Green Color Purity Control of Dual-Excitation Upconversion Display by Using Polymer/NaYF₄:Er³⁺ 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 Er³⁺ doped NaYF₄ (NaYF₄:Er³⁺) 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 (RE³⁺) were co-doped into NaYF₄:Er³⁺ (NaYF₄:Er³⁺, RE³⁺). Among those, NaYF₄ co-doped with Er³⁺ and Ce³⁺ (NaYF₄:Er³⁺, Ce³⁺) showed the highest green color purity under DW-NIR excitation. Furthermore, the excitation wavelengths of DW-UC were also investigated. Moreover, a NaYF₄:Er³⁺, Ce³⁺ 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/NaYF₄:Er³⁺, Ce³⁺ 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 (Er³⁺) and ytterbium (Yb³⁺) 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$_4$ (NaYF$_4$: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, NaYF$_4$: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 NaYF$_4$: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 NaYF$_4$: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 NaYF$_4$: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.](image-url)

## 2. Materials and methods
### 2.1. Materials
Yttrium(III) nitrate hexahydrate (Y(NO)$_3$·6H$_2$O), neodymium nitrate hexahydrate (Nd(NO$_3$)$_3$·6H$_2$O), and sodium fluoride (NaF) were purchased from Kanto Chemicals (Tokyo, Japan). Erbium(III) nitrate pentahydrate (Er(NO$_3$)$_3$·5H$_2$O) and cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O) were purchased from Sigma-Aldrich (St Luis, MO, USA). Holmium(III) nitrate pentahydrate (Ho(NO$_3$)$_3$·5H$_2$O) was purchased from Kojundo Chemical Laboratory (Saitama, Japan). Praseodymium(III) nitrate hexahydrate (Pr(NO$_3$)$_3$·6H$_2$O), ammonium fluoride, decahydronaphthalene, oleic acid, benzophenone, and pentaerythritol tetakis-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$_4$
NaYF$_4$:Er$^{3+}$ and NaYF$_4$ co-doped with Er$^{3+}$ and various rare-earth ions (NaYF$_4$: Er$^{3+}$, RE$^{3+}$) (RE$^{3+}$ = Ho$^{3+}$, Nd$^{3+}$, 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%), Y(NO$_3$)$_3$·6H$_2$O (9.8 mmol), Er(NO$_3$)$_3$·5H$_2$O (0.1 mmol), and
RE(NO)₃·nH₂O (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, ×3). The sample was then dried at 80 °C for 24 h. Subsequently, the samples were treated with NH₄F (800 mg) for 1 h at 550 °C to yield NaYF₄: 1% Er³⁺, 1% RE³⁺. Samples with different concentrations of RE³⁺ were prepared using a similar process.

2.3. UCL measurement

VIS-UCL spectra of the synthesized NaYF₄:Er³⁺, RE³⁺ 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 NaYF₄ (1.471). 10 vol% of NaYF₄:Er³⁺, RE³⁺ was dispersed in an immersion liquid and poured into a quartz cuvette. The UCL of NaYF₄:Er³⁺, RE³⁺ 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 NaYF₄:Er³⁺, RE³⁺ 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 NaYF₄:Er³⁺, RE³⁺

VIS-UCL of the NaYF₄:Er³⁺, RE³⁺ 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 NaYF₄:Er³⁺, RE³⁺ samples. The NaYF₄:Er³⁺ sample without RE³⁺ co-doping displayed strong green and red emissions. On the other hand, the absolute intensities of the green and red emissions of the RE³⁺ co-doped NaYF₄:Er³⁺ samples decreased. Particularly, the emission intensity of NaYF₄:Er³⁺, Pr³⁺ was quite low, and thus the I_G/I_R ratio of the NaYF₄:Er³⁺, Pr³⁺ could not be calculated. However, in the case of Nd³⁺, Ho³⁺, and Ce³⁺ co-doped samples, although the absolute intensities of the green and red emissions decreased with RE³⁺ doping, the I_G/I_R ratio of these samples increased, showing a higher green color purity.

Notably, NaYF₄:Er³⁺, Ce³⁺ showed the highest I_G/I_R ratio among the RE³⁺ co-doped samples, which was about 6 times larger than that of the NaYF₄:Er³⁺ sample without RE³⁺ doping. This result is probably due to the effect of energy transfer between Ce³⁺ and Er³⁺. As shown in Fig. 2(b), Ce³⁺ possesses only one energy level [19], which strongly affects the SW-UCL process of Er³⁺ under 1550 nm excitation. In the case of SW-UCL of Er³⁺, the UCL (650 nm) arise from three-step excitation under 1550 nm-light irradiation. In doped Ce³⁺, the 4I_{11/2} state relaxes into the 4I_{13/2} state, thus interrupting the SW-UCL (660 nm). Therefore, Ce³⁺ 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 RE³⁺ ions resulted in similar effects leading to an increase in the I_G/I_R ratio, the effects were much smaller than that of Ce³⁺ co-doping. This is probably because Ce³⁺ possesses only one energy level, as stated above, which caused efficient energy transfer between Ce³⁺ and Er³⁺. Therefore, Ce³⁺ is the best co-doping RE³⁺ ion for enhancing the
green color purity of the DW-UCL of NaYF₄:Er³⁺.

