Optics and Laser Technology 108 (2018) 456–465

Contents lists available at ScienceDirect

Optics and Laser Technology

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

Full length article

Photoluminescence and energy transfer in $Sr_3La(BO_3)_3$:Ce, Sm and Sr_2TiO_4:Sm, Eu phosphors

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A R T I C L E I N F O

Article history:
Received 4 March 2018
Received in revised form 23 June 2018
Accepted 16 July 2018

Keywords:
Phosphor
$Sr_3La(BO_3)_3$:Ce, Sm
Sr_2TiO_4:Sm, Eu
Photoluminescence
Energy transfer

A B S T R A C T

$Sr_3La(BO_3)_3$:Ce, Sm and Sr_2TiO_4:Sm, Eu phosphors were prepared via solid-state reaction method. The X-ray diffraction patterns, photoluminescence, diffuse reflectance spectra, decay curves and energy transfer mechanism of phosphors were investigated in detail. The photoluminescence properties of the phosphors indicated the Ce → Sm energy transfer in $Sr_3La(BO_3)_3$:Ce, Sm and Sm → Eu in Sr_2TiO_4:Sm, Eu. With the activator concentration increase, the characteristic emission intensity of activators increased firstly and then decreased. However, the emission intensity and the average decay times of the sensitizer gradually decreased, which was a strong evidence for energy transfer. The energy transfer efficiency of Ce → Sm in $Sr_3La(BO_3)_3$:0.03Ce, ySm were calculated to be 59.49% when $y = 0.03$ and Sm → Eu in Sr_2TiO_4:0.01Sm, yEu were calculated to be 90.51% when $y = 0.03$. The energy transfers Ce → Sm in $Sr_3La(BO_3)_3$ and Sm → Eu in Sr_2TiO_4 were both demonstrated to be dipole-dipole interactions. The quantum efficiency of $Sr_3La(BO_3)_3$:0.03Ce, 0.03Sm and Sr_2TiO_4:0.01Sm, 0.03Eu reached 45.5% and 19.1%, respectively, which indicated they could serve as efficient n-UV excitation blue-emitting and orange-emitting phosphors applied in w-LEDs, respectively.

1. Introduction

In recent years, white-light-emitting diodes (w-LEDs) have attracted the attention of many researchers, because its advantages such as energy saving, long serving time, high light efficiency and environmental friendliness [1–4]. Currently, the most common w-LEDs are made of phosphor-converted LEDs and the phosphor is a rare earth doped luminescence material [5–9]. The rare earth ions act as a significant role in the phosphors due to its specific electronic structure, the electron transition of 4f-4f or 4f-5d and rich emission energy levels [10–16]. With the development of the research and application the phosphors, using the energy transfer between rare earth ions to control the emission color of single matrix phosphor becomes an important research subject [17–21]. Therefore, so many researchers reported this kind of phosphors, for example, $Sr_3B_2O_6:Ce^{3+}$, Eu^{2+} [22], $Sc(PO_4)_7:Ce^{3+}$, Mn^{2+} [23], $KCaY(PO_4)_2:Ce^{3+},Tb^{3+}$ [24], $NaGdTiO_4:Sm^{3+}$, Dy^{3+} [25] et al.

Generally, the phosphors' emission color could be controlled by co-doping two or more kinds of rare earth ions which have energy transfer relationship. Ce^{3+} is often used to be a sensitizer in many phosphors that doping two kinds of rare earth ions, which is due to its strong 4f-5d absorption in UV region. So, the energy transfer from Ce^{3+} to activator can improve the emission intensity of activator under UV light excitation. And it is beneficial for enhancing the luminescence efficiency of phosphor applied in LEDs [24]. Sm^{3+} can act as activator in many compositions [26–30]. Meanwhile, Sm^{3+} can act as sensitizer in some phosphors [25]. However, the reports about the properties of Ce^{3+}-Sm^{3+} co-doped phosphors are scarce in the literature. There are a lot of literatures on Sm, Eu co-doped phosphors, but the study of the Sm, Eu co-doped titanates phosphors are very rare. In this work, we studied the photoluminescence properties and energy transfer in $Sr_3La(BO_3)_3$:Ce, Sm and Sr_2TiO_4:Sm, Eu by measuring the emission-excitation spectra, decay times and the quantum efficiency. As well, the energy transfer processes and mechanisms of Ce → Sm in $Sr_3La(BO_3)_3$:Ce, Sm and Sm → Eu in Sr_2TiO_4:Sm, Eu phosphors were discussed in detail.

