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Up-conversion luminescence in LaF₃:Ho³⁺ via two-wavelength excitation for use in solar cells

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An efficient broadband excited near-infrared to visible up-conversion is observed in LaF_3 :Ho³⁺ as the result of a two-wavelength excitation. The visible up-conversion emission intensity is greatly enhanced upon simultaneous excitation at 970 nm and 1150 nm, due to an energy transfer up-conversion mechanism. Multi-wavelength excitation based on the ground-state absorption, excited-state absorption, and phonon-coupled absorption of rare-earth ions results in an efficient broadband excited up-conversion emission, which may provide a new approach to fully harvest NIR solar energy and has potential application in solar cells.

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1 Introduction

Photon up-conversion (UC) from the near-infrared (NIR) to visible light in rare-earth (RE) doped materials has generated tremendous research interest, much of it focused on applications including photovoltaics, color displays, and biological imaging.1-6 The idea of adding an UC layer at the rear face of a photovoltaic device is very promising for enhancing the conversion efficiency of solar cells.7 However, the efficiencies of UC solar cells obtained experimentally have been extremely low and these merely serve as a proof of principle. The problem is that the efficiency of UC is very low, and the excitation spectral region is very narrow, in contrast to the solar spectrum, due to the nature of the 4f-4f transitions in RE ions. However, in solution, UC becomes broadband.8,9 Recently, Zou et al. reported the use of a cyanine dye molecule that enables the broadband excitation of NaYF₄ nanoparticles co-doped with Yb³⁺ sensitizer and Er³⁺ activator ions due to an energy transfer between the dye and Yb³⁺ ions.⁸ However, indirect excitation through heterogeneous energy transfer suffers from competitive energy loss. Moreover, the poor photostability of the dye hinders its application for long-term solar irradiation.¹⁰ Alternatively, Chen et al. demonstrated that broadband NIR photons excited to the visible-NIR region are up-converted due to a combination of the absorption bands of different RE ions

through core-shell nanofabrication, *i.e.*, $Er^{3+}:NaGdF_4@Ho^{3+}:NaGdF_4@NaGdF_4.$ ¹¹ However, it's hard to fully harvest solar energy, which has a continuous energy distribution, due to the discrete characteristic absorptions of RE ions. Moreover, heterogeneous doping will inevitably cause detrimental energy transfers between RE ions. Hence, it's necessary to find a new way to realize broadband excitation aimed at the complete utilization of solar energy.

Moreover, an up-converted emission with a high conversion efficiency is necessary for practical applications. One approach is to use multi-wavelength excitation. Energy transfer UC (ETU) between excited neighboring ions and excited-state absorption (ESA) can enhance the UC efficiency by decreasing the losses due to energy mismatches, in contrast to using a single wavelength. The creation of a blue-green UC laser has been achieved using a two-wavelength (one red and one NIR) pumping technique.¹²

In the case of solar energy, solar pumping can be considered as multi-wavelength excitation because the different wavelengths of light arrive at the same time. Herein, we propose a new strategy to enhance the UC emission efficiency and realize broadband excitation using RE ions through simultaneous two or multi-wavelength excitation. Ho³⁺ is used as an example RE ion, since its energy levels possess the ability to realize both NIR excitation and visible UC luminescence. Moreover, Ho³⁺ has relatively long-lived ⁵I₇ and ⁵I₆ excited states that can act as population reservoirs for UC processes.13 LaF3, which has a phonon cutoff frequency of approximately 350 cm⁻¹ and is a typical laser medium, is chosen as a host for efficient UC.14 We show that, by excitation with 970 nm and 1150 nm light, an intensive visible UC luminescence can be achieved. The UC mechanisms are elucidated through power dependence studies and lifetime measurements on samples under singlewavelength and two-wavelength excitation. Our approach, which possesses the features of broadband absorption and

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simultaneous excitation, is a new way to achieve efficient broadband excited UC emissions, and has the potential to enhance the conversion efficiency of solar cells.

