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The generation of energy transfer from Ce^{3+} to Eu^{3+} in $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors

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ABSTRACT

A series of $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors were synthesized by a co-precipitation method. The phase, microstructure and luminescence of the synthesized phosphors were investigated. In $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors with fixed Ce^{3+} and Eu^{3+} concentrations, the Tb^{3+} concentration has clear influence on emission intensities of Ce^{3+}, Tb^{3+} and Eu^{3+}. The Tb^{3+} plays a key role for the energy transfer bridge to connect the Ce^{3+} and Eu^{3+} ion pairs. Due to the energy transfer from Ce^{3+} to Eu^{3+} through Tb^{3+}, tunable luminescence was obtained for $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors by changing Tb^{3+} concentration.

1. Introduction

Energy transfer in phosphors with sensitizer and activator ion pairs means that part of excitation energy of an ion (sensitizer) transfers to another ion (activator) through a nonradiative process and subsequently enhances or generates the emission of the activator [1]. Due to the especially optical properties of phosphors containing energy transfer, they show potential application in a wide range field, such as solar cells [2], sensors [3], photocatalysis [4], white light emitting diodes [5] and bioimaging [6]. There are some reports of ion pairs occurring energy transfer in the hosts, such as Eu^{2+}/Mn^{2+} [7], $Ho^{3+}/Yb^{3+}/Tm^{3+}$ [8], Ce^{3+}/Tb^{3+} [9], Tb^{3+}/Eu^{3+} [10], Er^{3+}/Yb^{3+} [3,6], Yb^{3+}/Tb^{3+} [2], Ce^{3+}/Dy^{3+} [11], Eu^{3+}/Sm^{3+} [12] and Dy^{3+}/Eu^{3+} [13]. Generally speaking, an overlap between the emission spectrum of a sensitizer with the excitation spectrum of an activator means a possibility of energy transfer. It was been found in some Ce^{3+} and Eu^{3+} codoped phosphors that there is an overlap between the emission spectrum of Ce^{3+} with the excitation spectrum of Eu^{3+} but the energy transfer cannot occur due to the metal-metal charge transfer (MMCT) quenching [14]. An excited charge transfer state of $Ce^{3+} + Eu^{3+} = Ce^{4+} + Eu^{2+}$ has been proved to be responsible for this [15]. And it was also found that the energy transfer from Ce^{3+} to Eu^{3+} can be obtained by a Gd^{3+} chain [15–17] or a Tb^{3+} chain [18]. Further results of the energy transfer from Ce^{3+} to Eu^{3+} by a Tb^{3+} chain were reported by different researchers in the last several years [19–24].

$LaPO_4$, as a member of rare earth phosphates, was found over the years to have potential applications in some fields due to its low solubility in water, excellently thermal stability and high melting temperature [25–27]. And rare earth ions doped $LaPO_4$ has been used in devices of cathode ray tubes and fluorescent lamps [25]. To investigate the applications of rare earth ions doped $LaPO_4$ phosphors, some rare earth ions were doped into $LaPO_4$ host and the optical properties of them were investigated carefully. For example, Yang reported the synthesis and luminescent properties of $LaPO_4:Eu^{3+}$ microspheres and found the emission intensity can be enhanced by the spherical morphology [28]. Mi et al. synthesized $LaPO_4:Ce^{3+}$ phosphors and investigated the influence of experimental parameters on the morphology of product [29]. Dong et al. synthesized $LaPO_4:Ce^{3+}/Tb^{3+}$ phosphors and found the energy transfer from Ce^{3+} to Tb^{3+} in the obtained phosphors [30]. Oliveira et al. synthesized $LaPO_4:Eu^{3+}/Tb^{3+}$ phosphors and obtained tunable luminescence by changing the concentrations of doped ions [10]. However, there is no report of $Ce^{3+}/Tb^{3+}/Eu^{3+}$ tri-doped $LaPO_4$ phosphors. In this work, we report on the synthesis and luminescent properties of $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors. The results show that energy transfer from Ce^{3+} to Eu^{3+} through Tb^{3+} occurs in $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors.

2. Materials and method

A series of $LaPO_4:Ce^{3+}/Tb^{3+}/Eu^{3+}$ phosphors were synthesized by

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a co-precipitation method. La_2O_3 (99.95%), $(NH_4)H_2PO_4$ (99%), CeO_2 (99.99%), Tb_4O_7 (99.99%) and Eu_2O_3 (99.99%) were used as raw materials. All of raw materials were used directly without further purification. The mixture of glycerine and deionized water with a volume ratio of V_g:V_{dw} = 1:4 was used as the solvent. $NH_3{\cdot}H_2O$ was used to adjust the pH value of solution.

