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Luminescence and energy transfer of $La_5Si_2BO_{13}$: A (A=Ce^{3+}/Tb^{3+}/Eu^{3+}/Sm^{3+}) phosphors under UV excitation

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ABSTRACT

Ce^{3+}, Tb^{3+} co-doped and Ce^{3+}, Tb^{3+}, Eu^{3+}/Sm^{3+} tri-doped $La_5Si_2BO_{13}$ (LSBO) were synthesized by solid-state method. Green Tb^{3+} emission and red Eu^{3+}/Sm^{3+} emission could be efficiently sensitized by Ce^{3+}. Using Tb^{3+} concentration that predicted by empirical saturation distance (R_c=6–7Å), a terbium bridge is successfully formed and efficient $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}/Sm^{3+}$ energy transfer is realized in LSBO lattice. Under UV excitation, $La_5Si_2BO_{13}$: Ce^{3+}, Tb^{3+}, Eu^{3+}/Sm^{3+} system can achieve tunable emission from blue through yellowish-green to red by changing the Tb^{3+}/Eu^{3+}/Sm^{3+} concentration.

1. Introduction

Tb^{3+}/Eu^{3+}/Sm^{3+} ions, which possess linear green and red emission with superior color purity, are ideal activator ions for novel UV-excited luminescent materials. Unfortunately, the low oscillator strength and narrow line width of Tb^{3+}/Eu^{3+}/Sm^{3+} 4*f*-4*f* absorption transitions leads to a weak UV absorption, which greatly limit their luminescent performance [1]. Thus, it is necessary to find sensitizers for Tb^{3+}/Eu^{3+}/Sm^{3+} luminescence that could achieve strong excitation bands at UV region [2]. Due to its strong 4*f*-5*d* absorption in UV region, Ce^{3+} ion can be used as a sensitizer for Tb^{3+}/Eu^{3+}/Sm^{3+} ions to obtain strong green and red emission. However, unlike green-emitting Tb^{3+} ion, red-emitting Eu^{3+}/Sm^{3+} ion cannot be directly sensitized by Ce^{3+} ions due to metal–metal charge transfer (MMCT), that is, $Ce^{3+}+Eu^{3+}$ (Sm^{3+})$+Sm^{4+}+Eu^{2+}$ (Sm^{2+}), which quenches the luminescence of the sensitizer and makes the co-doped samples non-luminescent [3,4].

Aiming at realization of the sensitization effect between Ce^{3+}-Eu^{3+}/Sm^{3+}, circumvention of MMCT quenching is essential. As reported by Wen et al., a terbium bridge could be introduced to sensitize Eu^{3+}/Sm^{3+} ions and enhance the narrowband red emission with Ce^{3+} broadband UV absorption [5]. In order to achieve sufficient energy transfer, a host with compact structure is preferred since Tb^{3+}-Eu^{3+} energy transfer process is a short-distance interaction. Apatite-structure $La_5Si_2BO_{13}$ (LSBO) has a relative compact structure [space group: P63/m, $a=b=9.558$ Å, $c=7.212$ Å, $V=571.09$ Å^3, $Z=2$] [6], which makes it suitable host to realize an efficient $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}/Sm^{3+}$ energy transfer. In this article, we investigate the luminescence properties as well as the energy-transfer process of Ce^{3+}, Tb^{3+} co-doped and Ce^{3+}, Tb^{3+}, Eu^{3+}/Sm^{3+} tri-doped $La_5Si_2BO_{13}$.

2. Experimental

All samples $La_{5(1-x-y-z)}Si_2BO_{13}$: xCe^{3+}, yTb^{3+}, zEu^{3+}/Sm^{3+} ($x=0.01$, $y=0.02\sim0.50$, $z=0.01$) were synthesized by solid-state method. The stoichiometric amounts of raw materials SiO_2 (A.R.), H_3BO_3 (A.R.) (10% excessive as flux), La_2O_3 (A.R.), CeO_2 (A.R.), Tb_4O_7 (A.R.), Eu_2O_3 (A.R.) and Sm_2O_3 (A.R.) were thoroughly mixed by grinding. They were sintered at 1500 °C in a reducing (5% H_2+95% N_2) atmosphere for 5 h. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-IIIA diffractometer with Cu K_α radiation ($\lambda=1.5403$ Å). Photoluminescent excitation (PLE) and emission (PL) spectra and decay lifetimes were recorded on an EDINBURGH FLS920 Combined Fluorescence Lifetime & Steady State Spectrometer.