2 Experimental

2.1 Preparation of LaF₃:Ho³⁺ phosphors

LaF₃:Ho³⁺ (1, 5, 10 and 50 mol%) phosphors were prepared using a solid-state reaction method under a N₂ gas atmosphere. Stoichiometric amounts of LaF₃ (99.99%), HoF₃ (99.99%), and 10 wt% NH₄HF₂ (98%) were mixed, ground together, and then sintered at 1100 °C for 3 hours.

2.2 X-ray diffraction (XRD) analysis

XRD analysis was carried out using a RIGAKU D/MAX 2550/PC diffractometer (Japan) with a slit of 0.02° at a scanning speed of 5° min⁻¹ using Cu K_{α} radiation ($\lambda = 1.5406$ Å).

2.3 UC luminescence spectroscopy

The NIR excited UC emission and lifetime measurements of the phosphors were performed using an Edinburgh Instruments FLS900 steady/transient-state fluorescence spectrometer at room temperature. For the 970 nm excited UC emissions, a continuous wave semiconductor laser diode emitting at 970 nm was used. For the 1150 nm and two-wavelength (970 nm and 1150 nm) excited UC emissions and lifetime measurements, a tunable optical parametric oscillator (OPO) pumped using the third harmonic wavelength (355 nm) of a Q-switched YAG:Nd laser. The laser was tuned to 1150 nm in order to excite the samples with a 5 ns pulse at a repetition rate of 10 Hz.

3 Results and discussion

3.1 Crystal structure

XRD patterns showing reflections representative of pure phase LaF_3 are observed when different concentrations of Ho^{3+} ions (0, 1, 5, 10 and 50 mol%) are doped into the samples (Fig. 1).



Fig. 1 The XRD patterns of Ho^{3+} (0, 1, 5, 10 and 50 mol%) doped LaF₃ and the standard crystalline phase of LaF₃ (PDF no. 32-04833).

3.2 UC upon 970 nm excitation

During 970 nm laser excitation at room temperature, green emissions were observed from the Ho³⁺ doped LaF₃ powders. The intensity of these up-converted emissions depend on the doping concentration of Ho^{3+} , as shown in Fig. 2(a). The characteristic green and red emissions can be ascribed to the ${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺, respectively. The intensities of both the green and red emissions decreased as the Ho³⁺ concentration increased from 1 mol% to 50 mol%, which implies that there is an ever-present concentration quenching effect. Quantitative comparisons of the green and red emission intensities *versus* the concentration of Ho³⁺, are shown in Fig. 2(b). A sharper decrease of the green emission compared to the red emission causes a decrease of green/red intensity ratio. This may be due to the energy migration and loss of intra ions. In an attempt to analyse the energy migration process, we measured the power dependent UC intensity in LaF_3 :Ho³⁺ (1 mol%), as shown in Fig. 2(c). The plots of the green and red emissions versus the laser power exhibit gradients of 1.48. This indicates that more than one photon is responsible for populating the green and red emission levels. We suggest that the 970 nm laser excites the phonon-coupled levels of the ⁵I₆ state first, as shown in Fig. 2(d),¹⁵ followed by a second sequential photon excitation to the ⁵F₄ and ⁵S₂ levels, which is responsible for generating the up-converted green emission and was previously confirmed in a Lu₃Al₅O₁₂ host.¹⁶ For the red emission, population of the ${}^{5}F_{5}$ level by multiphoton nonradiative relaxation from the ⁵F₄ and ⁵S₂ levels is not possible because of the large energy gap (\sim 3000 cm⁻¹) compared to the maximum phonon energy of LaF_3 (~350 cm⁻¹).¹⁵ This could be confirmed by spectroscopy, which demonstrates that red emission is much weaker than green emission in the LaF₃ powders doped with lower concentrations of Ho³⁺, while the inverse intensity ratio was found in Lu₃Al₅O₁₂.¹⁶ In our case, the green/red intensity ratio decreases when the doping



