, PEMP and FA-321A (2:8 weight ratio) were mixed with 5 wt% benzophenone used as a photoinitiator. Then, the NaYF_4 : Er^{3+} , RE^{3+} samples were dispersed in the mixture (10 wt% of the mixture) and degassed. Subsequently, the mixture sample was dropped on a glass sheet

and irradiated with UV light (365 nm) for 24 h. DW-UCL was observed through a normal digital CCD camera under right-angled irradiation with two NIR excitation beams (Ex.1: 1470-1550 nm and Ex.2: 790-860 nm).

3. Results and discussion

3.1. Preparation and evaluation of UCL of NaYF_4 : Er^{3+} , RE^{3+}

VIS-UCL of the NaYF_4 : Er^{3+} , RE^{3+} samples were measured under DW-NIR (Ex.1: 1550 nm and Ex.2: 850 nm) excitation. Figure 2(a) shows the integrated green and red emission intensities and the I_G/I_R ratio of the NaYF_4 : Er^{3+} , RE^{3+} samples. The NaYF_4 : Er^{3+} sample without RE^{3+} co-doping displayed strong green and red emissions. On the other hand, the absolute intensities of the green and red emissions of the RE^{3+} co-doped NaYF_4 : Er^{3+} samples decreased. Particularly, the emission intensity of NaYF_4 : Er^{3+} , Pr^{3+} was quite low, and thus the I_G/I_R ratio of NaYF_4 : Er^{3+} , Pr^{3+} could not be calculated. However, in the case of Nd^{3+} , Ho^{3+} , and Ce^{3+} co-doped samples, although the absolute intensities of the green and red emissions decreased with RE^{3+} doping, the I_G/I_R ratio of these samples increased, showing a higher green color purity.

Notably, NaYF_4 : Er^{3+} , Ce^{3+} showed the highest I_G/I_R ratio among the RE^{3+} co-doped samples, which was about 6 times larger than that of the NaYF_4 : Er^{3+} sample without RE^{3+} doping. This result is probably due to the effect of energy transfer between Ce^{3+} and Er^{3+} . As shown in Fig. 2(b), Ce^{3+} possesses only one energy level [19], which strongly affects the SW-UCL process of Er^{3+} under 1550 nm excitation. In the case of SW-UCL of Er^{3+} , the UCL (650 nm) arise from three-step excitation under 1550 nm-light irradiation. In doped Ce^{3+} , the $^4\text{I}_{11/2}$ state relaxes into the $^4\text{I}_{13/2}$ state, thus interrupting the SW-UCL (660 nm). Therefore, Ce^{3+} co-doping considerably decreased the SW-UCL (660 nm) under 1550 nm excitation and increased the I_G/I_R ratio. Although co-doping with other RE^{3+} ions resulted in similar effects leading to an increase in the I_G/I_R ratio, the effects were much smaller than that of Ce^{3+} co-doping. This is probably because Ce^{3+} possesses only one energy level, as stated above, which caused efficient energy transfer between Ce^{3+} and Er^{3+} . Therefore, Ce^{3+} is the best co-doping RE^{3+} ion for enhancing the

green color purity of the DW-UCL of $\text{NaYF}_4:\text{Er}^{3+}$.

Fig. 2. DW-UCL intensities of $\text{NaYF}_4:\text{Er}^{3+}$, RE^{3+} . (a) Integrated emission intensity and I_G/I_R ratio of $\text{NaYF}_4:\text{Er}^{3+}$, RE^{3+} . The concentration of Er^{3+} and RE^{3+} were 1%, respectively. Excitation wavelengths were 850 nm and 1550 nm. (b) Energy diagram of DW-UCL and SW-UCL of Er^{3+} and Ce^{3+} .

