Highly efficient saturated visible up-conversion photoluminescent $Y_2O_3:Er^{3+}$ microspheres pumped with a 1.55 $\mu$m laser diode

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Highly efficient saturation up-conversion (UC) luminescent $Y_2O_3:Er^{3+}$ microspheres have been successfully prepared via a hydrothermal-homogeneous precipitation method. Bright visible luminescence can be clearly seen with a 1.55 $\mu$m laser diode excitation power as low as ~0.03 W cm$^{-2}$. The up-conversion (UC) emission spectra indicate that the strongest red emission with a peak situated at ~660 nm originated from the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition of $Er^{3+}$. The peaks situated at ~520 and 550 nm can be assigned to the transition from $^2H_{11/2} \rightarrow ^4S_{3/2}$ state to the ground state of $Er^{3+}$. The high efficient saturation up-conversion emission is related to the highly crystalline structure. These results indicate a new way to enhance UC radiation in rare-earth ion-doped materials prepared using a hydrothermal-homogeneous precipitation method.

1. Introduction

Lanthanide-doped up-conversion (UC) nanocrystals can convert absorbed near-infrared (NIR) light into a photoluminescence (PL) emission with high energy in the visible and/or ultraviolet (UV) regions due to the existence of real intermediate energy levels in lanthanide ions.$^{1–3}$ Highly efficient energy up-conversion in nanocrystals is desirable for numerous applications such as in efficient solar cells,$^4$ displays,$^5$ PL imaging,$^6$ sensing,$^7$ and biological labeling.$^8$ Recent UC studies focus on the design and synthesis of lanthanide-doped nanocrystals$^9–13$ due to the f- and d-ions possessing more than one metastable level that can be principally used to generate UC luminescence.$^8$ Due to the high phonon lattice energy and the defects of commonly used matrices for rare-earth ions,$^{14}$ it is still a great challenge to obtain an efficient up-conversion PL. The optical properties of trivalent lanthanide ions have been widely studied and the host materials investigated are mostly restricted to fluoride nanocrystals.$^{3,15–17}$ As a matter of fact, fluoride nanocrystals are not suitable as host materials due to their air sensitivity and toxicity from halides, which greatly limit their extensive applications.

Herein, it was critical to obtain new alternative host materials. Yttrium oxide ($Y_2O_3$) is a promising non-toxic host material for rare-earth dopants because of its wide range of transparency with wavelengths between 0.23 and 0.8 $\mu$m, relatively lower phonon cut-off energy and high thermal stability.$^{18,19}$ As a result, $Y_2O_3$ is an attractive erbium-doped host material. Much effort has been made on the UC in the $Er^{3+}$-doped material under 980 nm.$^{20,21}$ However, only a few studies have reported the UC emission of $Er^{3+}$ under 1.55 $\mu$m excitation.$^{19,22,23}$

To investigate the UC emission of $Er^{3+}$ from a 1.55 $\mu$m excitation to the visible or ultraviolet regions is of significance in several aspects, including IR quantum counters, the detection of surface plasmon, operation in the visible light region under excitation in the near infrared region, the development of bio-photonic materials used in the biological labeling and increasing the efficiency of energy conversion devices.$^{24}$ Furthermore, populating a certain UC emission of $Er^{3+}$ under 1.55 $\mu$m excitation is a higher-order process compared to that under 980 nm excitation, since the energy of a 1.55 $\mu$m photon is lower than that of a 980 nm photon.$^{22}$ Although the UC luminescence of $Er^{3+}$-doped $Y_2O_3$ nanocrystals under 1.55 $\mu$m excitation has been reported,$^{19,23}$ the required high excitation power density of these materials limits their applications.

In this study, $Y_2O_3:Er^{3+}$ microspheres were fabricated and their UC PL excited at 1.55 $\mu$m with high efficiency under excitation at a much lower power density were observed. A bright visible luminescence can be clearly observed with the naked eye under an excitation power as low as ~0.03 W cm$^{-2}$.

2. Experimental

2.1. Synthesis of the $Er^{3+}$-doped nanocrystals of $Y_2O_3$

$Y_2O_3$ nanocrystals doped with 1, 3, 5 and 7 mol% $Er^{3+}$ ions were synthesized via a simple hydrothermal method. For a typical
synthesis, 0.645 g of yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O, Aladdin Reagent Co. Ltd), 0.023 g of erbium trinitrate pentahydrate (Er(NO₃)₃·5H₂O, Aladdin Reagent Co. Ltd) and 0.357 g of hexamethylenetetramine (HMT, C₆H₁₂N₄, Mₑ = 140.19, Sinopharm Chemical Reagent Shanghai Co. Ltd) were dissolved in 17 mL of distilled water. The transparent solution was transferred into a 20 mL Teflon-lined stainless autoclave and subsequently sealed and heated at 180 °C for 24 h in an oven. The obtained precipitates were rinsed several times with deionized water and ethanol, and then dried in air at 60 °C. After being calcined at 700 °C for 4 h, the powders were collected for further characterization.

