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Enhanced visible to near infrared downshifting in Ce^{3+}/Yb^{3+}-co-doped yttrium aluminum garnet through Pr^{3+} doping

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ABSTRACT

Novel YAG:Ce^{3+}, Pr^{3+}, Yb^{3+} phosphors were synthesized using a high temperature solid state reaction method. The XRD patterns revealed that the obtained samples belong to the single phase YAG. The optical spectra demonstrated that Pr^{3+} could be a bridge to facilitate the energy transfer from Ce^{3+} to Yb^{3+} in the YAG host. Blue light excited Ce^{3+} and a yellow emission from Ce^{3+} together with a near infrared emission of Yb^{3+} was obtained. The effect of Pr^{3+} doping on the energy transfer efficiency was explored. When the doping concentration of Pr^{3+} increased, the yellow emission intensities of Ce^{3+} decreased and the near infrared emission intensity of Yb^{3+} increased monotonously. Hence, the efficiency of energy transfer from Ce^{3+} to Yb^{3+} is enhanced by the addition of Pr^{3+}, implying that the YAG:Ce^{3+}, Pr^{3+}, Yb^{3+} phosphors are promising downshifting materials and have the potential to be used in Si-based solar cells.

1. Introduction

The global crisis on energy and environment has produced a critical need for new energy sources which are clean, safe and sustainable[1–3]. Solar energy is the most abundant and renewable energy. When considering the diverse ways of solar energy utilization, solar cells based upon the photovoltaic effect have attracted the most attention. Currently, silicon-based solar cells dominate the marketplace but the efficiency of photoelectric conversion is low, limiting further wide application [4,5]. Because of the bandwidth limitations of the semiconductor, the response spectrum of the silicon solar cell mismatches the solar spectrum so that the silicon solar cell cannot take advantage of all the wavelengths of sunlight, causing an excessive waste of sunlight energy. Fortunately, through the modification of the solar spectrum by phosphors, it is possible to broaden the spectral response of the solar cell and improve the photoelectric conversion efficiency. The optical frequency conversion phosphors are usually coated on the surface of the solar cell, improving solar cell conversion efficiency in a very convenient and cheap way [6]. The high-energy part of the solar spectrum is between 350 and 550 nm, but the bandgap of monocrystalline silicon solar cells is at 1100 nm. If we use optical frequency conversion phosphors to transform the blue light into infrared light, the utilization of the solar spectrum will be enhanced greatly. Quantum cutting phosphors can convert one photon of high energy into two photons of lower energy and this kind of material is very suitable for solar cells to improve the photoelectric conversion efficiency [7]. Even downconversion phosphors, which change wasted high energy photons into the same number of useful lower energy photons, are also suitable [8]. The emission peak wavelength (1029 nm) of Yb^{3+} is close to the bandgap of monocrystalline silicon solar cells (1100 nm). In recent years, the energy transfer of trivalent rare earth ions to Yb^{3+} has been widely studied, and efficient energy transfers were found in Tb^{3+}-Yb^{3+}, Tm^{3+}-Yb^{3+}, Pr^{3+}-Yb^{3+}, Er^{3+}-Yb^{3+}, Ho^{3+}-Yb^{3+} co-doped powders, crystals, glasses and glass ceramics [9–13]. Although the energy transfer efficiency of downconversion can be very high, the electronic transitions between $4f^N$ levels of trivalent lanthanide ions are forbidden to first order so that the absorption cross sections are weak [14–16], thereby limiting the practical application of such materials in solar cells. In order to make effective downconversion, it is desirable that most of the high-energy part of the solar spectrum could be converted into two near-infrared photons. Otherwise, to enable effective downshifting, a sensitizer which has a broadband absorption is required. The ions Ce^{3+} and Eu^{2+} have strong and broad 4f-5d transitions, making them ideal sensitizers for downshifting.