Next, the concentrations of Ce^{3+} and Er^{3+} in $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} were optimized. Figure 3(a) shows the I_G/I_R ratio of $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} with different Er^{3+} and Ce^{3+} concentrations. The result indicates that the I_G/I_R ratio of $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} drastically changed with the doping amount and ratio of Er^{3+} and Ce^{3+} ions. For example, as shown in Fig. 3(b), the $\text{NaYF}_4: 1.5\% \text{Er}^{3+}$ sample displayed a strong line emission due to SW-UCL under 1550 nm excitation. Accordingly, the I_G/I_R ratio of $\text{NaYF}_4: 1.5\% \text{Er}^{3+}$, $0\% \text{Ce}^{3+}$ was quite low (Fig. 3(a)). In contrast, Ce^{3+} co-doped samples showed a high I_G/I_R ratio. Particularly, $\text{NaYF}_4:$

$0.5\% \text{Er}^{3+}$, $0.5\% \text{Ce}^{3+}$ showed the highest I_G/I_R ratio. As shown in Fig. 3(c), $\text{NaYF}_4: 0.5\% \text{Er}^{3+}$, $0.5\% \text{Ce}^{3+}$ displayed an ideal “point emission” under dual-wavelength excitation at 850 nm and 1550 nm, while the line emission under 1550 nm was effectively inhibited. From these results, it is concluded that $\text{NaYF}_4: 0.5\% \text{Er}^{3+}$, $0.5\% \text{Ce}^{3+}$ is the best composition for DW-UCL display applications. Thus, we focused on the $\text{NaYF}_4: 0.5\% \text{Er}^{3+}$, $0.5\% \text{Ce}^{3+}$ sample for further characterization.

Fig. 3. DW-UCL of $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} with different Er^{3+} and Ce^{3+} concentrations. (a) I_G/I_R ratio of $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} with various Er^{3+} and Ce^{3+} ratio. (b) Visible emission image of $\text{NaYF}_4: 1.5\% \text{Er}^{3+}$. (c) Visible emission image of $\text{NaYF}_4: 0.5\% \text{Er}^{3+}$, $0.5\% \text{Ce}^{3+}$. Excitation wavelengths were 850 nm and 1550 nm.

3.2. Excitation wavelength optimization for DW-UC green point luminescence of $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+}

As mentioned above, the emission intensity of the DW-UCL of the rare-earth doped ceramics changes with changing excitation wavelengths [17]. To investigate the effect, the

DW-UCL intensity and the I_G/I_R ratio of NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ were evaluated under various excitation wavelengths (Ex.1: 1470-1500 nm and Ex.2: 790-860 nm) to optimize the wavelength of the excitation lights. Figure 4(a) shows the integrated DW-UCL emission intensity and the I_G/I_R ratio of the NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ sample in the VIS wavelength region. The sample was excited under DW-NIR excitation (Ex.1: 1470-1500 nm and Ex.2: 790-860 nm). As shown in Fig. 4(a), the integrated VIS emission intensity decreased with decreasing Ex.1 (1470-1500 nm) wavelength. However, on the contrary, the I_G/I_R ratio increased with decreasing Ex.1 (1470-1500 nm) wavelength. This is probably due to the effect of the excitation level of Er³⁺. The first excitation level of Er³⁺ (⁴I_{13/2}) gives rise to an absorption peak at about 1550 nm. Thus, both the SW-UCL and DW-UCL were enhanced by increasing the Ex.1 (1470 – 1500 nm) wavelength, which corresponds to the first excitation level of Er³⁺ (⁴I_{13/2}). Therefore, 1470 nm can be considered the best Ex.1 wavelength for enhancing the green color purity, despite the decrease in the integrated emission intensity.

Furthermore, the Ex.2 wavelength (790-860 nm) was also optimized. Fig. 4(b) shows the integrated DW-UCL intensity and the I_G/I_R ratio of the NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ sample in the VIS wavelength region under DW-NIR excitation (Ex.1: 1550 nm and Ex.2: 790-860 nm). The result shows that the I_G/I_R ratio is almost unchanged with the variation of the Ex.2 wavelength. Additionally, the integrated VIS emission intensity was almost constant over the 800 nm Ex. 2 wavelength range. However, obviously, a strong emission was observed at 790 nm Ex.2 excitation wavelength. This is probably because the two energy levels of Er³⁺ correspond to the green emission of the DW-UCL (⁴S_{3/2} and ²H_{11/2}) [20], thus increasing the I_G/I_R ratio. Hence, 790 nm can be considered as the best Ex.2 excitation wavelength, which accords a strong VIS emission intensity and a high I_G/I_R ratio. From these results, it is concluded that the combination of 1470 nm Ex.1 and 790 nm Ex.2 is the best combination of the excitation wavelengths to achieve a pure and strong green emission from NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ under DW-NIR excitation.