In a typical synthesis, 3.6 mmol of La_2O_3, 0.4 mmol of CeO_2, 0.5 mmol of Tb_4O_7 and 0.2 mmol of Eu_2O_3 were dissolved into 70 mL of HNO_3 and the residual HNO_3 was removed through a heating process. Then, 100 mL of glycerine solution was added and heated up to 50 °C under magnetic stirring for 30 min (named solution A). Meanwhile, 11 mmol of $(NH_4)H_2PO_4$ was also dissolved into 100 mL glycerine solution at 50 °C under magnetic stirring for 30 min (named solution B). Subsequently, the pH values of two solutions were adjusted to be 9 by adding appropriate amount of $NH_3{\cdot}H_2O$ and mixed under magnetic stirring for 30 min at 50 °C. After that, the solution A was poured into a dropping funnel and dropped into the solution B at 50 °C under magnetic stirring. The sediment product was washed for several times by deionized water and ethanol and dried for 20 h at 80 °C. Finally, the product was calcined at 900 °C and ground carefully for the measurements.

The phase of the synthesized phosphors was confirmed by XRD technique using a Rigaku-Dmax 2500 diffractometer (Cu Kα radiation, λ = 0.15405 nm). The morphology and structure of the samples were inspected by an FEI Tecnai G2 S-Twin transmission electron microscope (TEM) with an accelerating voltage of 120 kV. FTIR measurements were carried out on a Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The excitation and emission spectra were obtained using an Edinburgh Instrument FLS920 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All of measurements for excitation and emission spectra were carried out after the spectral response corrections of excitation source, monochrometer and detector.

3. Results and discussion

Fig. 1 presents the XRD patterns of $LaPO_4$:4 mol%Ce^{3+}, $LaPO_4$:4 mol%Tb^{3+}, $LaPO_4$:4 mol%Eu^{3+} and $LaPO_4$:4 mol%Ce^{3+}/20 mol%Tb^{3+}/4 mol%Eu^{3+} phosphors. All of diffraction peaks are well accordance with the JCPDs card no. 32-0493, suggesting that Ce^{3+}, Tb^{3+} and Eu^{3+} have doped into $LaPO_4$ hosts and formed solid solutions. And all other phosphors have the similar XRD patterns. The XRD results demonstrate the monoclinic phase of the Ce^{3+}/Tb^{3+}/Eu^{3+} single or tri-doped $LaPO_4$ phosphors. It also can be seen that the diffraction peaks shift to higher 2θ angels comparing with the standard data of JCPDs card no. 32-0493. In $LaPO_4$ host, Ce^{3+} (1.196 Å, CN = 9), Tb^{3+} (1.095 Å, CN = 9) and Eu^{3+} (1.120 Å, CN = 9) are expected to substitute La^{3+} (1.216 Å, CN = 9) sites due to their similar ionic radii [31,32]. The slightly smaller ionic radii of substituted ions induce the diffraction peaks shift to higher 2θ angels. The microstructure of the synthesized phosphors was investigated by TEM. Fig. 2 gives the TEM images of $LaPO_4$:4 mol%Ce^{3+}, $LaPO_4$:4 mol%Tb^{3+}, $LaPO_4$:4 mol%Eu^{3+} and $LaPO_4$:4 mol%Ce^{3+}/20 mol%Tb^{3+}/4 mol%Eu^{3+} phosphors. The phosphors have nearly spherical shape and the size is in the range of 40–115 nm.

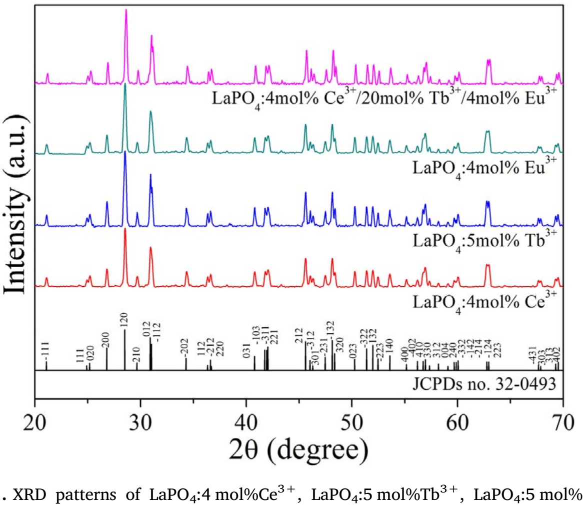

Fig. 1. XRD patterns of $LaPO_4$:4 mol%Ce^{3+}, $LaPO_4$:5 mol%Tb^{3+}, $LaPO_4$:5 mol%Eu^{3+} and $LaPO_4$:4 mol%Ce^{3+}/20 mol%Tb^{3+}/4 mol%Eu^{3+} phosphors.

