Journal of Luminescence 203 (2018) 121–126

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Resonant energy transfer and near-infrared emission enhanced by tri-doped Sr_2SiO_4: Ce^{3+}, Tb^{3+}, Yb^{3+} phosphors for silicon solar cells

Lege Wang, You-Fen Li*, Zhen Wang, Ru Yang*, Yaoyao Tong, Liangliang Sun

Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Keywords:
Sr_2SiO_4
Phosphor
Energy transfer
Near-infrared
Solar cells

ABSTRACT

A novel tri-doped Sr_2SiO_4: Ce^{3+}, Tb^{3+}, Yb^{3+} phosphor was prepared using a conventional solid reaction. The resonant energy transfer (ET) with $Ce^{3+} \rightarrow Tb^{3+}$ through electric dipole-dipole interactions was demonstrated with luminescent spectra and decay lifetime curves. Upon UV photon excitation at 372 nm of Tb^{3+} ions and 350 nm of Ce^{3+} ions, Yb^{3+} emissions were detected in the near-infrared (NIR) region with a main peak at 977 nm, which belonged to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and corresponding perfectly with silicon solar cell maximum spectral responses. The NIR emission intensity of Sr_2SiO_4: Ce^{3+}, Tb^{3+}, Yb^{3+} was almost 125 times greater than that of Sr_2SiO_4: Yb^{3+}, which demonstrated that the 4*f*–5*d* luminescence of Ce^{3+} could be used to sensitize the Tb^{3+}–Yb^{3+} down-conversion process. This tri-doped $Ce^{3+}-Tb^{3+}-Yb^{3+}$ system offered potential applications for NIR down-conversion phosphors for silicon solar cells.

1. Introduction

Ultraviolet (UV) and visible (VIS) to near-infrared (NIR) down-conversion (DC) phosphors doped with rare earth (RE) ion crystals have been extensively studied for their potential applications in silicon solar cells (SSC) [1–3]. Among RE ions, Yb^{3+} has a simple energy level with a single excited level (~1.2 eV), roughly in line with the silicon band gap (~1.1 eV) [4,5]. Therefore, much research has focused on RE^{3+}–Yb^{3+} co-doped materials (RE = Tb [6,7], Tm [8,9], Pr [10,11], and Er [12,13]) to adjust the solar spectrum to enhance the efficiency of SSC. However, RE^{3+} (RE = Tb, Tm, Pr, Er) have weak and line-like absorption in the VIS region by reason of the proscribed nature of *f*–*f* transitions, preventing the absorption of a large part of the broad band of distributed sunlight [14]. Because of the accepted 4*f*–5*d* transition, Ce^{3+} could be a perfect donor ion, having a wide and strong absorptive capacity in the desired spectral region [15]. Ce^{3+} is an efficient sensitizer for absorbing the UV and VIS portions of the solar spectrum and its excitation energy efficiently transfers to the $^5D_4$ state of Tb^{3+} for the Tb^{3+}–Yb^{3+} NIR process in other hosts [16], such as Ca_2BO_3Cl [17], YAG [18], $KSrPO_4$ [19], and borate glass [20]. Nevertheless, Duan*et al. have discovered that the energy transfer (ET) direction between Ce*$^{3+}$ and Tb^{3+} is closely linked to the matrix in Ce^{3+}/Tb^{3+} co-doped $Re_2Si_4N_6C$ Re = Lu, Y, and Gd) luminescent materials [21]. In $Lu_2Si_4N_6C$ and $Y_2Si_4N_6C$ matrix co-doped Ce^{3+}/Tb^{3+}, the dominant direction of ET is $Ce^{3+} \rightarrow Tb^{3+}$. In contrast, in the $Gd_2Si_4N_6C$ matrix, the ET dominant direction is exactly the opposite. Therefore, the ET mechanism in such a system requires further analysis and evidence to explore for a more efficient wide absorption band NIR conversion system.

The presence of ET among $Ce^{3+}-Tb^{3+}-Yb^{3+}$ prompted us to employ this process in our tri-doped silicate phosphors in view of the silicate's good mechanical and chemical stability. In this paper, the fabrication and performance of Sr_2SiO_4: Ce^{3+}, Tb^{3+}, Yb^{3+} phosphor, based on the resonant ET, were reported. This material cropped UV photons and displayed an extremely increased NIR emission of Yb^{3+} ion, located at ~1000 nm and at ~125-fold that of Sr_2SiO_4: Yb^{3+}, which demonstrated that the 4*f*–5*d* luminescence of Ce^{3+} could be used to sensitize the Tb^{3+}–Yb^{3+} down-conversion process. This tri-doped $Ce^{3+}-Tb^{3+}-Yb^{3+}$ system will be utilized as a platform for NIR down-conversion phosphor for silicon solar cells.