3. Results and discussion

Fig. 1a shows the crystal structure of $La_5Si_2BO_{13}$ together with the coordination environments of the La^{3+} sites. In $La_5Si_2BO_{13}$ host, there are two kinds of La^{3+} sites which are named La(1) and

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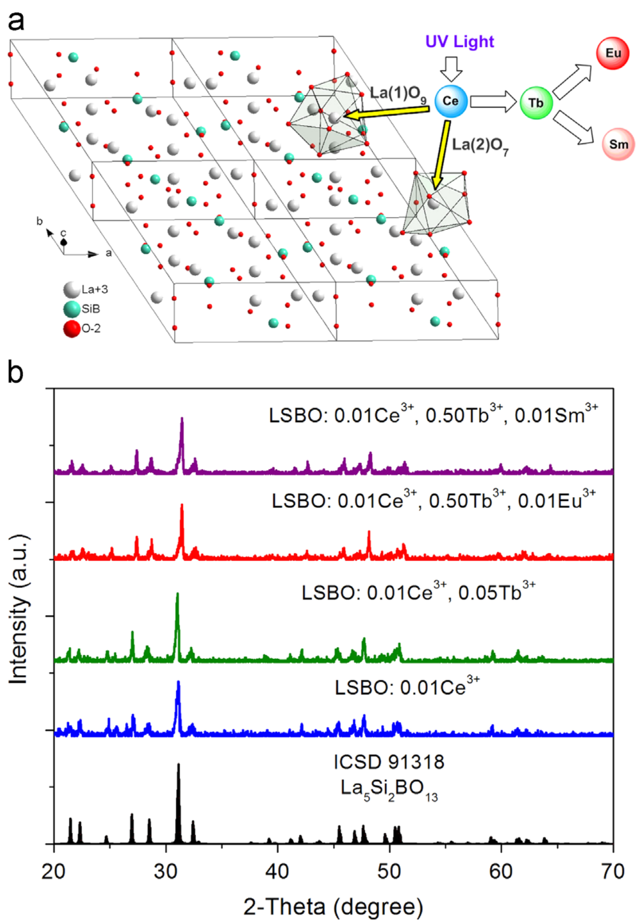

Fig. 1. The unit cell structure of $La_5Si_2BO_{13}$ (a) and the typical XRD patterns of phosphors (b).

La(2). La(1) is nine-fold coordinated 4*f* site with C_3 point symmetry and La(2) is 7-coordinated 6 *h* site with C_s point symmetry. The trivalent rare-earth ion ($Ce^{3+}/Tb^{3+}/Eu^{3+}/Sm^{3}$) as the dopant is expected to substitute the La^{3+} sites in LSBO host lattice on account of the same valence and close ionic radius between Ln^{3+} and La^{3+}.

Fig. 1b presents the XRD patterns of representative samples LSBO: $0.01Ce^{3+}$, LSBO: $0.01Ce^{3+}$, $0.05Tb^{3+}$, LSBO: $0.01Ce^{3+}$, $0.50Tb^{3+}$, $0.01Eu^{3+}$ and LSBO: $0.01Ce^{3+}$, $0.50Tb^{3+}$, $0.01Sm^{3+}$, respectively. It is found that all the diffraction peaks can be indexed to standard data of hexagonal-phase $La_5Si_2BO_{13}$ (ICSD 91318) [6]. Besides, the diffraction peaks shift slightly to the higher angle side with further doping of $Ce^{3+}/Tb^{3+}/Eu^{3+}/Sm^{3+}$, which is due to the smaller ionic radius of $Ce^{3+}/Tb^{3+}/Eu^{3+}/Sm^{3+}$ ion (1.01/0.92/0.95/0.96 Å) compared to La^{3+} (1.03 Å). The results suggest that dopant ions were effectively incorporated into the La^{3+} site along with contraction of the unit cell.

The PLE and PL spectra of LSBO: $0.01Ce^{3+}$ sample is shown in Fig. 2a. Under 280 nm excitation, LSBO: $0.01Ce^{3+}$ presents a blue emission band with an emission peak locates at 418 nm. Corresponding PLE spectrum consists of two broad excitation bands at 280 and 345 nm, which nearly cover the whole UV region and are assigned to Ce^{3+} 4*f*-5*d* allowed transitions.

Fig. 2b depicts the spectral characteristics of LSBO: $0.01Ce^{3+}$, $0.05Tb^{3+}$. The PLE spectrum monitored with $^5D_4 \rightarrow {}^7F_5$ emission (542 nm) of the Tb^{3+} ion shows not only the Tb^{3+} spin-allowed $4f^8$–$4f^75d^1$ transition band at 248 nm, but also the Ce^{3+} strong absorption band centered at 280 and 345 nm. The presence of the Ce^{3+} excitation band suggests energy transfer from Ce^{3+} to Tb^{3+}. Under the 280 nm excitation (the characteristic adsorption peak of Ce^{3+}), LSBO: $0.01Ce^{3+}$, $0.05Tb^{3+}$ sample exhibits the sensitized Tb^{3+} green $^5D_4$–^7F_J (J=6, 5, 4, 3) emission along with weaken Ce^{3+} blue emission.