Fig. 2 (a) UC emission spectra of Ho^{3+} (1, 5, 10 and 50 mol%) doped LaF₃ upon 970 nm excitation. (b) Plots of the green and red emission intensities and the green/red intensity ratio *versus* the concentration of Ho^{3+} . (c) The power dependent green and red emission intensity changes in LaF₃:Ho³⁺ (1 mol%). (d) An energy level diagram showing the 970 nm excited UC mechanism of Ho³⁺ in LaF₃.

concentration of Ho³⁺ increases. This implies that cross relaxation occurs (CR1: ${}^{5}F_{4}$, ${}^{5}S_{2}$ + ${}^{5}I_{8} \rightarrow {}^{5}I_{4}$ + ${}^{5}I_{7}$), as shown in Fig. 2(d), which results in a decrease of the green emission.¹⁷ Since the ${}^{5}I_{7}$ level possesses a longer lifetime of >10 ms, subsequent up-converted red emission occurs due to the excited state absorption of one 970 nm photon.¹⁸ In addition, the concentration dependent red emission quenching may be due to a sequential non-radiative relaxation from the ${}^{5}F_{5}$ level to the ${}^{5}I_{5}$ level followed by cross relaxation (CR2: ${}^{5}I_{5} + {}^{5}I_{8} \rightarrow {}^{5}I_{7} + {}^{5}I_{7}$).¹⁷

3.3 UC upon 1150 nm excitation

Upon 1150 nm excitation, the same transitions of Ho³⁺ (${}^{5}S_{2} \rightarrow$ ${}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$) are observed compared to the case of 970 nm excitation, however, the red emission is more intense than the green emission, as shown in Fig. 3(a). The green and red emissions have optimum intensities at 5 mol% Ho³⁺ (Fig. 3(b)). When the Ho³⁺ concentration is increased above this value, the UC emissions becomes less efficient. This can be explained by the appearance of concentration quenching based upon cross relaxations between neighbouring ions. The transient evolution of the emission helps us to achieve a better understanding of the UC emission mechanism. As shown in Fig. 3(c) and its inset, the transient evolution of the emission at 650 nm in LaF₃:Ho³⁺ (5 mol%) exhibits an initial rise before decaying. If sequential two-photon excitation was the only mechanism in UC, then the red emission should not demonstrate any rise time because the pulse width of the excitation laser is only 10 ns. The initial rise is related to a non-radiative phonon relaxation that causes population of the ⁵F₅ energy level, even during the absence of a laser pulse, as depicted in Fig. 3(d). The decay section could be fitted using a tri-exponential equation corresponding to decay mechanisms occurring via different depopulation channels. The average decay time was determined using the following equation:19



Fig. 3 (a) UC emission spectra of Ho^{3+} (1, 5, 10 and 50 mol%) doped LaF₃ upon 1150 nm excitation. (b) Plots of the green and red emission intensities *versus* the concentration of Ho^{3+} . (c) Transient evolution of the red emission (650 nm) under 1150 nm excitation, with the data fitted in order to obtain the average decay time in LaF₃:Ho³⁺ (5 mol%). The inset shows an expansion of the initial emission. (d) Energy level diagram showing the 1150 nm excited UC mechanism of Ho³⁺ in LaF₃.

$$\tau_{\text{decay}} = \sum_{i=1}^{n} A_i \tau_i^2 / \sum_{i=1}^{n} A_i \tau_i$$
(1)

where A_i and τ_i are the amplitude and lifetime corresponding to the level of the depopulation channel *i*, respectively, and n = 3. The calculated average decay time is equal to 1.2 ms. For the green emission, its relative weak intensity limits the measurement of the transient emission. A possible three-photon related UC process, along with the cascade relaxation ${}^5G_5 \rightarrow {}^5F_3 \rightarrow {}^5S_2$, is shown in Fig. 3(d), which is in agreement with the transition probability distribution observed from the emission spectra.¹⁵

