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1. Introduction

Fossil fuels including coal, oil, and natural gas constitute the foundation of world energy. While obtaining energy through the combustion of fossil fuels, by-products such as billions of tons of carbon dioxide and massive numbers of compounds containing arsenic, sulphur and plumbum accelerate the greenhouse effect as well as pollute the ecological environment.^{1,2} Developing a renewable and carbon-free energy source is an urgent mission to satisfy the ever-growing world energy demand.^{2–4} The sun irradiates about 10⁵ terawatts of solar power to the earth's surface annually, which exceeds the total amount of global consumption by thousands of times.⁵ The silicon-based solar cell is the most extensive photovoltaic (PV) device on the market and occupies 80% market share of the world's solar cell industry.⁶ However, sub-band gap transmission loss restricts the improvement of conversion effi-

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Enhancing IR to NIR upconversion emission in Er³⁺-sensitized phosphors by adding Yb³⁺ as a highly efficient NIR-emitting center for photovoltaic applications

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Near-infrared (NIR) to visible upconversion (UC) luminescence in activator Er^{3+} and sensitizer Yb^{3+} codoped systems has been extensively studied. In this work, we report the results of Er^{3+} -sensitized Yb^{3+} NIR UC emission at ~1000 nm originating from ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition under infrared (IR) excitation at ~1500 nm responsible for $Er^{3+} \, {}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ transition absorption. The IR to NIR UC is a desirable strategy to increase solar light utilization by reducing the spectral mismatch between the solar spectrum and crystalline silicon (c-Si) solar cells. $Er^{3+} \, \text{singly}$ doped phosphors are mostly used for realizing the IR to NIR UC emission derived from $Er^{3+} \, {}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ transition centered also at ~1000 nm. The efficiency of this transition, however, is limited by multiphonon relaxation and radiative transition to the ${}^{4}I_{13/2}$ state. Here, Yb^{3+} ions are codoped in Y_2O_3 : Er^{3+} , and NIR UC emission with the intensity enhanced 1.5 times is achieved due to efficient energy transfer from Er^{3+} to Yb^{3+} and highly efficient Yb^{3+} emission. The influence of the dopants' concentrations on UC dynamics is studied. The optimal concentration under IR excitation is 5% Er^{3+} and 1% Yb^{3+} . Our results indicate that introducing Yb^{3+} ions in Er^{3+} singly doped phosphors may notably improve the IR to NIR UC performance.

ciency of commercial PV devices even for the crystalline silicon (c-Si) solar cell with a small band gap of 1.12 eV. This means that only the radiation with wavelength shorter than 1100 nm in the air mass 1.5 (AM 1.5) spectrum can be utilized by c-Si solar cells and at least 20% of the solar irradiation is lost.^{4,7} A promising strategy for mitigating the transmission loss is to convert sub-band gap photons into available photons by upconversion (UC) materials.^{8,9} The maximum theoretical efficiency of a c-Si PV cell with an additional upconverter can be elevated to 40.2% for non-concentrated sunlight, which exceeds the Shockley–Queisser limit (30%).¹⁰

The UC luminescence (UCL) phenomenon has generated enormous interest due to its unique luminescence features and potential applications in 3D displays, solar cells, biomarkers, optical anti-counterfeiting, optical temperature sensing, etc.^{11–21} High-efficiency UCL could often be observed in lanthanide ion (Ln^{3+}) doped materials owing to the abundant and long-lived intermediate energy levels of trivalent rare earth ions. Typically, Er^{3+} ions have an absorption band in the 1430– 1600 nm region originating from the ${}^{4}\text{I}_{15/2} \rightarrow {}^{4}\text{I}_{13/2}$ transition and can emit four UC emissions centered at 1000, 820, 660, and 560 nm that can be absorbed by c-Si solar cells. Shalav *et al.* applied β -NaYF₄: Er^{3+} phosphors as an upconverter to enhance the efficiency of bifacial c-Si solar cells for the first

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Fig. 1 (a) XRD patterns of the prepared samples and the standard diffraction data of Y_2O_3 . (b) Enlarged (622) peaks of various XRD patterns.