Fig. 2. DW-UCL intensities of NaYF₄:Er³⁺, RE³⁺.
(a) Integrated emission intensity and $I_G/I_R$ ratio of NaYF₄:Er³⁺, RE³⁺. The concentration of Er³⁺ and RE³⁺ were 1%, respectively. Excitation wavelengths were 850 nm and 1550 nm. (b) Energy diagram of DW-UCL and SW-UCL of Er³⁺ and Ce³⁺.

Next, the concentrations of Ce³⁺ and Er³⁺ in NaYF₄:Er³⁺, Ce³⁺ were optimized. Figure 3(a) shows the $I_G/I_R$ ratio of NaYF₄:Er³⁺, Ce³⁺ with different Er³⁺ and Ce³⁺ concentrations. The result indicates that the $I_G/I_R$ ratio of NaYF₄:Er³⁺, Ce³⁺ drastically changed with the doping amount and ratio of Er³⁺ and Ce³⁺ ions. For example, as shown in Fig. 3(b), the NaYF₄: 1.5% Er³⁺ sample displayed a strong line emission due to SW-UCL under 1550 nm excitation. Accordingly, the $I_G/I_R$ ratio of NaYF₄: 1.5% Er³⁺, 0% Ce³⁺ was quite low (Fig. 3(a)). In contrast, Ce³⁺ co-doped samples showed a high $I_G/I_R$ ratio. Particularly, NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ showed the highest $I_G/I_R$ ratio. As shown in Fig. 3(c), NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ 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 NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ is the best composition for DW-UCL display applications. Thus, we focused on the NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ sample for further characterization.

Fig. 3. DW-UCL of NaYF₄:Er³⁺, Ce³⁺ with different Er³⁺ and Ce³⁺ concentrations. (a) $I_G/I_R$ ratio of NaYF₄:Er³⁺, Ce³⁺ with various Er³⁺ and Ce³⁺ ratio. (b) Visible emission image of NaYF₄: 1.5% Er³⁺. (c) Visible emission image of NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺. Excitation wavelengths were 850 nm and 1550 nm.

3.2. Excitation wavelength optimization for DW-UC green point luminescence of NaYF₄:Er³⁺, Ce³⁺

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 NaYF\(_4\): 0.5% Er\(^{3+}\), 0.5% Ce\(^{3+}\) 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 NaYF\(_4\): 0.5% Er\(^{3+}\), 0.5% Ce\(^{3+}\) 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 Er\(^{3+}\). The first excitation level of Er\(^{3+}\) (\(^{4}I_{13/2}\)) 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 Er\(^{3+}\) (\(^{4}I_{13/2}\)). 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 NaYF\(_4\): 0.5% Er\(^{3+}\), 0.5% Ce\(^{3+}\) 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 Er\(^{3+}\) correspond to the green emission of the DW-UCL (\(^{5}S_{3/2}\) and \(^{2}H_{11/2}\)) [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 NaYF\(_4\): 0.5% Er\(^{3+}\), 0.5% Ce\(^{3+}\) under DW-NIR excitation.

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

Finally, as a proof of concept, transparent and flexible polymer composites containing NaYF\(_4\):Er\(^{3+}\), Ce\(^{3+}\) 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/NaYF\(_4\): 0.5% Er\(^{3+}\), Ce\(^{3+}\) 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 NaYF\(_4\):Er\(^{3+}\) without Ce\(^{3+}\) co-doping. Therefore, a typical DW-UCL material, Ce\(^{3+}\) non-doped
NaYF₄:Er³⁺ is unsuitable for DW-UCL displays. On the other hand, as shown in Fig. 5(c), in the case of polymer/NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ 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 NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ embedded transparent composite has great potential for display applications.

![Fig. 5. DW-UCL of transparent and flexible polymer/NaYF₄:Er³⁺, Ce³⁺ composite. (a) Room light image of the transparent composite without DW-NIR excitation. (b) Line emission image of the transparent polymer/NaYF₄: 0.5% Er³⁺ composite. Excitation wavelength: 850 nm and 1550 nm. (c) Point emission image of the transparent polymer/NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ composite. Excitation wavelength: 790 nm and 1470 nm.](image)

4. Conclusion

In conclusion, we reported the synthesis and evaluation of NaYF₄ co-doped with Er³⁺ and various rare-earth ions for optimizing the monochromatic UC green emission. The \( \frac{I_G}{I_R} \) ratio of NaYF₄:Er³⁺ effectively increased upon co-doping with various RE³⁺ ions. Particularly, NaYF₄:Er³⁺, Ce³⁺ showed the highest \( \frac{I_G}{I_R} \) ratio. Additionally, the doping concentration of Er³⁺ and Ce³⁺ ions in NaYF₄ were optimized as 0.5 mol% Er³⁺ and 0.5 mol% Ce³⁺ for the highest \( \frac{I_G}{I_R} \) ratio. Furthermore, the excitation wavelengths of the DW-UC were also optimized. The NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ sample showed the largest \( \frac{I_G}{I_R} \) 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 NaYF₄: 0.5% Er³⁺, 0.5% Ce³⁺ 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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