3.4 UC upon two-wavelength co-excitation (970 nm + 1150 nm)

Two laser beams were focused onto the same point of a sample to simulate the principle of broadband excitation. The characteristic green and red emissions can be ascribed to the ⁵F₄, ${}^5S_2 \rightarrow {}^5I_8$ and ${}^5F_5 \rightarrow {}^5I_8$ transitions of Ho³⁺ and are similar to those observed in the single-wavelength excitation cases (Fig. 2(a) and 3(a)). Both the ${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ emission are greatly enhanced in comparison with the singlewavelength excitation cases, as shown in Fig. 4(a). Fig. 4(b) shows the enhancement of the intensity ratio between the twowavelength excitation case and the single-wavelength excitation cases, i.e., 5.4 and 25-fold enhancements for the green emission and 43.6 and 38.6-fold enhancements for the red emission for the 970 nm and 1150 nm excitation, respectively. As shown in Fig. 4(c), the transient emission at 650 nm in LaF_3 :Ho³⁺ (1 mol%) upon co-excitation exhibits much longer rise and decay times compared to the 1150 nm excitation. Typically a delayed rise time is a clear indicator of an energy transfer process. Thus, we can attribute this behavior to the preferential population of the ⁵F₅ level of neighbouring ions, which are heterogeneously excited, as shown as the ETU process in



Fig. 4 (a) UC emission spectra of LaF₃:Ho³⁺ (1 mol%) upon 970 nm, 1150 nm and two-wavelength (970 nm + 1150 nm) excitation. (b) Intensity ratios of the two-wavelength excited green and red emissions compared to the single-wavelength excited emissions. (c) Transient evolution of the red emission (650 nm) under two-wavelength excitation and data fitting in order to determine the rise time and average decay time in LaF₃:Ho³⁺ (1 mol%). (d) An energy level diagram showing the two-wavelength excited UC mechanism of Ho³⁺ in LaF₃.

Fig. 4(d),^{20,21} which is different to the ESA populations in the single-wavelength excitation cases (Fig. 2(d) and 3(d)). A pair of Ho³⁺ ions, which are initially both excited to the intermediate ${}^{5}I_{6}$ level; in a second step one Ho³⁺ ion non-radiatively transfers its excitation energy to its partner which is thus excited to the ${}^{5}F_{5}$ level in the visible. Considering an ion pair with three levels, 1, 2 and 3, which correspond to the ${}^{5}I_{8}$, ${}^{5}I_{6}$, and ${}^{5}F_{5}$ levels, respectively, the transient process could be modeled as the difference between two exponential components as follow:^{21,22}

$$I(t) = k(\exp(-(2W_2 + W_t)t) - \exp(-W_3t))$$
(2)

where k is a constant and W_2 and W_3 are the intrinsic single ion decay rate constants of levels 2 and 3, respectively. W_t is the rate constant of the energy transfer. The decay rate is determined by the lesser rate of W_3 (or $2W_2 + W_t$), while the greater of the two rates describes the rise. The average rise time of in the twowavelength excitation case is calculated to be 0.77 ms, while the average decay time is 13 ms. In the 1150 nm excitation case, the average decay time is 1.1 ms, while the rise time is too short to be calculated. Similar transient behaviour was observed for the green emission, where the average rise time and decay time are 0.36 ms and 5.2 ms, respectively, upon two-wavelength excitation. Thus, as shown in Fig. 4(d), the ETU process ${}^{5}I_{6}$ + ${}^{5}I_{6} \rightarrow {}^{5}I_{8} + {}^{5}F_{4}$, ${}^{5}S_{2}$, can be attributed to the green emission mechanism. The shorter rise time of green emission compared to red emission, is in agreement with the emission intensity enhancement. The reason for this is that for a higher emission efficiency, photons have to interact with the medium for a longer time.22

