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Competitive absorption of Eu^{3+} and Tb^{3+}codoped in $NaGd(PO_3)_4$ phosphors

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ABSTRACT

Energy transfer has been generally utilized for the sensitization of luminescence in phosphors. It is common that excitation of donor can be transferred efficiently to acceptor. However, energy transfer should be investigated in association with the transfer efficiency from donors to activators. To accomplish this, energy transfer from Gd^{3+} to Eu^{3+} and Tb^{3+} was investigated. It was found that the transfer efficiency from Gd^{3+} to Eu^{3+} is higher than that from Gd^{3+} to Tb^{3+} because there are less energy mismatches between the emission of Gd^{3+} and the absorption of Eu^{3+} than that between Gd^{3+} and Tb^{3+} in the host $NaGd(PO_3)_4$.

1. Introduction

Energy transfer from an excited center (energy donor) to an unexcited center (energy acceptor) is practically utilized for the sensitization of luminescence in phosphors to enhance the emission efficiency. For example, the 4f–5d transition of Ce^{3+} is often used to sensitize Tb^{3+} luminescence in phosphors for fluorescent tubes [1,2]. To increase the conversion efficiency of crystalline Si solar cells, investigations on the efficient downconversion energy transfer using Yb^{3+} as an acceptor have been done recently, such as the Pr^{3+}–Yb^{3+} couple codoped in the host SrF_2, [3] Er^{3+}–Yb^{3+} couple in $Cs_3Y_2Br_9$, [4] Tb^{3+}–Yb^{3+} couple codoped in the host YPO_4, [5] and Ce^{3+}–Yb^{3+} couple codoped in the host Y_2SiO_5 [6]. In $LiGdF_4$:Eu^{3+}, upon excitation of Gd^{3+} with a high-energy photon, two visible photons can be emitted by Eu^{3+} through an efficient two-step energy transfer from Gd^{3+} to Eu^{3+} with a quantum efficiency approaching 200 percent [7]. And the energy absorbed by Gd^{3+} excited with a $\lambda_{ex} = 273$ nm can be transferred simultaneously to three activators (Eu^{3+}, Tb^{3+} and Dy^{3+}) in the host $GdPO_4$ and a single-phase solid-state white light nanophosphor has been fabricated by triply doping the monoclinc $GdPO_4$ twined particles with appropriate concentration of Eu^{3+}, Tb^{3+} and Dy^{3+} [8].

As we have known, Gd^{3+} ion is often chosen to be used as a sensitizer because of its special energy levels. In our previous works, the polyphosphates $NaGd(PO_3)_4$ containing Gd^{3+} ions in the host was confirmed as a good host for rare-earth ions activated phosphors and the energy absorbed by Gd^{3+} in the host $NaGd(PO_3)_4$ can be transferred efficiently to Ce^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}, respectively [9–12]. Now that the excitation of donor can be transferred to different acceptors, respectively, it is necessary to investigate which acceptor can get more energy from donor when two or three activators are doped simultaneously in the same host for developing new phosphors with high luminescence efficiency. In order to study the competitive absorption phenomenon of two acceptors from one donor, the energy transfer processes from Gd^{3+} to Eu^{3+} and Gd^{3+} to Tb^{3+} ions in the host $NaGd(PO_3)_4$ were investigated respectively in present work.

2. Experimental

A series of polycrystalline samples of $NaEu_xGd_{(1-x-y)}Tb_y(PO_3)_4$ ($x = 0.01$–0.20, $y = 0.01$–0.20) were synthesized by a high temperature solid-state reaction methods. Stoichiometric amounts (Na/RE/P = 1:1:4) of analytical reagent grade Na_2CO_3, $NH_4H_2PO_4$ and 99.99% pure rare-earth oxides (Gd_2O_3, Tb_4O_7 and Eu_2O_3) were used as raw materials. The pulverous mixtures were ground in an agate mortar and then calcinated at 973 K (700 °C) for 40 h in a corundum crucible through a carbothermal reduction method for the formation of trivalent terbium (Tb^{3+}) [13].

The X-ray powder diffraction analyses were carried out with a Rigaku D/max 2200 vpc X-ray powder diffractometer (Cu Kα radiation, 40 kV, 30 mA) at room temperature (RT), and the data were collected with $2\theta = 10$–$60°$, step size = 0.02°.