time.²² Subsequently, some other host materials such as fluoride glass, NaGdF₄, Gd₂O₂S, and CaTiO₃ were also adopted to explore the application of UCL materials in enhancing the efficiency of silicon-based PV devices.^{23–26} Fischer *et al.* in 2015 reported an external upconversion quantum yield (UCQY) as high as 9.5% for monocrystalline BaY₂F₈:Er³⁺ upon monochromatic excitation at 1520 nm. This value is similar to its internal UCQY (10.1%) and higher increases in the short-circuit current density are achieved compared with using microcrystalline β -NaYF₄:Er³⁺, which can be well understood that transparent materials show stronger absorption and less scattering in comparison to opaque phosphors.²⁷ Therefore, developing transparent or potentially transparent UCL materials is essential for taking full advantage of solar energy.

Rare earth doped Y_2O_3 is usually studied in fields of high power infrared (IR) solid state lasers and UCL by virtue of its excellent stability and relatively low phonon energy (~600 cm⁻¹) in oxides.^{28,29} Y_2O_3 possesses a cubic crystalline phase which makes it possible to prepare it into a transparent ceramic.³⁰ However, compared with fluoride, its phonon energy is still large, which will decrease the emission efficiency of the Er^{3+ 4}I_{11/2} level and thereby lower the UCQY of the nearinfrared (NIR) emission. To address this issue, a feasible idea is to introduce new emission centers with high-efficiency NIR emission.³¹⁻³⁴ Yb³⁺ ions have a quite simple energy level diagram and extremely large energy gap ($\sim 10000 \text{ cm}^{-1}$), which enable their emission to be free from the influence of the matrix phonon.³⁵ In addition, the energy transfer (ET) can take place from Er³⁺ to Yb³⁺ ions and the emission energy of Yb³⁺ is beyond the band gap of c-Si. Consequently, the incorporation of Yb³⁺ might possibly enhance the NIR UCL intensity upon IR excitation. Some studies have reported the down-conversion luminescence of Ln³⁺ and Yb³⁺ ion codoped materials.^{36,37} Nevertheless, in the sensitizer Er³⁺ and activator Yb³⁺ doubly doped systems, the investigation on the IR to NIR upconversion luminescence kinetics is very limited.

In this work, the central topics focus on the enhancement of ~1000 nm NIR UCL under ~1500 nm IR excitation and the dynamic process involved, which is different from the common visible (VIS) UCL phenomenon excited by a 980 nm NIR laser. Codoping with Yb³⁺ ions leads to the enhancement of NIR UCL intensity, which is beneficial to improving the silicon solar cell efficiency. The energy transfer upconversion (ETU) is considered to be the dominant excitation mechanism for NIR UCL through analyzing the power dependencies, temporal evolutions and energy diagrams. Furthermore, we also studied the impacts of dopant contents on the luminescence dynamic process.

2. Experimental section

2.1 Sample preparation

 Y_2O_3 polycrystalline powder phosphors with the chemical formula $(Y_{1-x-y}Er_xYb_y)_2O_3$ (x = 0-12.5%; y = 0-20%) were



Fig. 2 (a) Normalized UCL spectra of Y_2O_3 :5%Er in NIR (black line) and VIS (red line) regions. Absorption curve of $Er^{3+} \, {}^4l_{15/2} \rightarrow {}^4l_{13/2}$ transition (magenta line). AM 1.5 solar spectrum (blue line) and spectral response of c-Si (purple dash line). (b) UCL spectra of Y_2O_3 :5% Er in the range of 780–1100 nm. The red solid line shows the full spectrum shape of ${}^4l_{11/2} \rightarrow {}^4l_{15/2}$ transition obtained using the Triax550 spectrometer. (c) The dependence of NIR UC intensities upon Er^{3+} concentration.