2. Experimental

Reagent grade $SrCO_3$, SiO_2, CeO_2, Tb_4O_7, and Yb_2O_3 were employed as raw materials and were weighed stoichiometrically and mixed thoroughly with an agate mortar and pestle, with 5 wt% B_2O_3 (A.R.) was added as flux. The mixture was subsequently settled into an alumina crucible and calcined at 1100 °C for 3 h in a reducing atmosphere. Then, the samples were cooled passively to room temperature and then reheated again.

The resulting products' compositions were analyzed using an X-ray diffractometer (XRD; Neo X D/Max-2500VB2, Rigaku Corp., Tokyo, Japan) with Cu-K$_\alpha$ radiation. The emission or photoluminescent (PL)

---

* Corresponding authors.
E-mail addresses: yfli@mail.buct.edu.cn (Y.-F. Li), ruyang@mail.buct.edu.cn (R. Yang).

https://doi.org/10.1016/j.jlumin.2018.06.016
Received 27 February 2018; Received in revised form 19 May 2018; Accepted 7 June 2018

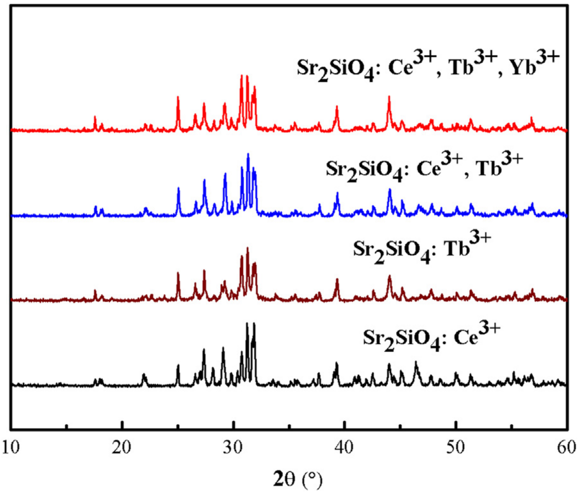

Fig. 1. XRD patterns of specimens doped with different ions.

spectra and photoluminescence excitation (PLE) were obtained using an F97Pro fluorescence spectrophotometer (Shanghai Lengguang Technology Co., Ltd., Shanghai, China) with a 150 W Xe lamp. The NIR excitation and emission spectra were registered using a FLS 980 steady/transient fluorescence spectrometer (Edinburgh Instruments Ltd., EH54 7DQ, UK) with a 150 W Xe lamp. All tests were at room temperature.

3. Results and discussion

3.1. Luminescence and ET in $Ce^{3+}-Tb^{3+}$ co-doped Sr_2SiO_4

The synthesized samples were consistent with standard Sr_2SiO_4, as confirmed by XRD (Fig. 1). The emission and excitation spectra of Tb^{3+} or Ce^{3+} solely doped and Ce^{3+}–Tb^{3+} co-doped Sr_2SiO_4 phosphors were measured (Fig. 2). The emission and excitation spectra of Sr_2SiO_4: $0.04Ce^{3+}$ was at 414 nm and the excitation spectrum involved a wider band, ranging from 230 to 400 nm and originating from the 4*f*–5*d* transition for Ce^{3+} (Fig. 2a). In addition, the emission spectrum was composed of an asymmetric broadband. Under near UV excitation of 357 nm, the peak located at 321 nm was attributed to $4f^05d^1 \rightarrow 4f^15d^0$ transitions of Ce^{3+}. The influence of Ce^{3+} concentration in the Sr_2SiO_4 phosphor on emission intensity was investigated and it was clear that, as the Ce^{3+} concentration increased, the emission intensity was found to increase and then decrease (Fig. 2d). The maximum emission intensity obtained when Ce^{3+} concentration was 0.04.

The emission and excitation spectra of Sr_2SiO_4: Tb^{3+} showed that the Sr_2SiO_4 excitation spectrum displayed a number of bands ranging from 300 and 400 nm in monitoring at 545 nm for Tb^{3+}, which was attributed to *f*–*f* transitions of Tb^{3+} within the $4f^8$ configuration (Fig. 2b). At 372 nm excitation, the emission peaks included 489, 545, 587, and 622 nm, which contributed to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of Tb^{3+}. The optimal Tb^{3+} concentration was also found to be 0.16 (Fig. 2e).