The UV–visible luminescence spectra and luminescence decay curves at RT were recorded on an Edinburgh FLS 920 combined fluorescence lifetime and steady state spectrometer, which was equipped with a time-correlated single-photon counting (TCSPC) card. A 450 W xenon lamp was used as the excitation source for the UV–visible spectra and a blue-sensitive photomultiplier tube (R1527 PMT) was used for the emission spectra recording. The excitation light source for the determination of luminescence decay curves was provided by a 60 W µF flash lamp with a pulse width of 1.5–3.0 µs.

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3. Results and discussion

3.1. X-ray powder diffraction of $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$

In order to characterize the phase purity of the samples, X-ray powder diffraction (XRD) measurements were performed for all samples. As examples, the XRD patterns of samples $NaEu_{0.05}Gd_{0.90}Tb_{0.05}(PO_3)_4$, $NaEu_{0.15}Gd_{0.70}Tb_{0.15}(PO_3)_4$, $NaEu_{0.01}Gd_{0.79}Tb_{0.20}(PO_3)_4$ and $NaEu_{0.20}Gd_{0.79}Tb_{0.01}(PO_3)_4$ were plotted in Figure 1, indicating that all samples are of single phase and in good agreement with the reported powder patterns in JCPDS standard card numbered 47-0657 [$NaGd(PO_3)_4$].

3.2. UV–visible luminescence spectra of $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$

Figure 2 shows the UV–visible excitation spectra of the sample $NaEu_{0.05}Gd_{0.90}Tb_{0.05}(PO_3)_4$ at RT. Curve a is the excitation spectrum monitored Eu^{3+} emission at 611 nm and curve b is the excitation spectrum monitored Tb^{3+} emission at 544 nm. The absorption peaks in the range of 280–450 nm (curve a) correspond to the f–f transitions of Eu^{3+} ions and the absorption peaks in the range of 280–450 nm (curve b) correspond to the f–f transitions of Tb^{3+} ions in the host lattice. The broad bands at about 254 and 284 nm (curve b) are ascribed to the spin-forbidden f–d transition of Tb^{3+} ions. The sharp peaks at about 273 and 311 nm (curve a and b) are attributed to the $^8S_{7/2} \rightarrow {}^6I_J$ and $^8S_{7/2} \rightarrow {}^6P_J$ transitions within Gd^{3+} ions, indicating the energies absorbed by Gd^{3+} can be transferred to both Eu^{3+} and Tb^{3+} in this sample.

Figure 3 shows the emission spectra of $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$ under 273 nm UV excitation at RT. The emission peaks with the maxima at about 489 and 544 nm are due to the transitions from the excited state $^5D_4$ to the ground states ^7F_J ($J = 6$ and 5, respectively) of Tb^{3+}, and the peaks in the range from 580 nm to 630 nm are the characteristic red emission peaks of Eu^{3+} ions corresponding to the transitions from $^5D_0$ to ^7F_J ($J = 1$ and 2, respectively). The appearance of intensive green emission of Tb^{3+} and red emission of Eu^{3+} under 273 nm UV excitation correspond to the transition from $^8S_{7/2}$ to $^6I_{7/2}$ within Gd^{3+} ions indicates that the absorbed energy by Gd^{3+} ions can be transferred efficiently to both Tb^{3+} ions and Eu^{3+} ions synchronously. Comparing the emission spectra of these three samples $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$ ($x = 0.05$, 0.10 and 0.15), it can be observed that the intensities of Eu^{3+} emission at 611 nm go up gradually with the increasing of Eu^{3+} doping concentration while the intensities of Tb^{3+} emission at 544 nm go down gradually with the increasing of Tb^{3+} doping concentration in $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$. The ratio of the intensity of red emission at 611 nm to the intensity of green emission at 544 nm increase from 3.38 to 6.15 as the x value in $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$ goes up from 0.05 to 0.15. In our previous reports, it was observed that both Eu^{3+} ions and Tb^{3+} ions doped in the host $NaGd(PO_3)_4$ have no quenching concentration when the doping concentration of Eu^{3+} or Tb^{3+} reaches 20.0 at.%. [10,11]. Therefore, it was inferred that the energy transfer from Gd^{3+} to Eu^{3+} should be more efficient than that from Gd^{3+} to Tb^{3+}.