Fig. 3 UCL spectra of Y_2O_3 :5% Er, yYb under IR excitation. The inset shows the Yb³⁺ concentration dependence of the integrated NIR UC intensities.

synthesized *via* a sol–gel method. First, certain quantities of high-purity rare earth oxides Y_2O_3 (4 N), Er_2O_3 (5 N) and Yb_2O_3 (5 N) were dissolved in nitric acid (G.R.) with incessant stirring. An appropriate amount of de-ionized water was added to prepare the corresponding nitrate solution after the excess HNO₃ was removed by heating. After that, these obtained nitrate solutions were mixed and consecutively stirred according to relevant stoichiometric ratios. Subsequently, citric acid (the molar ratio of rare earth ions to citric acid was maintained at 1:2) and anhydrous ethanol were added into the above mixed solution and kept stirring for about 1 h. The homogeneous solution was dried in an oven until a xerogel was formed and then preheated at 600 °C for 5 h. Finally, the precursor was ground in an agate mortar and further calcined at 1600 °C for 5 h to obtain the final samples.

2.2 Measurements and characterization

The crystalline phase and structure were analyzed by X-ray power diffraction (XRD) in the range from 15° to 70° using a Bruker D8 Focus diffractometer with Cu-K α radiation. Steadystate UCL spectra were recorded on a Triax550 spectrometer for the NIR region and a FLS920 spectrometer for the VIS region pumped with a 200 mW 1532 nm diode laser. A powercontrolled 1450 nm diode laser was selected as the excitation source for measuring the power density dependent UC emission intensity. An optical fiber spectrometer (QEPro, Ocean Optics) also served to measure the UCL spectra. The temporal evolutions of fluorescence intensities were detected by a Triax550 spectrometer and recorded using a Tektronix digital oscilloscope (TDS3052) while an optical parametric oscillator (OPO) was used as the excitation source. The absorption curve of $\mathrm{Er}^{3+4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ transition was converted from the diffuse reflectance (DR) spectrum using the Kubelka–Munk formula. A UV-3600plus spectrophotometer (Shimadzu) equipped with an integrating sphere was used to detect the DR spectrum. All the measurements were carried out at room temperature.

3. Results and discussion

3.1 Structure properties

To analyze the phase purities of the as-prepared samples, Er^{3+} singly doped and Er^{3+}/Yb^{3+} codoped Y_2O_3 phosphors were examined by XRD. The XRD patterns are presented in Fig. 1(a). As can be seen, all the patterns can be accurately indexed to the normal data of cubic Y_2O_3 (JCPDS# 86-1107) and no obvious other diffraction peaks from impurities and raw materials can be observed. The diffraction peaks slightly shifted to higher angles (see Fig. 1(b)) with the increase of doping concentration due to the substitution of Y^{3+} (0.90 Å) by smaller ionic radii Er^{3+} (0.89 Å) and Yb^{3+} (0.86 Å). The above results indicate that Er^{3+} and Yb^{3+} are completely incorporated into the host lattices without an apparent change of crystal phase.

3.2 Spectral properties

To evaluate the possibility of Er^{3+} -doped Y_2O_3 as UC material for improving the efficiency of the c-Si solar cell, the normalized UCL and absorption spectra of Y_2O_3 :5% Er are plotted together with the AM 1.5 solar spectrum and the spectral response curve of c-Si, as shown in Fig. 2(a). The absorption band centers at 1530 nm correspond to the transition from the ground state ${}^4I_{15/2}$ to the lowest excited state ${}^4I_{13/2}$, which overlaps with the IR (1420–1800 nm) part of the solar spectrum. Four UC emission peaks observed around 560, 660, 820



Fig. 4 Double logarithmic plots of UC intensities versus laser power density in (a) Y₂O₃:5% Er and (b) Y₂O₃:5% Er, 1% Yb.



Fig. 5 Temporal evolution of the luminescence intensities from $Er^{3+4}l_{11/2}$ level under three-wavelength excitation in (a) Y_2O_3 :5% Er and (b) Y_2O_3 :5% Er, 1% Yb (linear scale).