In order to obtain further insight into the reasons for the large emission enhancement from single-wavelength to twowavelength excitation, we further compared the UC luminescence dynamic processes of the two-wavelength excitation in different LaF₃:Ho³⁺ samples (1 mol%, 10 mol%, and 50 mol%), as shown in Fig. 5. The relatively strong emission at 650 nm was chosen as a typical example in order to analyze the mechanism by transient evolution. It can be clearly observed that the initial state of the transient evolution changed from a slow rise to a sharp decay with increasing Ho³⁺ concentration. In addition, there is an intermediate state, which combines the sharp decay and slow rise in the 10 mol% Ho³⁺ doped LaF₃ sample. This implies the coexistence of ETU and ESA in the UC process. ETU is the most efficient of the various two-photon UC processes because it is closest to the full resonance case.15 Thus, ETU processes show greater enhancements in their UC emissions than ESA processes, which is in accordance with the enhancement of the ratio of the emission intensity from 1 mol% to 50 mol% Ho³⁺ doping (see inset). Moreover, an apparent enhancement could be observed from single-wavelength to twowavelength excitation in LaF₃:Ho³⁺ (50 mol%) despite only ESA participating in the population of the ⁵F₄, ⁵S₂ and ⁵F₅ states. This is because the excitation energies of 1150 nm and 970 nm are in good agreement with the energies the ${}^{5}I_{8} \rightarrow {}^{5}I_{6}$, and $^5I_6 \rightarrow \ ^5F_{4,5}, \ ^5S_2$ transitions of $\text{Ho}^{3+},$ respectively, which decreases the energy mismatch of the two-photon UC process.



Fig. 5 Transient evolution of the red emission (650 nm) under two-wavelength excitation in the LaF₃:Ho³⁺ samples (1 mol%, 10 mol%, and 50 mol%). The inset shows the red emission intensity ratio between the two-wavelength excited case and 1150 nm excited case vs. the concentration of Ho³⁺.

3.5 Broadband UC based on multi-wavelength co-excitation

In principle, the solar spectrum is composed of numerous continuously distributed single wavelengths. Hence, the concept of a broadband UC based on multi-wavelength excitation leads to solar pumping as a possible approach for efficient UC. As illustrated in Fig. 6, NIR solar energy represented by the blue solid line could be absorbed by the ${}^{5}I_{6}$ and ${}^{5}I_{5}$ levels of Ho³⁺ for further excitation to higher energy levels in order to realize visible UC emission.¹⁵ In addition, the blue dotted lines show the NIR energy harvested *via* ESA and phonon-coupled absorption (PCA), which works the same way as in the 970 nm excited UC case (Fig. 2). With the simultaneous arrival of solar



Fig. 6 Schematic illustration of the broadband NIR harvesting of solar energy and subsequent visible emission after up-conversion by Ho³⁺. The solid yellow line shows part of the AM1.5 terrestrial solar spectrum. The solid red line shows visible up-conversion emission of Ho³⁺. The solid blue line shows the ground-state absorption (GSA) bands of Ho³⁺ corresponding to ⁵I₈ \rightarrow ⁵I₅, ⁵I₆ transitions. The blue dotted lines show the phonon-coupled absorption (PCA) and excited-stated absorption (ESA) bands.

energy to the material surface, the aforementioned processes work together to harvest a broad band of light and emit efficiently. Recently reported results concerning the enhanced photocatalytic activity of $YF_3:Yb^{3+},Tm^{3+}/TiO_2$ core-shell nanoparticles under NIR solar irradiation may be an example that shows the feasibility of using a broadband solar pumping method.²³

4 Conclusions

In conclusion, an efficient broadband excited NIR to visible upconversion was demonstrated using the two-wavelength excitation of LaF_3 :Ho³⁺. Efficient visible emissions were achieved by two-step population processes, *i.e.*, the ground state absorption occurs through 970 nm and 1150 nm excitation and then an energy transfer up-conversion occurs between neighbouring Ho³⁺ ions. Successful modeling of the broadband excited upconversion has been achieved through numerous continuously distributed single wavelength simultaneous excitations, describing a feasible concept for solar pumping up-conversion. This may find potential applications in solar cells to improve the conversion efficiency and should be useful for the design of UC converters containing other RE active centers.

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