



Upconversion- and cathodo-luminescence properties of Yb³⁺/Ho³⁺/Li⁺ tridoped Lu₆O₅F₈ nanoparticles



Linna Guo^{a,b}, Xiong Zheng^a, Sheng Zhang^a, Benliang Zhao^a, Yuhua Wang^{a,*}

^a Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, China

^b The college of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan, China

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ABSTRACT

Yb³⁺/Ho³⁺/Li⁺ tridoped Lu₆O₅F₈ as a novel phosphor was prepared by a coprecipitation method. It is found that Li⁺ doping could enhance the emission intensity of Yb³⁺/Ho³⁺ codoped Lu₆O₅F₈ both under the excitation at 980 nm and low-voltage electron beam. Under 980 nm laser excitation, the intensity of red emission is slightly stronger than that of green emission, generating an overall yellow output in Lu₆O₅F₈:20%Yb³⁺,1%Ho³⁺,x%Li⁺ (0 ≤ x ≤ 8) nanoparticles, and the reason for this phenomenon is discussed in detail. Meanwhile, under low-voltage electron beam excitation, spectral results demonstrated that the intensity of red emission is much stronger than that of green emission, yielding a red color output. Therefore, Lu₆O₅F₈:20%Yb³⁺,1%Ho³⁺,x%Li⁺ (0 ≤ x ≤ 8) nanoparticles have potential applications in luminescent display panels and field emission displays.

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1. Introduction

As is known to all, rare-earth (RE) ions doped up-conversion (UC) materials with unique optical properties have great potential applications in the fields of displays and biomedicine [1,2], such as light emitting devices, optical data storage, biomedical fluorescent labels, etc. Meanwhile, RE ions doped cathodoluminescence (CL) materials have the advantage of much higher spatial resolution, up to a few nanometers and can be applied to field emission displays (FEDs) [3].

For UC luminescence materials, relative studies mostly focus on the design of fluoride crystals which have been demonstrated to be one of the best host materials, due to their low phonon energy and wide transparent region [4]. However, fluorides have less favorable chemical, thermal and mechanical properties compared to oxides, and thus are hard to be prepared and handled [5]. Similarly, many efficient sulfide-based compounds have been explored as low-voltage phosphors, such as Y₂O₂S: Eu [6], Gd₂O₂S: Tb [7], SrGa₂S₄: Eu [8], etc. However, sulfide-based materials have many disadvantages, such as chemical instability, corrosion of the emitter cathode, and luminance saturation [9]. Recently, Oxyfluorides with high chemical stability and low phonon energy, are commonly considered as ideal host materials and are widely investigated [10].

Lu₆O₅F₈, as a new oxyfluoride matrix, is chosen as the investigated luminescent host in the present work.

Both Er³⁺ and Ho³⁺, which have ladder-like arrangement energy levels, are frequently used as activators to generate UCL emission under NIR excitation. In our previous work, Yb³⁺/Er³⁺ codoped Lu₆O₅F₈ UCNPs display intense UC emission, and the red emission is predominated in the UC spectra. By contrast, their CL emission is very weak. However, in our work it is found that the luminescence properties of Ho³⁺ are different from that of Er³⁺ whether under excitation at 980 nm or low electron beam excitation. Most reports about UC luminescence properties of Ho³⁺ show that the intensity of green emission is much higher than that of red emission, such as in Gd₃Ga₅O₁₂ (Ref. [11]), NaGdF₄ (Ref. [12]), Ln₂BaZnO₅ (Ref. [13]), La₂O₃ (Ref. [14]) and Zr₂O₃ (Ref. [15]), etc. Interestingly, in our work it is observed that the intensity of red emission of Ho³⁺ is higher than that of green emission in Lu₆O₅F₈ host. The dependence of excitation power on the visible and near-infrared (NIR) emissions as well as the energy levels of Yb³⁺ and Ho³⁺ has been investigated, and the above phenomenon is attributed to back energy transfer process from Ho³⁺ to Yb³⁺ and cross relaxation between two Ho³⁺ ions. This new UC emission color of Ho³⁺ will provide new possibilities for the design of more efficient devices for new applications. Moreover, we find intense red emission of Ho³⁺ in the Lu₆O₅F₈ host under low electron beam excitation, which is scarcely reported.

Due to its small ionic radius, Li⁺ ion can be doped easily into the host lattice substitutionally or interstitially, and this will break the

* Corresponding author.

