

Enhanced cooperative near-infrared quantum cutting in Pr³⁺-Yb³⁺ co-doped phosphate glass*

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Pr³⁺ and Yb³⁺ co-doped phosphate glasses are prepared to study their optical properties. Excitation and emission spectra and decay curves are used to characterize their luminescence. We demonstrate that upon excitation of Pr³⁺ ion with one high energy photon at 470 nm, two near-infrared (NIR) photons are emitted at 950–1100 nm (Yb³⁺:²F_{5/2} → ²F_{7/2}) through an efficient cooperative energy transfer (CET) from Pr³⁺ to Yb³⁺. The maximum energy transfer efficiency (ETE) and the corresponding quantum efficiency approach up to 90.17% and 190.17%, respectively. The glass materials might find potential application for improving the efficiency of silicon-based solar cells.

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In silicon solar cells, a single electron-hole pair is generated when the incoming photon energy is above 1.1 eV with the excess energy lost as heat. Thermalization losses can be reduced if the absorbed ultraviolet (UV) or visible (VIS) photons can be split into two or more near-infrared (NIR) photons. This kind of two-photon luminescence phenomenon by absorbing one high energy photon is called quantum cutting (QC)^[1-4]. In this case, the QC luminescence process can greatly enhance the solar cell efficiency. The visible QC has received considerable attention due to its potential application in silicon-based solar cells.

Rare earth (RE) ions with abundant energy levels are good candidates for QC. Yb³⁺ ions have a relatively simple energy level structure, and especially the energy level difference of Yb³⁺ is well matched with the bandgap of silicon solar cell. Hence, RE³⁺/Yb³⁺ co-doped downconversion (DC) phosphates which can modify solar spectra by cooperative energy transfer (CET) are suitable for greatly improving the conversion efficiency of Si solar cell. Recently, several groups reported DC from UV or VIS light to NIR light using rare earth ion pairs^[5-11]. Vergeer et al^[9] presented the experimental evidence for QC DC by CET from one Tb³⁺ ion to two Yb³⁺ ions in the Yb_xY_{1-x}PO₄: Tb³⁺ powder. Yb³⁺ ions can emit two NIR photons at 980 nm via the excitation of one Tb³⁺ ion with one blue photon. In addition, Zhang et al^[3,10,11] reported

NIR QC downconversion in RE³⁺/Yb³⁺ (RE:Pr, Tb and Tm) co-doped oxide powders on excitation of RE³⁺ with a blue photon, where two NIR photons (980 nm) could be emitted by Yb³⁺ through an efficient cooperative energy transfer from RE³⁺ to Yb³⁺.

Up to now, NIR QC phenomenon has been identified in many systems including powder phosphors^[7,9,10], crystals^[11,12], tri-nuclear complex^[13], thin-film phosphors^[14], glasses^[15,16] and glass ceramics^[6]. Glass has the advantages of low cost, easy preparation and high doping concentration of RE ions. Phosphate glasses were selected due to their excellent dissolvability and high transmittance of RE³⁺ ions in the UV region. In this paper, we demonstrate the NIR QC involving the emission of two NIR photons of Yb³⁺ for each UV photon of Pr³⁺ absorbed in phosphate glasses by CET. The results might be a good way to improve the efficiency of silicon-based solar cells.

The phosphate glasses used in this paper were prepared with the following composition of 50P₂O₅-45BaO-5Al₂O₃-0.5Pr³⁺- γ Yb³⁺ ($\gamma=0, 0.5, 1.0, 1.5, 2.0, 4.0, 6.0$) in mol% by the melting and quenching method using high-purity NH₄H₂PO₄, BaCO₃, Al(OH)₃, Pr₆O₁₁ and Yb₂O₃ as raw materials. Each batch of about 25 g was mixed homogeneously, and melted at 1300 °C for 30 min in corundum crucible in air. The melt was poured onto a brass plate, and then pressed to the thick-

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ness of about 2 mm with another brass plate. These glasses are circular in design with 4 cm diameter, a thickness of about 0.3 cm and good transparency. All these glasses were annealed at 400 °C for 2 h to remove thermal strains. For convenience, the samples are labeled as PYY (y = 0, 0.5, 1.0, 1.5, 2.0, 4.0, 6.0). The absorption spectra were measured by Perkin-Elmer Lamda 35 UV/VIS spectrophotometer. The excitation and emission spectra and the fluorescence decay curves in both visible and infrared regions were recorded by Hitachi F-4500 fluorescence spectrophotometer. All the measurements were carried out at room temperature.