2.2. Characterization

The morphology of the nanocrystals was characterized using field-emission scanning electron microscopy (FE-SEM Hitachi S-4800, 5 kV). The structure of the prepared powders was identified via X-ray diffraction (XRD) using a Rigaku Dmax2200 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 150 mA.

The UC luminescence spectra in the range of 300–800 nm were recorded on a 970CRT fluorescence spectrophotometer (Shanghai Precision Instrument Factory, slit: 3 nm). A 1.55 µm optical fiber laser (DS3-11312, BWT, Beijing Kaipulin Co., Ltd, China) with a continuous output maximum power of 2.0 W was used as the excitation source. All the spectral measurements were performed at room temperature.

3. Results and discussion

3.1. Crystal structure

Fig. 1 presents the XRD patterns of the samples after calcination. The diffraction patterns were in good agreement with the standard values of Y₂O₃ (JCPDS file No. 41-1105). No peaks from any other phase can be found, indicating no crystal structure change in the prepared particles co-doped with Er³⁺. The relatively high intensity of the peaks as well as the broad diffraction feature indicate the small grain size and high crystallinity of Y₂O₃: Er³⁺. The FE-SEM image of the particles (Y₂O₃:Er 3%) shows microspheres (Fig. 2a). Sheets were observed to be the building blocks of the microspheres, as shown Fig. 2b.

3.2. UC emissions

The UC emissions of the particles were studied in the visible UC spectra from 400–750 nm. Fig. 3 shows the UC spectra in the range of 400–750 nm for the Y₂O₃:Er³⁺ sample under excitation with an unfocused laser beam at 1.55 µm. Three up-conversion PL bands centered at 520, 550 and 652 nm were clearly resolved under a weak excitation power (0.01 W), which corresponded to the transitions from the 2H₁₁/₂, 4S₃/₂ and 4F₉/₂ state to the ground 4I₁₅/₂ state of Er³⁺, respectively. The effect of the Er³⁺ ion concentration on the UC emission spectrum can be observed, Fig. 3. The UC emission intensity increases gradually upon increasing the concentration of Er³⁺. Due to the quenching effect, the UC emission intensity decreases at a higher doping level. The highest UC emission intensity was achieved in the sample with 3 mol% Er³⁺.

The UC emission of the sample can be seen clearly at an excitation power as low as ~0.03 W cm⁻² (inset of Fig. 3). Table 1 summarizes the recent study on Er³⁺ doped or co-doped Y₂O₃ compounds for comparison. This clearly demonstrates that the Y₂O₃:Er³⁺ microspheres prepared here have the lowest pumping power/pump power and the highest UC efficiency. In this case, the high efficiency of up-conversion observed for our Y₂O₃:Er³⁺ microspheres under 1.55 µm excitation can be attributed to the highly crystalline structure, which is due to the homogeneous and slow nucleation process throughout the solution utilizing HMT hydrolysis. HMT can form a homogenous solution at low temperature. As the temperature of the solution increases, HMT begins to hydrolyze slowly and subsequently, the pH of the solution increases, which in turn sustains a homogenous pH level in the solution to avoid the agglomeration of the primary particles, leading to slow nucleation. With the slow nucleation process throughout the homogeneous solution, highly crystalline Y₂O₃ microspheres are synthesized. The microspheres with well-crystallized structures exert a strong crystal field around the dopant ions and minimize the energy loss of the dopant ion arising from crystal defects. Consequently, the Y₂O₃:Er³⁺ microspheres with highly crystalline structures show a highly efficient UC emission.