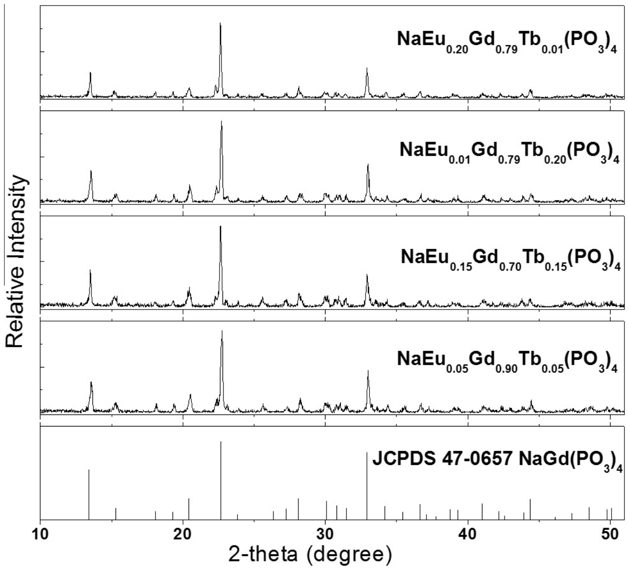

Figure 1. XRD patterns of samples $NaEu_xGd_{(1-x-y)}Tb_y(PO_3)_4$ and JCPDS 47-0657 [$NaGd(PO_3)_4$] as a reference.

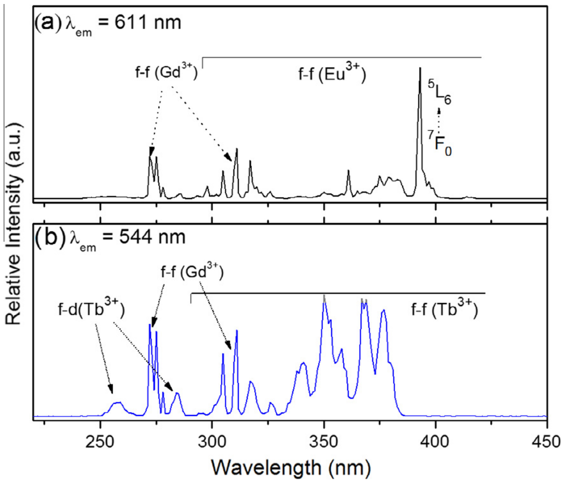

Figure 2. Excitation spectra of $NaEu_{0.05}Gd_{0.90}Tb_{0.05}(PO_3)_4$ at RT. (a) monitored Eu^{3+} emission at 611 nm, (b) monitored Tb^{3+} emission at 544 nm.

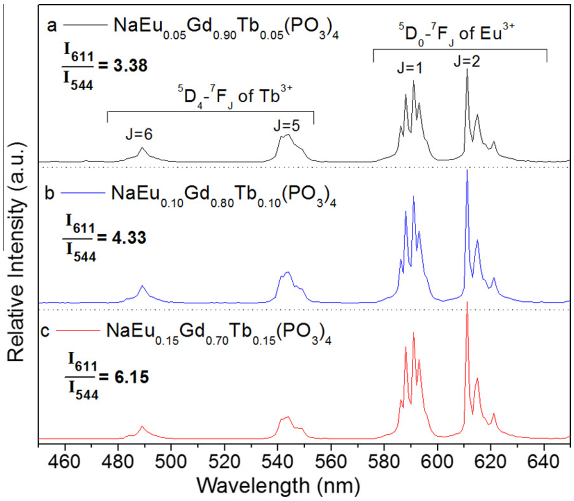

Figure 3. Emission spectra of $NaEu_xGd_{(1-2x)}Tb_x(PO_3)_4$ under 273 nm UV excitation at RT.

3.3. Luminescence decay properties of $NaEu_xGd_{(1-x-y)}Tb_y(PO_3)_4$

In order to further investigate the competitive absorption of Eu^{3+} and Tb^{3+} from Gd^{3+}, the Eu^{3+} and Tb^{3+} doping concentration dependence of the luminescence decay curves of Gd^{3+} $^6P_{7/2} \rightarrow {}^8S_{7/2}$ luminescence at 311 nm in $NaEu_xGd_{(1-x-y)}Tb_y(PO_3)_4$ were measured, respectively. Figure 4 shows the decay curves of the Gd^{3+} emission at 311 nm as a function of Eu^{3+} doping concentration in