Fig. 4. Measurement of DW-UCL intensity of NaYF₄:Er³⁺, Ce³⁺ under various DW excitation wavelengths. (a) Integrated intensity of VIS-UC emission and I_G/I_R ratio under 850 nm and different excitation wavelengths (1470-1500 nm). (b) Integrated intensity of VIS-UC emission and I_G/I_R ratio under 1550 nm and different excitation wavelengths (790-860 nm). Rare-earth concentration: 0.5% Er³⁺ and 0.5% Ce³⁺.

3.3. Preparation and evaluation of transparent and flexible DW-UCL composites

Finally, as a proof of concept, transparent and flexible polymer composites containing NaYF₄:Er³⁺, Ce³⁺ were prepared and its DW-UCL was observed. The polymer sheet was prepared by photopolymerization under UV irradiation. As shown in Fig. 5(a), the obtained polymer sheet with a thickness of about 5 mm appeared transparent and was flexible enough for bending. Figure 5(b) shows the DW-UCL image of the polymer/NaYF₄: 0.5% Er³⁺ composite under DW-NIR excitation (1550 nm as Ex.1 and 850 nm as Ex.2). As shown in the image, a strong line emission under 1550 nm excitation was observed for NaYF₄:Er³⁺ without Ce³⁺ co-doping. Therefore, a typical DW-UCL material, Ce³⁺ non-doped

$\text{NaYF}_4:\text{Er}^{3+}$ is unsuitable for DW-UCL displays. On the other hand, as shown in Fig. 5(c), in the case of polymer/ NaYF_4 : 0.5% Er^{3+} , 0.5% Ce^{3+} composite, a strong “point emission” was observed at the cross point of the two excitation lights without the line emission of 1550 nm excitation. These results clearly indicate that the NaYF_4 : 0.5% Er^{3+} , 0.5% Ce^{3+} embedded transparent composite has great potential for display applications.

Fig. 5. DW-UCL of transparent and flexible polymer/ $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} composite. (a) Room light image of the transparent composite without DW-NIR excitation. (b) Line emission image of the transparent polymer/ NaYF_4 : 0.5% Er^{3+} composite. Excitation wavelength: 850 nm and 1550 nm. (c) Point emission image of the transparent polymer/ NaYF_4 : 0.5% Er^{3+} , 0.5% Ce^{3+} composite. Excitation wavelength: 790 nm and 1470 nm.

4. Conclusion

In conclusion, we reported the synthesis and evaluation of NaYF_4 co-doped with Er^{3+} and various rare-earth ions for optimizing the monochromatic UC green emission. The I_G/I_R ratio of $\text{NaYF}_4:\text{Er}^{3+}$ effectively increased upon co-doping with various RE^{3+} ions. Particularly, $\text{NaYF}_4:\text{Er}^{3+}$, Ce^{3+} showed the highest I_G/I_R ratio. Additionally, the doping concentration

of Er^{3+} and Ce^{3+} ions in NaYF_4 were optimized as 0.5 mol% Er^{3+} and 0.5 mol% Ce^{3+} for the highest I_G/I_R ratio. Furthermore, the excitation wavelengths of the DW-UC were also optimized. The NaYF_4 : 0.5% Er^{3+} , 0.5% Ce^{3+} sample showed the largest I_G/I_R ratio under the combination of 790 nm and 1470 nm excitation lights. Moreover, for the demonstration of transparent and flexible display application, a composite of a transparent and flexible polymer with the NaYF_4 : 0.5% Er^{3+} , 0.5% Ce^{3+} crystals was prepared, which showed a strong DW-UC point emission. Therefore, the obtained transparent DW-UCL material is a promising candidate for the non-projection-type transparent and flexible displays.

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