and 1000 nm are assigned to the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}, {}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2},$ ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ transitions of Er³⁺, respectively. All the UC emission bands locate within the absorption range of the silicon solar cell, implying that they can all be absorbed by the c-Si solar cell. These characteristics signify that Er³⁺-doped Y₂O₃ has potential to be an UC layer to enhance the utilization of the solar spectrum by silicon solar cells. It is worth noting that the VIS and NIR UCL spectra were recorded on two different detectors and were normalized individually. In order to compare the relative intensities of distinct emission bands, an optical fiber spectrometer (QEPro high performance, Ocean Optics) was employed to monitor the total emission bands simultaneously (shown in Fig. 2(b)). Unfortunately, only the high-energy portion of the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ transition (black solid line) can be detected because the cutoff wavelength of our fiber spectrometer is around 980 nm. Nevertheless, it is still easy to recognize that the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ emission is the dominant UC emission and the ratio of its intensity to the overall UC intensity is approximately 99%. In other words, the UCL band around 1000 nm makes the most important contribution for the enhancement of solar spectral utilization. Fig. 2(c) shows the dependence of the NIR UC intensity on Er³⁺ concentration. The UC intensity at 1000 nm increases first with increasing Er³⁺ concentration and reaches a maximum value at 5%, and then decreases for higher Er³⁺ contents due to concentration quenching.

However, the emission efficiency of the ${}^{4}I_{11/2}$ level varies from around 100% to 10% or much lower in different host materials. It will remain at a high value in host materials with low phonon energy such as fluorides, halides and sulfides because more than six phonons are needed to make up the energy gap (~3600 cm⁻¹). Comparatively, it usually presents a low value in oxides or glasses due to the most population of ${}^{4}I_{11/2}$ non-radiative decay to the next lower excited state ${}^{4}I_{13/2}$ by multiphonon relaxation. In the Y₂O₃ matrix, only approximately 40% of the population of the ${}^{4}I_{11/2}$ state will radiate to the ground state and emit NIR emission centered at 1000 nm.³⁸ In contrast, the emission efficiency of Yb³⁺ ions can reach as high as 100% due to the enormous energy gap. Furthermore, highly efficient ET can take place from Er³⁺ to Yb³⁺ in view of their superb resonant energy levels.³⁹ One feasible method to enhance the NIR UCL intensity is to transfer the energy from the inefficient emission center to the efficient ones.

The NIR UCL spectra of Y₂O₃:5% Er, yYb under IR excitation are shown in Fig. 3, and the dependence of the integrated UC intensity upon Yb³⁺ concentration is shown in the inset of Fig. 3. Apparently, the optimal component for the strongest NIR UC emission is considered to be Y2O3:5% Er, 1% Yb and the NIR emission is enhanced 1.5 times compared with the sample without Yb³⁺. Even for the sample with only 0.5% Yb, the UC intensity is strengthened by a factor of 1.44, which reveals the effective ET from Er³⁺ to Yb³⁺ and the high emission efficiency of the $Yb^{3+2}F_{5/2}$ level. The decrease of the NIR UC intensity for higher Yb³⁺ concentrations might be caused by energy migration to defects and energy back transfer from Yb³⁺ to Er³⁺. In addition, one can also observe that the NIR UC emission spectral shape markedly changes with the increase of Yb³⁺ concentration, indicating that the NIR luminescence center ratio of $Er^{3+} {}^{4}I_{11/2}$ to Yb^{3+} ${}^{2}F_{5/2}$ is greatly affected by the content of Yb³⁺ ions.

3.3 Upconversion mechanisms upon ⁴I_{13/2} excitation

It is generally believed that the number of the IR photons (*n*) absorbed in the UC process could be confirmed by the dependence of the UCL intensity (*I*) *versus* the pump power (*P*) according to the equation: $I \propto P_{(IR)}^{n}$.⁴⁰ In double logarithmic coordinates (see Fig. 4), the slopes (*n*) for the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ (560 nm), ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ (660 nm), ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$ (820 nm), and ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ (1000 nm) transitions of Er^{3^+} for the Y₂O₃:5% Er sample are 3.83, 2.93, 2.09, and 1.87, respectively. As for

Table 1 Decay and rise times of the NIR emissions in Y_2O_3 :5% Er and Y_2O_3 :5% Er, 1% Yb upon different excitation wavelengths