3.3. UC mechanisms

Fig. 4 shows the energy levels of the Er³⁺ ions as well as the proposed UC pathways under an unfocused laser excitation at 1.55 µm. Three photon processes for green and red UC emission were observed and the mechanisms can be seen in Fig. 4. The Er³⁺ ions are directly excited by the 1.55 µm photons from the ground 4I₁₅/₂ state (217 cm⁻¹) to the first excited 4I₁₃/₂ state (6712 cm⁻¹). Multi-step excited state absorption (ESA) processes lead to the population of the higher states of the Er³⁺ ions. The 4I₁₃/₂ state of the Er³⁺ ions can absorb excitation photons via...
ESA and jump to the $^4I_{9/2}$ (12597 cm$^{-1}$) state. Some ions at the $^4I_{9/2}$ state are promoted via ESA to the $^2H_{11/2}$/$^4S_{3/2}$ (18583/19337 cm$^{-1}$) states. The other $^4I_{9/2}$ states of the Er$^{3+}$ ions are relaxed non-radiatively (no absorbing energy required) to the $^4I_{11/2}$ state (10346 cm$^{-1}$) (process “a” in Fig. 4) and then excited to the $^4F_{9/2}$ state (15455 cm$^{-1}$) through adsorbing energy transfer (ET) energy.32 The shorter ion–ion distance between the doping ions can strengthen the multi-polar ion–ion interactions.33 With the assistance of lattice phonons, the $^4I_{13/2}$ state of the Er$^{3+}$ ions can be excited to the $^2H_{11/2}$/$^4S_{3/2}$ and $^4I_{9/2}$ states via energy transfer. The $^4F_{9/2}$ state can also be populated via non-radiative relaxation from the $^4S_{3/2}$ state (process “b” from Fig. 4). The different processes can lead the population of higher excited Er$^{3+}$ states, which rely either on multi-step state absorption or energy transfer UC mechanisms.3 Since the concentration of doped Er$^{3+}$ in the product is high enough, the energy transfer UC is believed to be the dominant mechanism due to the strong multi-polar ion–ion interactions induced by the short ion–ion distance.27 A three-photon green emission at $\sim$520/550 nm corresponds to the radiative decay from the $^2H_{11/2}$/$^4S_{3/2}$ state to the ground state of Er$^{3+}$. A strong three-photon red emission at $\sim$652 nm corresponds to the $^4I_{9/2} \rightarrow ^4I_{15/2}$ transition of Er$^{3+}$.3

To understand the UC mechanisms, the pump power dependent UC intensity ($I_{UC}$) was measured. For an unsaturated UC process, the number of photons required to populate the upper emitting state can be obtained by the relation $I_{UC} \propto P^n$, where $P$ is the pump laser power and $n$ is an integer corresponding to

$$I_{UC} \propto P^n$$

![Fig. 2](image_url) (a) The FE-SEM image of the Y$_2$O$_3$:Er$^{3+}$ microspheres and (b) the high-magnification image of a single microsphere.

![Fig. 3](image_url) The up-conversion emission spectra of the Y$_2$O$_3$:Er$^{3+}$ microspheres under 10 mW excitation at 1.55 μm using an unfocused laser beam (pump density of only $\sim$0.03 W cm$^{-2}$). The inset is the photographic image of the up-conversion photoluminescence of the Y$_2$O$_3$:Er$^{3+}$ 3% microspheres.

![Fig. 4](image_url) The energy level diagram of the Er$^{3+}$ ions and the proposed mechanisms for the up-conversion process.

### Table 1

<table>
<thead>
<tr>
<th>Dopant ion</th>
<th>Host lattice</th>
<th>Pump power density/pump power</th>
<th>Preparation method</th>
<th>Excitation (nm)</th>
<th>Ref.</th>
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<tr>
<td>Er$^{3+}$</td>
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<td>This work</td>
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<tr>
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<td>18</td>
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<td>Solid-state reaction</td>
<td>1550</td>
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the excitation photon number required for the population of the emitting state.\(^{19,34}\) As shown in Fig. 5, \(n \approx 1\) was observed for the 520, 550, and 652 nm three-photon UC radiations at the low pumping power density range from \(\sim 0.03\) to 0.3 W cm\(^{-2}\). This demonstrates the occurrence of a saturation process for the generation of the UC.\(^{34}\) For any up-conversion mechanism, the dependence of the UC emission intensity on the pump power is expected to decrease in the slope, which is due to the competition between a linear decay and a up-conversion process for the depletion of the intermediate exited states. Pollnau \textit{et al.} attributed this phenomenon to the “saturation” process.\(^{35}\) The photon process can be decreased by saturation effects induced via the intrinsic radiation characteristics of rare-earth ions.\(^{36}\) Usually, for a specific rare-earth ion, the lower the energy level is, the longer the lifetime will be.\(^{37,38}\) In the \(\text{Y}_2\text{O}_3\) host lattices, the trivalent erbium ion (\(\text{Er}^{3+}\)) has a ladder-like system of long-lived excited states.\(^{39}\) These long-lived intermediate excited states can thereby have energy reservoirs, whose function is similar to the ground state when populating the emitting state.\(^{19,34}\) A ss h o w ni nF i g .5 ,

4. Conclusions

Highly efficient saturation up-conversion photoluminescence has been demonstrated in \(\text{Er}^{3+}\) doped \(\text{Y}_2\text{O}_3\) microspheres under excitation with a telecom-wavelength at 1.55 \(\mu\)m. Due to the highly crystalline structures, the intensities of the three-photon (maxima at \(\sim 520, \sim 550\) and \(\sim 652\) nm) up-conversion emission are high under a low power excitation (\(\sim 0.03\) W cm\(^{-2}\)). This work provides a way to synthesize \(\text{Er}^{3+}\) doped \(\text{Y}_2\text{O}_3\) microspheres that could evoke wide interests in the biophotonic, photovoltaic and photonic applications of these crystals.

Notes and references


