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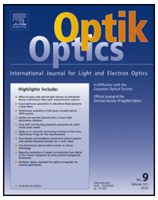

Original research article

Broadband down-conversion of near-infrared emission in Bi^{3+}-Yb^{3+} co-doped $Y_3Al_5O_{12}$ phosphors

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ABSTRACT

An efficient near-infrared (NIR) down-conversion (DC) process has been demonstrated in Bi^{3+}-Yb^{3+} co-doped $Y_3Al_5O_{12}$ phosphors. The excitation spectra, emission spectra and decay curves were measured to prove the occurrence of energy transfer (ET) from $Bi^{3+} \rightarrow Yb^{3+}$. Upon the excitation of UV photons, NIR emission has been obtained at 1028 nm through the energy transfer from $^3P_1$ energy level of Bi^{3+} to $^2F_{5/2}$ energy level of Yb^{3+}. Quantum efficiency related to Yb^{3+} concentration is calculated and the maximum efficiency reaches 138%. Our results suggested that these phosphors might have a potential application for the down-conversion process to improve the efficiency of Si-based solar cells.

1. Introduction

The c-Si solar cells have been developed quickly in the past few decades because they can generate electricity environmental-friendly [1,2]. A major problem limiting the conversion efficiency of c-Si solar cells is the spectral mismatch between the solar spectrum and the energy band gap of silicon ($E_g \sim 1.12$ eV or 1100 nm), which makes the conversion efficiency around 29% only [1,3]. For high energy photons, the energy loss in Si solar cells results from the thermalization of carriers whose energy is much higher than the band gap of Si, and might be reduced considerably if ultraviolet (UV)/blue photon ($300\,nm < \lambda < 500\,nm$) can be cut into two near-infrared (NIR) photons ($\lambda_{abs} < 1100\,nm$) and then absorbed by Si [4].

Down-conversion (DC) materials can convert one high energy photon into two low energy photons to whom Si solar cells have a good spectral response [5,6]. Therefore, they are a promising candidate to enhance the efficiency of Si solar cells. The maximum conversion efficiency of the solar cells was predicted up to ~39.63% [4]. Thus, the DC phosphors have attracted much attention in recent years [7–10].

The phosphors with two or more kinds of rare-earth (RE) ions are one of the suitable candidates for DC process because of RE ions' rich energy level structure which allows an efficient spectral conversion [11–16]. Yb^{3+} is a desirable RE ion as an emitter due to its high luminescence quantum efficiency and the emission band from 920 nm to 1100 nm which is just close to the band gap of Si [17]. To find a suitable RE ion as an absorber (sensitizer), some RE^{3+} ions (RE = Tb, Tm, Pr, Er, Nd and Ho) have been introduced into the phosphors. However, their weak and narrow absorption owing to the luminescent nature of

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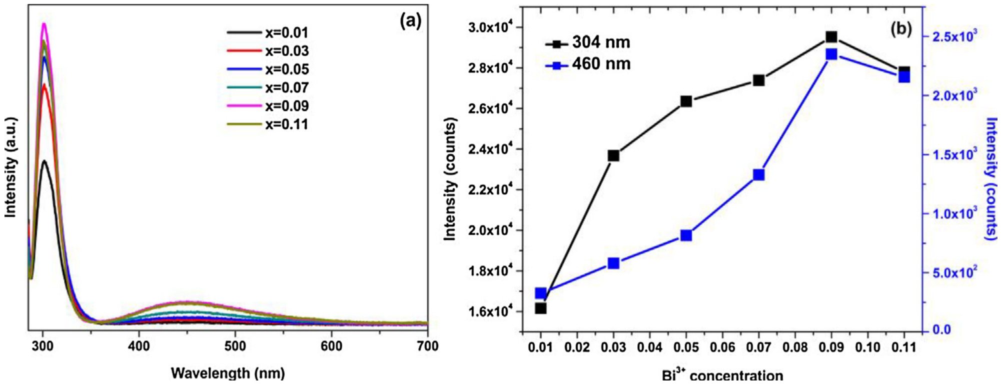

Fig. 1. (a) Emission spectra for singly doped $Y_{3-x}Al_5O_{12}$: xBi^{3+} phosphors with various Bi^{3+} concentrations (x = 0.01, 0.03, 0.05, 0.07, 0.09 and 0.11) upon the excitation wavelength of 275 nm and (b) Variation of intensity of the emission peaks of 304 nm and 460 nm with respect to doping concentration of Bi^{3+}.