	Ex (nm)	$\tau_{ m D} \ ({ m ms})$	$\tau_{\rm R} ({\rm ms})$
Y ₂ O ₃ :5% Er	1500	4.70	1.73
	980	2.87	_
	800	2.95	
Y ₂ O ₃ :5% Er, 1% Yb	1500	4.20	1.19
	980	1.99	_
	800	2.03	

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the doubly doped sample (Y₂O₃:5% Er, 1% Yb), the slopes for the emission bands at 560, 660, 820, and 1000 nm (${}^{4}I_{11/2} \rightarrow$ ${}^{4}I_{15/2}$ and ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$) are 3.88, 2.98, 2.01, and 1.98, respectively. These observations imply that UC emissions from ${}^{4}S_{3/2}$, ⁴F_{9/2}, and ⁴I_{9/2} levels are assigned to four-, three-, and twophoton processes, respectively. Moreover, the introduction of the Yb³⁺ ion does not affect the relationship between the 1000 nm UCL intensity and the excitation power. For two samples, they all exhibit a quadratic dependence of the NIR UCL on pump power, signifying that the population of Yb³⁺ ²F_{5/2} mainly comes from $\mathrm{Er}^{3+}\,{}^{4}I_{9/2}$ and ${}^{4}I_{11/2}$ through ET. It is well understood that the contribution of the Er^{3+ 4}S_{3/2} and ⁴F_{9/2} states to the Yb3+ UCL via ET can be neglected because the involved green and red levels are higher order UC processes. Herein, the ET from $\text{Er}^{3+} ({}^{4}\text{I}_{11/2} \rightarrow {}^{4}\text{I}_{15/2})$ to $\text{Yb}^{3+} ({}^{2}\text{F}_{5/2} \leftarrow {}^{2}\text{F}_{7/2})$ is generally believed to be the major excitation path of Yb³⁺ in consideration of their insignificant energy mismatch and the large population ratio between ${}^{4}I_{11/2}$ and ${}^{4}I_{9/2}$ (see Fig. 2(b)).

The temporal evolutions of the UC intensities from diverse energy levels will be conducive to unraveling UC mechanisms for different emitting states. Considering that NIR UCL represents about 99% of the total UCL, we will concentrate on investigating the dynamic process of NIR UCL in the following section. As shown in Fig. 5(a), the NIR fluorescence decays in Y_2O_3 :5% Er were measured upon pulsed excitation at three different wavelengths. The temporal evolutions of NIR luminescence were presented in linear scale to study the whole kinetic process. Under 1500 nm excitation, the ${}^{4}I_{11/2}$ UC emission exhibits a slow rise before the decay and the rising part starts from zero, which means that ETU is the dominant UC mechanism. The rise and decay times of the UC fluorescence curves upon IR pulsed excitation can be fitted by the equation:⁴¹

$$I(t) = A(e^{-t/\tau_{\rm D}} - e^{-t/\tau_{\rm R}})$$
(1)

where τ_D and τ_R represent the decay and rise times, respectively. A is a constant. The fitting results are listed in Table 1. In the case of low excitation densities and long-lived feeding states, $\tau_{\rm D}$ strongly depends on the lifetimes of the donor and acceptor involved in the ETU process. In addition, $\tau_{\rm R}$ is mainly influenced by the lifetime of the emitting level. In order to identify whether the rise is caused by the MPR process from the 4I9/2 level, the luminescence decay curves of the $^4I_{11/2}$ level under direct excitation into $^4I_{9/2}$ and $^4I_{11/2}$ states were also measured and shown in Fig. 5(a). They both show immediate decay processes, indicating that the rising process under 1500 nm excitation is due to ETU. Moreover, these two decay curves almost coincide, which signifies that the ${}^{4}I_{9/2}$ can rapidly non-radiate to the ⁴I_{11/2} level due to the small energy gap and relatively large phonon energy in Y₂O₃. Furthermore, it needs to be mentioned that the $({}^{4}I_{13/2}, {}^{4}I_{13/2}) \rightarrow$ $({}^{4}I_{15/2}, {}^{4}I_{11/2})$ UC mechanism is impossible due to the large energy mismatch (~3000 cm⁻¹).²⁵ As shown in Fig. 5(b), an analogous temporal evolution can be observed for the Y₂O₃:5% Er, 1% Yb sample except for the different rise and decay times, suggesting that the introduction of Yb³⁺ does not influence the UC mechanism upon IR excitation.