Fig.1 presents the photoluminescence excitation (PLE) and photoluminescence (PL) spectra of PYY (y = 1.0) sample by monitoring the $^3P_0 \rightarrow ^3H_6$ transition of Pr^{3+} at 606 nm and the $Yb^{3+}: ^2F_{5/2} \rightarrow ^2F_{7/2}$ emission at 980 nm. In the PLE spectra (Fig.1(a)), three excitation bands centered at 445 nm, 470 nm, 482 nm are observed corresponding to the $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ transitions of Pr^{3+} , respectively. The excitation bands from Pr^{3+} in the PLE spectrum of the $Yb^{3+}: ^2F_{5/2} \rightarrow ^2F_{7/2}$ emission demonstrate the occurrence of energy transfer (ET) from Pr^{3+} to Yb^{3+} .

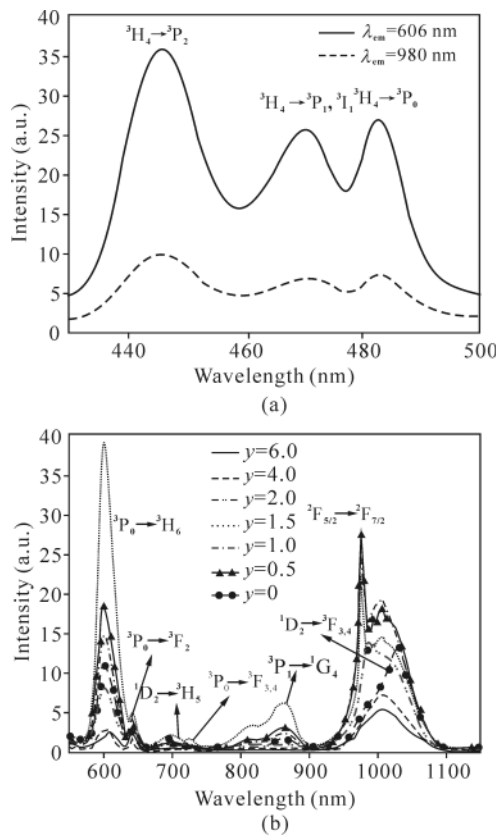


Fig.1(a) PLE spectra of the $Pr^{3+}: ^3P_0 \rightarrow ^3H_6$ emission at 606 nm; **(b)** Visible-NIR PL spectra of all studied glasses with 470 nm excitation

Excitation at 470 nm gives rise to emissions from Pr^{3+} to Yb^{3+} ions as shown in the PL spectra (Fig.1(b)). The peaks at

606 nm, 643 nm, 694 nm, 722 nm, 863 nm and 1030 nm in the region of 600–1100 nm are assigned to the electronic transitions of $^3P_0 \rightarrow ^3H_6$, $^3P_0 \rightarrow ^3F_2$, $^1D_2 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3F_{3,4}$, $^3P_1 \rightarrow ^1G_4$ and $^1D_2 \rightarrow ^3F_{3,4}$, respectively. Meanwhile, the characteristic emission band locates at 900–1100 nm corresponding to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb^{3+} ions. Also two peaks in the infrared region of Yb^{3+} emission can be shown as a sharper peak located at 980 nm and a broader peak centered at 1006 nm. From the comparison of the emission spectra in the visible region and the NIR region with 470 nm excitation, we find that the visible emission intensities of Pr^{3+} are significantly reduced with increase of Yb^{3+} contents ranging from 0 to 4.0 mol%, and especially the intensity of the $^3P_0 \rightarrow ^3H_6$ emission of Pr^{3+} decreases quickly with the incorporation of Yb^{3+} into samples. It is noted that the emission intensity of Yb^{3+} increases almost linearly with Yb^{3+} concentration up to 1.0 mol% at the cost of Pr^{3+} emission. It is another evidence of the cooperative ET from Pr^{3+} to Yb^{3+} . Significant emission quenching is observed when the concentration is higher than 1.0 mol%.

The experimental results above clearly show that ET by a cooperative mechanism is the dominant process. The possible DC mechanism is illustrated in Fig.2. From the schematic energy level diagram of the Pr^{3+}/Yb^{3+} system, we can confirm that NIR QC occurs at the 3P_0 level of Pr^{3+} . The $Pr^{3+}: ^3P_0 \rightarrow ^3H_4$ transition is located at the energy which is approximately twice the energy of $Yb^{3+}: ^2F_{5/2} \rightarrow ^2F_{7/2}$ transition, and Yb^{3+} has no other levels in the UV region. After excitation of $Pr^{3+}: ^3P_0$ level by 470 nm photons, the excited Pr^{3+} ion transfers its energy to two Yb^{3+} ions through a cooperative DC mechanism of $Pr^{3+}: ^3P_0 \rightarrow Yb^{3+}: ^2F_{5/2} + Yb^{3+}: ^2F_{7/2}$. Then the radiative transition of $Yb^{3+}: ^2F_{5/2} \rightarrow ^2F_{7/2}$ occurs, generating two 980 nm photons.