It has been reported that broadband absorption of Ce^{3+} plays an important role as a sensitizer for the near infrared quantum cutting to Yb^{3+} [17], but the efficiency is not high because the cooperative energy transfer from Ce^{3+} to Yb^{3+} is regarded as a high order

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process. Besides, the downshifting energy transfer process may occur by metal–metal charge transfer [18].

YAG ($Y_3Al_5O_{12}$) is an oxide with good thermal stability. The Y^{3+} sites of YAG can be substituted by rare earth ions. The strong crystal field strength on doped Ce^{3+} ions leads to 4f → 5d emission transitions situated in the visible region and the energy matches twice that of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+}. The ion Pr^{3+} is often used as activator in oxides. The energy transfer from Ce^{3+} to Pr^{3+} is well-known in oxides [19,20]. Furthermore, evidence for quantum cutting from Pr^{3+} to Yb^{3+} has been put forward [21–23]. Hence, in order to compensate for the weak $4f^2$–$4f^2$ absorption of Pr^{3+}, we investigated the tri-doped system YAG:Ce^{3+},Pr^{3+},Yb^{3+} to determine the energy transfer efficiency in this refractory material.

In this paper, the broadband-sensitized downconversion luminescent YAG:Yb^{3+},Ce^{3+},Pr^{3+} phosphors were synthesized using a traditional high temperature solid state reaction method. The effect of the doping concentration and mechanism of Pr^{3+} on the energy transfer efficiency from Ce^{3+} to Yb^{3+} was explored.

2. Experimental

2.1. Materials and synthesis

All white powder samples were synthesized using a conventional high temperature solid state reaction method. The starting materials were Al_2O_3 (99.5%, Guangzhou Chemical Reagent Factory), Y_2O_3 (99.99%, Aladdin Shanghai), CeO_2 (99.99%, Aladdin Shanghai), Pr_6O_{11} (99.99%, Aladdin Shanghai), Yb_2O_3 (99.99%, Aladdin Shanghai). The stoichiometric amounts of raw materials were weighed out and then mixed and milled thoroughly for 1 h in an agate mortar. Afterwards, the homogenous mixtures were transferred to an alumina crucible and heated up to 1500 °C at a rate of 5 °C min^{-1} and calcined at 1500 °C for 6 h in a tube furnace in a reducing atmosphere (90% N_2 + 10% H_2 mixed flowing gas), and then cooled down to 500 °C at a rate of 5 °C min^{-1}, finally cooling down naturally to room temperature.

2.2. Characterization

The phase purity and crystalline structure of all as-obtained powder samples were examined by a MSAL XD II powder diffractometer (Beijing PGENERAL) using Cu Kα radiation (λ = 1.5406 Å) at 36 kV tube voltage and 20 mA tube current with a scanning step of 0.02° over the 2θ range from 10° to 70°. The photoluminescence (PL) and excitation spectra were measured by a Hitachi F-7000 Fluorescence Spectrophotometer (Tokyo) equipped with a xenon lamp (150 W) as excitation source. The slit widths of excitation and emission were set as 2.5 nm and the scanning rate was 1200 nm/min under 400 V working voltage. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD powder patterns

Fig. 1 displays the XRD patterns of YAG:0.06Ce^{3+}; YAG:0.1Pr^{3+}; YAG:0.06Ce^{3+}, 0.06Pr^{3+}, 0.15Yb^{3+} and shows that the samples have good crystalline quality. All the diffraction peaks can be indexed to a pure eulytite-type structure that coincides with the standard JCPDS (No. 33-0040) card. There are no observable diffraction peaks related to impurities, indicating that the doping ions may be incorporated into the YAG crystal lattice *via* the substitution of the Y^{3+} sites by Ce^{3+}, Pr^{3+}, and Yb^{3+}.