The simplified energy level scheme with the dominant NIR UCL and the proposed UC mechanism are shown in Fig. 6. First, the Er^{3+} ions are excited to the ${}^{4}\text{I}_{13/2}$ level upon IR excitation through ground state absorption. The higher excited state $({}^{4}\text{I}_{9/2})$ can be populated primarily by the $({}^{4}\text{I}_{13/2}, {}^{4}\text{I}_{13/2}) \rightarrow ({}^{4}\text{I}_{15/2}, {}^{4}\text{I}_{9/2})$ process. The radiative transition $({}^{4}\text{I}_{9/2} \rightarrow {}^{4}\text{I}_{15/2})$ produces the UC emission centered at 820 nm. As discussed above, the fast and efficient MPR process makes the population of ${}^{4}\text{I}_{9/2}$ almost relax down to the ${}^{4}\text{I}_{11/2}$ state,



Fig. 7 Temporal evolution of the NIR UC emission in (a) Er^{3+} -doped and (b) Er^{3+}/Yb^{3+} codoped Y_2O_3 for different dopant concentrations upon pulsed excitation at 1500 nm.

Table 2 Decay and rise times of the NIR emissions in $Y_2O_3{:}xEr$ and $Y_2O_3{:}5\%$ Er, yYb series of samples upon 1500 nm excitation

Y ₂ O ₃ :xEr			Y ₂ O ₃ :5% Er, <i>y</i> Yb		
x (%)	$\tau_{\rm D} ({\rm ms})$	$\tau_{\rm R} ({\rm ms})$	y (%)	$\tau_{\rm D} \ ({\rm ms})$	$\tau_{\rm R} ({\rm ms})$
2.5	5.71	2.15	0	4.70	1.73
5	4.70	1.73	0.5	4.44	1.38
7.5	3.14	1.06	1	4.20	1.19
10	2.09	0.58	3	3.96	0.84
12.5	1.50	0.36	5	3.86	0.65

from where the most intense UCL centered at 1000 nm generates. Nevertheless, the emission efficiency of the ${\rm Er}^{3+}$ ${}^{4}I_{11/2}$ level in trace doped Y_2O_3 is only ~45%, ten percent of which will radiate to the ${}^{4}I_{13/2}$ state. In other words, most of the population of the ${}^{4}I_{11/2}$ level is wasted. In contrast, the emission efficiency of Yb^{3+} is high due to the tremendous energy gap. After codoping Yb^{3+} ions, the ${\rm Er}^{3+}$ ions in the ${}^{4}I_{11/2}$ levels can transfer their energy to Yb^{3+} in the ground state followed by the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ radiative transition at ~1000 nm. Thereby, the NIR UCL could be boosted by the replacement of inefficient ${\rm Er}^{3+}$ with the efficient Yb^{3+} .

3.4 Dopant concentration dependence of the UC dynamics

It is widely known that energy transfer is closely related to the dopant concentration. Therefore, the NIR UCL decay curves were measured (Fig. 7) for different doping concentrations to further comprehend the UCL dynamic process. The decay curves are fitted according to eqn (1) and the obtained rise and decay times are listed in Table 2. The decrease of the rise time along with the increase of Er^{3+} concentration in

Table 3 Lifetimes of ~1500 nm and ~1000 nm emissions under direct excitation in Y_2O_3 :xEr and Y_2O_3 :5% Er, yYb samples

V O •rFr	Lifetime (ms)		$Y_2O_3:5\%$	Lifetime (ms)	
$\frac{1}{x}(\%)$	${}^{4}I_{13/2}$	${}^{4}I_{11/2}$	$\frac{EI, yID}{y(\%)}$	${}^{4}I_{13/2}$	${}^{4}I_{11/2} + {}^{2}F_{5/2}$
0.1	9.42	2.70	0	8.97	2.87
2.5	11.51	2.95	0.5	9.09	2.39
5	8.97	2.87	1	8.82	1.99
7.5	5.07	2.23	3	8.90	1.33
10	2.94	1.57	5	9.30	1.03
12.5	1.84	1.17			