E-mail address: wyh@lzu.edu.cn (Y. Wang).

symmetry of the crystal field around the RE ions, leading to the enhancement of luminescence intensity [16,17]. Herein, $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\%\text{Ho}^{3+},x\%\text{Li}^+$ ($0 \leq x \leq 8$) nanoparticles were prepared to explore new optical properties on the basis of the luminescent efficiency and intensity increment by Li^+ doping. Therefore, in this paper we provide the optical properties of $\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Li}^+$ -doped $\text{Lu}_6\text{O}_5\text{F}_8$ nanocrystals, which would further broaden the research area of this matrix.

2. Experimental

$\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\%\text{Ho}^{3+},x\%\text{Li}^+$ ($0 \leq x \leq 8$) nanoparticles were prepared by a coprecipitation method and subsequent calcination route [16]. Phase identification was performed via XRD analysis (XRD, Model D/MAX-2400 V, Rigaku, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation. The size, shape and structure of the as-prepared samples were characterized by SEM (S-4800). In the measurements of UC emission, a continuous 980-nm laser diode (LD) was used for excitation source, and the emissions were collected using a HORIBA JOBIN YVON Fluorolog-3 Spectrofluorometer system. Low-voltage CL spectra were obtained using a modified Mp-Micro-S instrument.

3. Results and discussion

The representative XRD patterns of a series of $\text{Lu}_6\text{O}_5\text{F}_8:20\% \text{Yb}^{3+},1\% \text{Ho}^{3+},x\%\text{Li}^+$ ($0 \leq x \leq 8$) samples calcinated at 590°C for 4 h are shown in Fig. 1(a). It is obvious that the locations and relative intensities of the diffraction peaks coincide well with the PDF card of $\text{Lu}_6\text{O}_5\text{F}_8$ described in Ref. [16], indicating that Li^+ ions have been dissolved into the $\text{Lu}_6\text{O}_5\text{F}_8$ host. Fig. 1(b) shows the morphology and size of $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\%\text{Ho}^{3+},3\%\text{Li}^+$ which is chosen as an example, indicating the uniform agglomerated particles with rough surface and average size of about 45 nm were obtained.

Under 980 nm LD excitation at the pump power of 274.4 mW, the corresponding UC emission spectra of the as-prepared samples with different Li^+ concentrations are shown in Fig. 2(a). Evidently, the emission intensities of $\text{Ho}^{3+}: {}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ transition around 540 nm, ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ transition around 665 nm and ${}^5\text{F}_4 \rightarrow {}^5\text{I}_7$ transition around 750 nm increased remarkably with increasing Li^+ concentration from 0 to 5 mol%, and then decreased with further doping of Li^+ . This may be due to the fact that pairing or aggregation of activator ions at high concentration will lead efficient resonant energy transfer between Yb^{3+} and Ho^{3+} , and a fraction of energy migration to distant killer or quenchers followed by the appearance of quenching behaviour [18]. To the best of our knowledge, the intensity of red UC emission is usually weaker than that of green emission in $\text{Yb}^{3+}/\text{Ho}^{3+}$ couple [11–15], while spectral results demonstrated that the red emission is slightly intense than green

emission in our investigated system, which was different from most cases. To understand the mechanism of the UC process, we have performed power dependence studies of $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\% \text{Ho}^{3+}$ and $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\%\text{Ho}^{3+},5\%\text{Li}^+$, as shown in Fig. 2(b). In terms of every emission peak at 540, 665 and 756 nm, a plot of all the three $\ln I$ versus $\ln P$ yields a straight line with slope $n \approx 2$, indicating that all the three emissions are two-photon process whether doping Li^+ ions or not. As none of these plots show a threshold for UC emission, a photon avalanche mechanism could be ruled out [19], and the UC emission should therefore be arisen from sequential transfer of absorption energy from excited Yb^{3+} to Ho^{3+} . Typically for the $\text{Ho}^{3+}/\text{Yb}^{3+}$ couple, Yb^{3+} absorbs the excitation energy and transfers it to Ho^{3+} ions. The weaker green and NIR UC luminescence (relative to the red emission) was ascribed to the transition from the ${}^5\text{F}_4, {}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ and ${}^5\text{F}_4, {}^5\text{S}_2 \rightarrow {}^5\text{I}_7$ states, respectively, while $\text{Ho}^{3+} ({}^5\text{F}_5) \rightarrow {}^5\text{I}_8$ transition yields slightly stronger red emission. In fact, nonradiative deactivation of $\text{Ho}^{3+} ({}^5\text{S}_2)$ could happen in three ways (shown in Fig. 2(c)) [20]:

Pathway 1 Phonon relaxation of $\text{Ho}^{3+} ({}^5\text{S}_2, {}^5\text{F}_4)$ to ${}^5\text{F}_5$

Pathway 2 Cross relaxation between two Ho^{3+} ions, $\text{Ho}^{3+} ({}^5\text{S}_2, {}^5\text{F}_4) + \text{Ho}^{3+} ({}^5\text{I}_7) \rightarrow \text{Ho}^{3+} ({}^5\text{F}_5) + \text{Ho}^{3+} ({}^5\text{I}_6)$

Pathway 3 Back energy transfer from Ho^{3+} to Yb^{3+} , $\text{Ho}^{3+} ({}^5\text{S}_2, {}^5\text{F}_4) + \text{Yb}^{3+} ({}^2\text{F}_{7/2}) \rightarrow \text{Ho}^{3+} ({}^5\text{I}_6) + \text{Yb}^{3+} ({}^2\text{F}_{5/2})$

Direct excitation of $\text{Ho}^{3+} ({}^5\text{S}_2, {}^5\text{F}_4)$ energy level with 540 nm light did not result in any detectable red emission, implying that the feeding of ${}^5\text{F}_5$ level by ${}^5\text{S}_2$ through multiphonon relaxation (pathway 1) should be minimal. While the occurrence of Ho^{3+} to Yb^{3+} back energy transfer was obvious from study of the NIR emission of Yb^{3+} under excitation at 450 nm (inset of Fig. 2(a)), and this strongly supports that pathway 3 is a key contributor to the deactivation of $\text{Ho}^{3+} ({}^5\text{S}_2)$. Pathway 3 will cause the green emission decreasing, and a decrease in green emission should be accompanied by an increase in red emission. In short, pathway 2 and 3 build up the population of $\text{Ho}^{3+} ({}^5\text{F}_5)$ level red-emitting at the expense of green-emitting level of $\text{Ho}^{3+} ({}^5\text{S}_2, {}^5\text{F}_4)$, leading to the stronger red emission compared with that of green. Additionally, the CIE coordinates are also investigated, as shown in Fig. 2(d). It could be easily seen that the CIE coordinates of samples doping Li^+ or not are located in the yellow region basically.

By contrast, $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+}, 1\%\text{Ho}^{3+}, x\%\text{Li}^+$ nanoparticles exhibit much stronger red emission (relative to the green emission) under excitation of a low voltage electron beam. As shown in Fig. 3(a), under accelerating voltage of 4 kV, filament current of 70 mA, the CL spectra of $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+}, 1\%\text{Ho}^{3+}, x\%\text{Li}^+$ ($0 \leq x \leq 8$) samples give the characteristic transitions of Ho^{3+} centered at 489 nm (2.54 eV), 543 nm (2.28 eV) and 627 nm (1.98 eV), respectively. Similar to UC emission spectra, upon increasing Li^+ concentration, peaks of the three typical emissions did not shift, while the integrated emission magnified first and

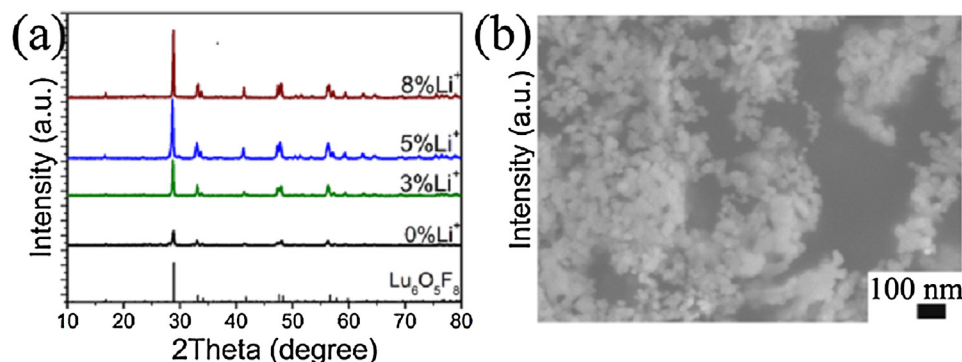


Fig. 1. (a) X-ray diffraction patterns of $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\%\text{Ho}^{3+},x\%\text{Li}^+$ ($0 \leq x \leq 8$) nanoparticles; (b) SEM image of $\text{Lu}_6\text{O}_5\text{F}_8:20\%\text{Yb}^{3+},1\%\text{Ho}^{3+},3\%\text{Li}^+$ as an example.

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