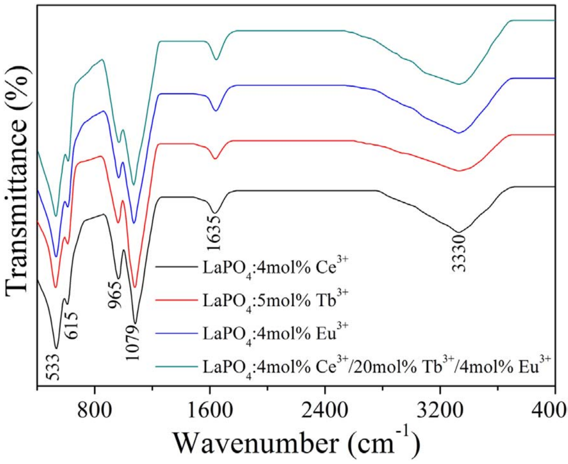

Fig. 2. FTIR spectra of $LaPO_4$:4 mol%Ce^{3+}, $LaPO_4$:5 mol%Tb^{3+}, $LaPO_4$:5 mol%Eu^{3+} and $LaPO_4$:4 mol%Ce^{3+}/20 mol%Tb^{3+}/4 mol%Eu^{3+} phosphors.

Fig. 3 shows the FTIR spectra of $LaPO_4$:4 mol%Ce^{3+}, $LaPO_4$:4 mol%Tb^{3+}, $LaPO_4$:4 mol%Eu^{3+} and $LaPO_4$:4 mol%Ce^{3+}/20 mol%Tb^{3+}/4 mol%Eu^{3+} phosphors. Characteristic vibrations of PO_4^{3-} are clearly shown. The absorption bands at 533 cm^{-1} and 615 cm^{-1} are in the ν_4 vibration region corresponding to the O=P-O and O-P-O bending modes and the absorption bands at 965 cm^{-1} and 1079 cm^{-1} are in the ν_3 vibration region corresponding to the P-O stretching mode [28]. The separation of absorption band in the ν_3 vibration region is a characteristic of monoclinic $LaPO_4$ phase [31]. The absorption bands at 1635 cm^{-1} and 3330 cm^{-1} correspond to the bending and stretching vibrations of –OH group coming from the physically adsorbed water [9].

The luminescent properties of Ce^{3+}, Tb^{3+} and Eu^{3+} single doped $LaPO_4$ phosphors were firstly investigated. Fig. 4 shows the excitation and emission spectra of $LaPO_4$:4 mol%Ce^{3+} (A), $LaPO_4$:5 mol%Tb^{3+} (B) and $LaPO_4$:4 mol%Eu^{3+} (C) phosphors. The excitation spectrum of $LaPO_4$:4 mol%Ce^{3+} consists of two bands respectively peaking at 252 nm and 320 nm, which originates from the transitions of Ce^{3+} from the ground $^2F_{5/2}$ state to different 5d levels [33]. Under the excitation at 320 nm, $LaPO_4$:4 mol%Ce^{3+} shows emission spectrum with two peaks locating at 342 nm and 364 nm, which comes from the partly allowed transitions of the lowest component of the ^2D state to the spin-orbit components of the $^2F_{5/2}$ and $^2F_{7/2}$ states of Ce^{3+} [34]. The excitation spectrum of $LaPO_4$:5 mol%Tb^{3+} consists of some excitation bands in the range of 250–400 nm, which can be assigned to the f-f transitions of Tb^{3+} [35]. Under the excitation at 270 nm, the $LaPO_4$:5 mol%Tb^{3+} shows four emission bands in the range of 450–650 nm, which corresponds to the $^5D_4 \rightarrow {}^7F_{6,\ 5,\ 4,\ 3}$ transitions of Tb^{3+} [30]. It can be seen from the Fig. 4A and B that there is overlap between the emission spectrum of Ce^{3+} with the excitation spectrum of Tb^{3+}, suggesting the possible occurrence of energy transfer from Ce^{3+} to Tb^{3+}. The excitation spectrum of $LaPO_4$:4 mol%Eu^{3+} consists of a strong and broad excitation band peaking at 270 nm and several weaker excitation bands in the range of 340–550 nm. The excitation band peaking at 270 nm is the charge transfer band (CTB) corresponding to the transition from the 2p orbital of oxygen to the 4 f