4f-4f forbidden transitions limits their practical applications in solar cells as only a small fraction of the solar spectral range can be harvested [18].

Some researchers reported that Ce^{3+} ion might be a good broadband sensitizer for Yb^{3+}because its allowed electric dipole transitions can take place from 4f ground state to the 5d excited one [19,20]. But the energy transfer from $Ce^{3+}$to Yb^{3+}, which is completed possibly via the charge transfer state (CTS),will not be able to give a high quantum cutting efficiency [21].

Most of these published works mainly focus on the systems with RE ions, and less attention has been given to the combination of metal ions and RE ions for DC luminescence [22]. In fact, some metal ions with broadband and spin-allowed absorption in the UV–blue region can also be used as the excellent sensitizer for Yb^{3+} ions. Because metal ion systems are much more sensitive to chemical and structural variations than RE ion systems, this allows us to tune the absorption spectrum to match the solar spectrum below 500 nm through chemical modifications of the host lattice [23].

Bi^{3+} ions have the ionic diameter similar to RE ions and can be excited by the high energy photons [24,25].They provide a possibility of using a metal ion instead of a RE ion as the sensitizer in the DC phosphors. In this paper, we try to prepare Bi^{3+}-Yb^{3+} co-doped $Y_3Al_5O_{12}$ phosphors as DC materials. Their luminescence properties have been investigated, and the energy transfer mechanism of $Bi^{3+} \rightarrow Yb^{3+}$has also been discussed.

2. Experimental procedure

The Bi^{3+}-Yb^{3+} co-doped $Y_3Al_5O_{12}$ phosphors have been prepared by the solid-state reaction method. The raw materials including Y_2O_3 (99.99%), Al_2O_3 (99.99%), Bi_2O_3 (99%) and Yb_2O_3 (99.99%) were accurately weighed according to the ratio of Y_{3-x-z} Al_5O_{12}: xBi^{3+}, zYb^{3+} (x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.11; z = 0.05, 0.1, 0.15, 0.2, 0.25). Then, the weighed materials were thoroughly mixed in an agate mortar for 30 min. After that, the mixed powders were transferred into an alumina crucible and subsequently fired at 1600 °C for 6 h in a chamber furnace. Finally, the samples were cooled down to room temperature and ground again thoroughly into powders before the characterization process. The excitation and emission spectra of the phosphors were recorded by Ocean Optics MAYA 2000PRO and the decay lifetime measurements were performed by using a FM-4P-TCSPC spectro-fluorometer (Horiba Jobin Yvon). All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1(a) shows the emission spectra of $Y_{3-x}Al_5O_{12}$: xBi^{3+} phosphors with various doping concentrations of Bi^{3+}underthe excitation of the wavelength at 275 nm. There are two broad emission peaks at 304 nm and 460 nm, which correspond to the allowed transitions from the excited $^1P_1$ and $^3P_1$ states to the ground state $^1S_0$ of Bi^{3+} [26]. Moreover, it can be identified that the luminescent intensity of Bi^{3+} increases gradually with its concentration upto 0.09. After that, the emission intensity decreases due to the concentration quenching effect [27,28]. The variation of intensities of the emission peaks at 304 nm and 460 nm with doping concentration of $Bi^{3+}$is shown in Fig. 1(b). Clearly, the optimal concentration of Bi^{3+} in $Y_3Al_5O_{12}$ phosphors is x = 0.09 and this concentration is further used for the co-doping process.

The excitation and emission spectra of Bi^{3+}-Yb^{3+} co-doped $Y_3Al_5O_{12}$ phosphors are shown in Fig. 2. A broad excitation band ranging from 250 to 300 nm is observed at the monitoring wavelength of 304 nm and 460 nm, as shown in Fig. 2(a). The peak at 275 nm can be ascribed to the transition from the ground state to the excited states of Bi^{3+}. Moreover, a similar excitation spectrum monitored at 1028 nm is also obtained, which can be considered as a direct evidence for the energy transfer from Bi^{3+} to Yb^{3+} [29].

Fig. 2(b) exhibits the emission spectra of Bi^{3+}-Yb^{3+} co-doped phosphors with various concentrations of Yb^{3+} (z = 0.05, 0.1, 0.15, 0.2, 0.25) and a fixed concentration of Bi^{3+} (x = 0.09) under an excitation wavelength of 275 nm. The intensity of broad emission band for Bi^{3+}: $(^1P_1$-$^3P_1) \rightarrow {}^1S_0$ transition decreases monotonously with the increasing concentration of Yb^{3+}. Apart