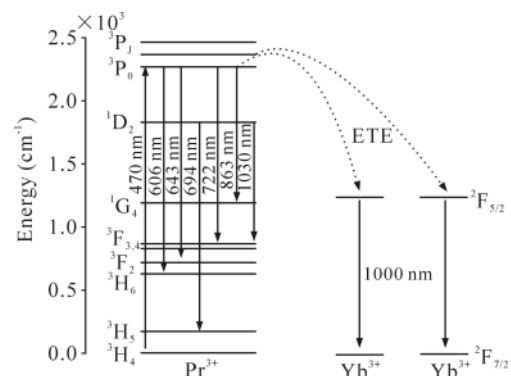


Fig.2 Schematic energy level diagram of Pr^{3+}/Yb^{3+} co-doped glasses with 470 nm excitation

The decay curves of all studied samples with 606 nm emissions under the excitation of 470 nm light are shown in Fig.3. When the ion concentration is large enough, energy transfer

appears, and the decay curves become non-exponential. The decay curve of the 0.6 mol% Pr³⁺ singly-doped glass exhibits a nearly single exponential decay with decay time of 88.91 μs. However, with the increase of the Yb³⁺ concentration from 0 to 6.0 mol%, the lifetime decreases rapidly from 88.91 μs to 12.68 μs. We fit the decay curves of all samples by equation

$$y = Ae^{-x/\tau} \quad (1)$$

where A is a constant of the first order fitting, x stands for wavelength, and τ represents the lifetime of all samples. Using this equation which is used to calculate the energy transfer efficiency (ETE), the efficiency of the energy transfer from the Yb³⁺ to quenching centers could be obtained from the luminescence decay curves of Yb³⁺ emission. When the Yb³⁺ content increases, the lifetime of Yb³⁺ becomes shorter, which verifies the Yb³⁺ concentration quenching process.

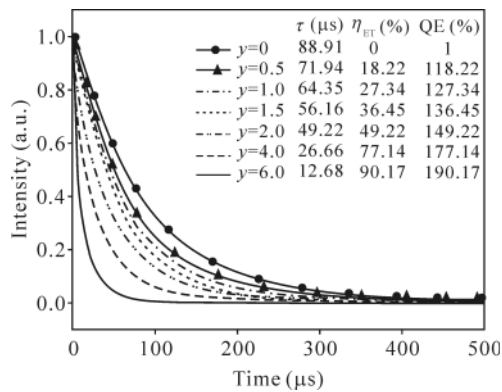


Fig.3 Decay lifetime of Pr³⁺:³P₀ → ³H₆ luminescence (606 nm) under excitation of 470 nm and corresponding ETE and QE of all studied glasses

Based on the decay curves, the ETE (η_{ET}) and the quantum efficiency (QE) are determined in Fig.3. The ETE is defined as the ratio of Pr³⁺ ions which are depopulated by ET to Yb³⁺ ions over the total number of Pr³⁺ ions excited. The total QE (η_{QE}) can be defined as the ratio of emitted photons to the photons which are absorbed, assuming that all excited Yb³⁺ ions decay radiatively. This assumption leads to an upper limit of the QE. By dividing the Pr³⁺ mean lifetime in the Pr³⁺/Yb³⁺ couple by the Pr³⁺ lifetime in the Yb³⁺ free glasses, the η_{ET} is obtained as a function of Yb³⁺ concentration^[1,9],

$$\eta_{ET} = \eta_{x\%Yb} = 1 - \frac{\int I_{x\%Yb} dt}{\int I_{0\%Yb} dt} \quad (2)$$

where I is the luminescence intensity as a function of time t , I_0 is the maximum of I , and x represents the Yb³⁺ concentration. The relationship between η_{ET} and η_{QE} can be taken as below^[7,9],

$$\eta_{QE} = \eta_{Pr}(1 - \eta_{ET}) + 2\eta_{ET} \quad (3)$$

where η_{Pr} stands for the Pr³⁺. Ignoring the non-radiative en-

ergy loss by defects and impurities, η_{Pr} is set to 1.

The lifetime of Pr³⁺ is determined by using the data in Fig.3, and the corresponding ETE and QE are also calculated. It is presented that the ETE increases and achieves a maximum value of 90.17 % when Yb³⁺ doping concentration equals 6.0 mol%. Supposing there is no loss of non-radiation by defects and impurities, the maximum QE of 190.17 % is obtained.

In summary, we conclude that phosphate glasses with Pr³⁺/Yb³⁺ as dopant ions are successfully prepared, and their optical properties are characterized. Upon excitation into ³P₀ level of Pr³⁺ at 470 nm, efficient energy transfer from Pr³⁺ to Yb³⁺ is observed. An efficient NIR QC in the studied glasses is demonstrated, which involves the conversion of the visible photon from Pr³⁺ into the NIR Yb³⁺ emission with the optimal QE of 190.17 %. These results indicate the potential prospect for enhancing efficiency of solar cells by downconversion.

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