The PL and PLE of Sr_2SiO_4 phosphor co-doped with Ce^{3+} and Tb^{3+} were investigated and the experimental results shown in Fig. 2c. Emissions by Ce^{3+} (414 nm, 5d → 4 f) and Tb^{3+} (480–650 nm, $^5D_4 \rightarrow {}^7F_J$, J = 6, 5, 4, 3) were both produced with excitation at 350 nm. The peak intensity of Sr_2SiO_4: $0.04Ce^{3+}$, $0.06Tb^{3+}$ at 414 nm was significantly lower than that of $Sr_{1.96}SiO_4$: $0.04Ce^{3+}$ (Fig. 2a). Meanwhile, the emission peak intensity located at 545 nm was clearly higher than that of $Sr_{1.94}SiO_4$: $0.06Tb^{3+}$, resulting from the existence of ET between Ce^{3+} and Tb^{3+} (Fig. 2c). In accordance with Dexter sensitization theory [22], Ce^{3+} was considered as an ideal sensitizer for Tb^{3+} when the emission waveband of Ce^{3+} was superimposed with the excitation waveband of Tb^{3+}. Comparison of Fig. 2a and b, with a dotted line, made clear the significant superimposition over 350 and 450 nm, which was concluded to be the effective ET for $Ce^{3+} \rightarrow Tb^{3+}$ that occurred on the Sr_2SiO_4 host, as expected.

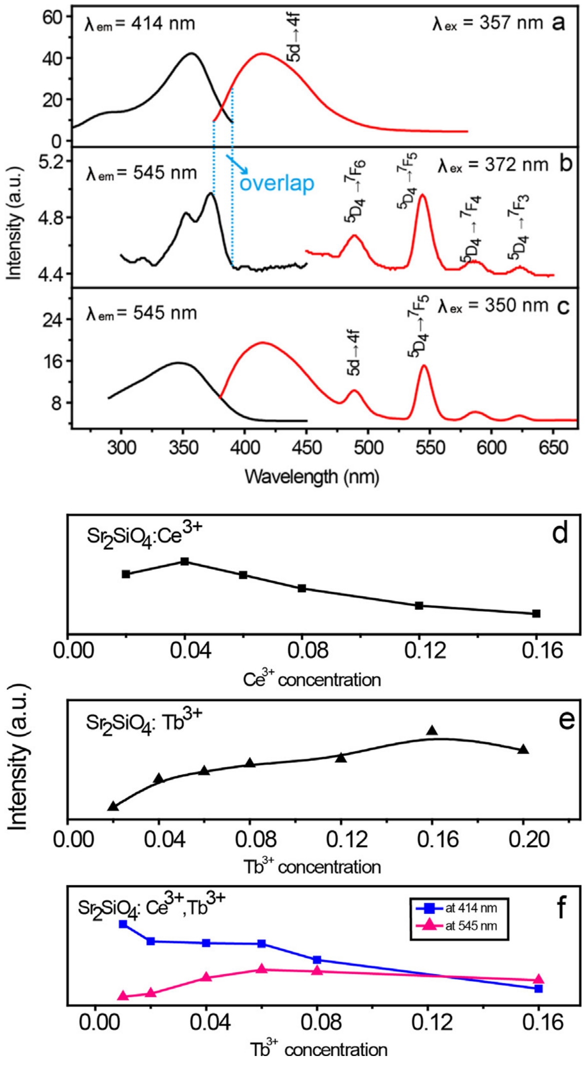

Fig. 2. Excitation and emission spectra of phosphors in left: (a) Sr_2SiO_4: $0.04Ce^{3+}$, (b) Sr_2SiO_4: $0.06Tb^{3+}$, and (c) Sr_2SiO_4: $0.04Ce^{3+}$, $0.06Tb^{3+}$. The relative PL intensities in right: (d) Sr_2SiO_4: xCe^{3+}, (e) Sr_2SiO_4: yTb^{3+}, and (f) Sr_2SiO_4: $0.04Ce^{3+}$, yTb^{3+}.

Based on the results of Fig. 2d and e, the Ce^{3+} content was fixed at 0.04 and the emission intensity observed, with changes in Tb concentration in co-doping, so as to obtain the quenching concentration. Conversely, a fixed Tb^{3+} content of 0.16 was used to investigate the effects of Ce concentration changes. The emission intensity of Ce^{3+} was found to decrease monotonically with increasing of Tb^{3+} emission, while the Tb^{3+} quenching concentration was determined with 0.06 (Fig. 2f). The optimal component ratio of co-doped phosphor was thus Sr_2SiO_4: $0.04Ce^{3+}$, $0.06Tb^{3+}$, which was lower than that of solely-doped Sr_2SiO_4: Tb^{3+}.

To analyze the ET process of $Ce^{3+} \rightarrow Tb^{3+}$, a resonant ET mechanism with two main aspects was proposed that involved multipolar and exchange interactions [23]. The amount of space R_c between the sensitizer and activator was used as the judgment criteria and R_c must be < 5 Å in the ET mechanism for the exchange interaction, which was calculated as [24]

$$Rc \approx 2\left(\frac{3V}{4\pi x_c Z}\right)^{1/3} \tag{1}$$