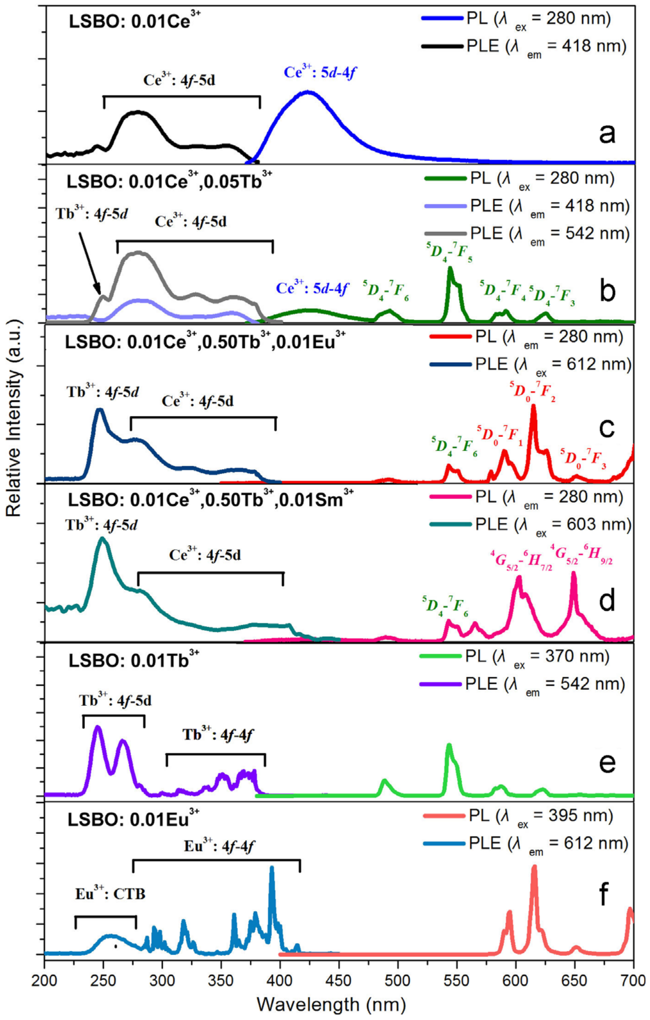

Fig. 2. The PLE and PL spectra of representative LSBO: Ce^{3+}, Tb^{3+}, Eu^{3+}/Sm^{3+} samples.

As seen in Fig. 2c, PLE spectrum of LSBO: $0.01Ce^{3+}$, $0.50Tb^{3+}$, $0.01Eu^{3+}$ monitoring Eu^{3+} emission at 613 nm has similar profile with the PLE band of LSBO: Ce^{3+}, Tb^{3+}, which covers the broad UV range (200–400 nm) and gives direct evidence of sensitized Eu^{3+} by $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ energy transfer. The strong absorption peak at 248 nm is related to the spin-allowed $4f^8 \rightarrow 4f^75d^1$ ($\Delta S=0$) transition of Tb^{3+}, the intensity of which is greatly enhanced because of the relative high Tb^{3+} content. Similar phenomenon could be found in $Sr_3Y(PO_4)_3$: Eu^{2+}, Tb^{3+}, Sm^{3+} system [7]. Under 280 nm excitation, sensitized Eu^{3+} red emission with main peaks at 591, 614, 620 nm is found, which are assigned to $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3) transitions. Due to efficient $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ energy transfer, both Ce^{3+} blue emission and Tb^{3+} green emission are hardly observed. The dominant red emission peak at 613 nm is attributed to Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition, because Eu^{3+} ions are occupying non-centrosymmetric La sites in $La_5Si_2BO_{13}$ host.

Fig. 2d shows the PLE and PL spectrum for LSBO: $0.01Ce^{3+}$, $0.50Tb^{3+}$, $0.01Sm^{3+}$. Under Ce^{3+} excitation at 280 nm, intense red emission of Sm^{3+} $^4G_{5/2} \rightarrow {}^6H_J$ (J=5/2, 7/2, 9/2) transitions are exhibited in PL spectrum. The PLE spectrum that monitoring Sm^{3+} red emission at 603 nm consists of strong broad bands with significant contribution from both Ce^{3+} and Tb^{3+}, indicating that the successful sensitization of Sm^{3+} ion emission by Ce^{3+} using Tb^{3+} bridge in the LSBO lattice.