Er³⁺ singly doped samples reflects the nature of the rapid energy migration and high population density of the ⁴I_{13/2} intermediate level in the initial state. The higher Er³⁺ concentration shortens the average spatial distance between two Er³⁺ ions in the ⁴I_{13/2} excited state and promotes the generation of energy transfer upconversion.41 However superfluous Er3+ ions will accelerate energy migration to defects and impede the generation of UCL. The decay time also exhibits a monotonous decline when the Er³⁺ concentration increases, which can be ascribed to concentration quenching. As the Yb³⁺ concentration increases in doubly doped samples, the abatement of the rise time reveals that the average lifetime of NIRemitting centers is shortened because of the shorter radiative lifetime of $Yb^{3+}\ ^2F_{5/2}$ than that of $Er^{3+}\ ^4I_{11/2}.^{42}$ It is usually agreed that a small amount of Yb³⁺ codoping will hardly affect the lifetime of $Er^{3+4}I_{13/2}$ owing to the similar ionic radii and the characteristics between rare earth elements. Hence, the decay time should be approximately the same in doubly



Fig. 8 The fluorescence decay curves of (a and c) ~1500 nm and (b and d) ~1000 nm emissions for different dopant concentrations upon direct excitation in singly and doubly doped samples, respectively.

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doped samples under 1500 nm excitation, because the donor and acceptor are both Er^{3+} ions in the ${}^{4}I_{13/2}$ level. In Fig. 7(b), the curves of the decay process are almost parallel, implying that their decay rates are similar and roughly equal to twice that of the ${}^{4}I_{13/2}$ level. However, the fitting results of decay time (Table 2) show a slight drop on increasing Yb³⁺ concentration. We consider that the reason for this phenomenon is that the pulse excitation density is not low enough and some fast decay processes of the ${}^4\mathrm{I}_{13/2}$ level may exist. The fluorescence decay curves of ~1500 nm and ~1000 nm emissions (Fig. 8) upon direct excitation into the emitting states were also measured to acquire useful information for studying the UC dynamics. The corresponding lifetimes are collected in Table 3. From Fig. 8(a and c) one can observe that the lifetime of the ${}^{4}I_{13/2}$ level is strongly related to Er^{3+} concentration and is independent of the incorporation of Yb³⁺ as previously expected. Additionally, the decay curves deviate from the single exponential function except for the 0.1% Er^{3^+} , which reflects the existence of some fast decay processes under \sim 1500 nm excitation in this work. Both Er³⁺ and Yb³⁺ contents can influence the decay rate of NIR-emitting levels due to energy transfer and rapid energy migration, as shown in Fig. 8(b and d). These down-conversion lifetimes exactly indicate the validity of analyses about UC dynamics mentioned above.

4. Conclusion

A series of Er³⁺ and Yb³⁺ doped Y₂O₃ UC phosphors with various doping concentrations were synthesized by a sol-gel method. Unlike the extensive studies about the VIS UCL characteristics of Y₂O₃:Er³⁺/Yb³⁺ upon 980 nm excitation, here we investigated the IR to NIR UCL properties. Yb³⁺ ions were doped as activators rather than sensitizers. For the optimum Er^{3+} singly doped concentration (5%), 99% of the overall UCL comes from the ⁴I_{11/2} emitting state under IR excitation. The ~1000 nm NIR UC emission intensity increased 1.5 times under the circumstance of 1% Yb3+ codoping. The energy loss caused by the MPR process from the ${}^{4}I_{11/2}$ level was mitigated via introducing Yb³⁺ ions as highly efficient NIR emission centers, which was believed to be the reason for the enhancement of NIR luminescence. The ETU is the dominant excitation mechanism for the NIR UCL. Concentration dependencies indicate that the optimization of concentration is necessary to keep a balance between helpful ETU and harmful quenching. The present results may be beneficial to the enhancement of IR to NIR UCL in host materials with large phonon energies.

Conflicts of interest

The authors declare no competing financial interest.

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