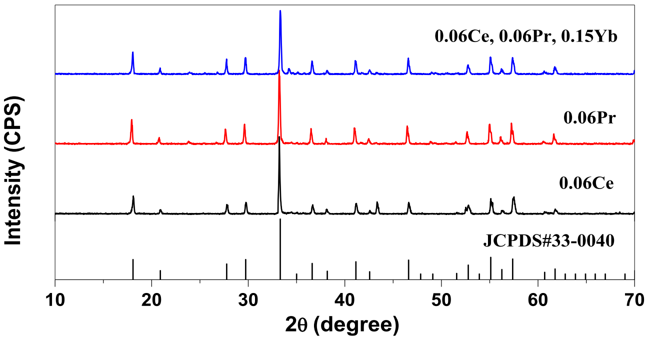

Fig. 1. XRD patterns of YAG:0.06Ce^{3+}; YAG:0.1Pr^{3+} and YAG:0.06Ce^{3+}, 0.06Pr^{3+}, 0.15Yb^{3+}.

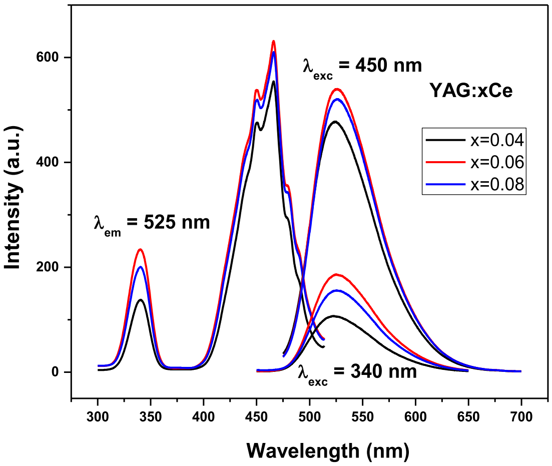

Fig. 2. Excitation (λ_{em} = 525 nm) and emission (λ_{ex} = 340, 450 nm) spectra of YAG: xCe^{3+} (x = 0.04, 0.06, 0.08). The xenon lamp lines decorate the excitation peak.

3.2. Photoluminescence (PL) of YAG:Ce^{3+} phosphors

Fig. 2 shows the excitation and emission spectra of $Y_{3-x}Al_5O_{12}$: xCe^{3+} (x = 0.04, 0.06, 0.08). The excitation spectrum monitored at the wavelength of 525 nm displays two broad bands. The broad feature ranging from 310 to 360 nm, peaking at 340 nm, is ascribed to the $4f^1 {}^2F_{5/2} \rightarrow 5d(2)$ transition of Ce^{3+} ions and the second broad band from 400 to 510 nm, peaking at 450 nm, corresponds to the transition to 5d(1). Upon 310 nm and 450 nm excitation, the PL spectrum exhibits a strong broad emission band from 480 to 650 nm, peaking at 525 nm, due to orbital and spin parity-allowed transitions from the lowest component of the 5d state, 5d(1), to the $^2F_{5/2}$ and $^2F_{7/2}$ levels of Ce^{3+}. Besides, the relative intensities of both the excitation and emission increased with increased doping concentrations of Ce^{3+}, and then decreased due to concentration quenching when the doping concentration of Ce^{3+} exceeded x = 0.06. The optimal concentration of Ce^{3+} singly doped YAG is determined to be 0.06.

3.3. Photoluminescence of YAG:Pr^{3+} phosphors

Fig. 3a (red) exhibits the excitation spectra of YAG:Pr^{3+} by monitoring the emission of Pr^{3+} at 608 nm. The emission spectra of YAG:Ce^{3+} under the excitation wavelength of 310 nm is superimposed in black. The excitation spectral features correspond to narrow-band weak $4f^2$–$4f^2$ transitions of Pr^{3+} ions between 450 and 520 nm [$^3H_{4,5} \rightarrow {}^1I_6$, ^3P_J (J = 0–2)]. There is a spectral overlap in the range of 480 ~ 550 nm between the excitation spectrum of YAG:Pr^{3+} and the emission spectra of YAG:Ce^{3+}, indicating the

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