2. Experimental

The $Sr_3La(BO_3)_3$:Ce, Sm and Sr_2TiO_4:Sm, Eu phosphors were synthesized by high temperature solid-state method. Analytical reagent grade $SrCO_3$, H_3BO_3, TiO_2, NH_4HF_2 and spectrographically pure (99.99%) La_2O_3, CeO_2, Sm_2O_3, Eu_2O_3 were selected as the raw materials. All of the above mentioned chemical reagents were

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https://doi.org/10.1016/j.optlastec.2018.07.043

produced from Sinopharm Chemical Reagent Co., Ltd. They were weighted according to stoichiometric ratios. Then, the starting materials were sufficiently grinded and mixed in an agate mortar. After that, the raw materials of $Sr_3La(BO_3)_3$:Ce, Sm were placed in a corundum crucible and annealed in a reducing ($N_2/H_2 = 95:5$) atmosphere for 4 h at 1250 °C. The heating rate was controlled to be 6 °C/min until the target temperature and cooling ramps were 3 °C/min. The raw materials of Sr_2TiO_4:Sm, Eu were placed in a corundum crucible and annealed in the air for 6 h at 1200 °C (a little H_3BO_3/NH_4HF_2 was added as flux). In this case, the heating rate was controlled to be 5 °C/min until the holding temperature before being cooled inside the furnace to room temperature. Finally, the phosphors were obtained in the form of powders.

The phase composition of the samples was characterized by X-ray diffraction (XRD-D/max2200pc, Japan) technique using Cu Kα radiation ($\lambda = 0.154$ nm). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the phosphors were researched by Hitachi F-4600 fluorescence spectrophotometer equipped with a 150 W Xe lamp as the excitation light source. The ultraviolet-visible (UV–vis) diffuse reflection spectra were measured using a UV–vis–NIR Spectrophotometer (DRS, Cary 5000, Agilent, U.S.A.) in the range of 200–800 nm. The photoluminescence decay curves were measured by Edinburgh Instruments FS5 spectrofluorimeter equipped with a 150 W Xe lamp as an excitation source. The quantum efficiency (QE) measurement was conducted on a fluorescence spectrometer (FS5, Edinburg, U.K.) equipped with an integrating sphere (150 mm inside diameter) coated with barium sulfate. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Phase identification

The XRD patterns of the samples $Sr_3La(BO_3)_3$, $Sr_3La(BO_3)_3$:0.03Ce, $Sr_3La(BO_3)_3$:0.03Sm, $Sr_3La(BO_3)_3$:0.03Ce, 0.03Sm are shown in Fig. 1. It was regrettable that the JCPDS card of $Sr_3La(BO_3)_3$ had not been found now. However, it was clear that all of the diffraction peaks of samples could be proved to the pure structure with the standard data of closely related compound $Ba_3Dy(BO_3)_3$ (JCPDS No.50-0098) [31]. The peaks in the XRD patterns were noticeably shifted to higher diffraction angles compared with JCPDS NO.50-0098 due to the ionic radii difference between Sr and Ba ($r_{Sr}^{2+} < r_{Ba}^{2+}$) (the ionic radii of La and Dy are close). Compared with the patterns of the host material $Sr_3La(BO_3)_3$, the rare earth ions doped phosphors showed the similar diffraction peaks and did not have any changes in the position of diffraction peaks. This indicated that the rare earth ions doping had little influence on the crystal structure of the host material due to low doping level.

The XRD patterns of the samples Sr_2TiO_4:0.01Sm, Sr_2TiO_4:0.03-Eu, Sr_2TiO_4:0.01Sm, 0.03Eu are shown in Fig. 2. It could be seen that most of the peaks match well with the JCPDS No. 39-1471. However, there was a strong impurity peak at 31.8 °, it was identified as the diffraction peak of the compound $Sr_4Ti_3O_{10}$. The raw materials TiO_2 had relatively high melting temperature (1850 °C), which hindered the chemical reaction of TiO_2 with SrO, therefore it was difficult to gain highly purified Sr_2TiO_4 crystal phase. But by comparing the three strongest peaks of the XRD patterns, the samples could be determined as Sr_2TiO_4.

3.2. Photoluminescence and energy transfer in $Sr_3La(BO_3)_3$:Ce, Sm

The photoluminescence and photoluminescence excitation spectra of $Sr_3La(BO_3)_3$:0.03Ce, $Sr_3La(BO_3)_3$: 0.03Sm, and $Sr_3La(BO_3)_3$: 0.03Ce, 0.03Sm samples are shown in Fig. 3, respectively. The PLE spectrum of $Sr_3La(BO_3)_3$:0.03Ce monitored at 442 nm showed an intense broad excitation band centered at 342 nm, which were assigned to $4f \rightarrow 5d$ transition of Ce^{3+}. The broad excitation band from 250 nm to 400 nm was significant for the excitation absorption of the n-UV LED chip. Under the 342 nm excitation, the PL spectrum of $Sr_3La(BO_3)_3$:0.03Ce displayed an asymmetric broad band from 350 nm to 650 nm with the center at around 442 nm [32–36]. The PLE spectrum of $Sr_3La(BO_3)_3$:0.03Sm monitored at 603 nm contained five excitation bands from 320 nm to 550 nm and the most strong one centered at 405 nm, which corresponding to *f-f* transition of Sm^{3+}. Moreover, the PL spectrum of $Sr_3La(BO_3)_3$:0.03Sm under the excitation of 405 nm only emerged three peaks at 566 nm, 603 nm, 651 nm, which was attributed to $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2 and 9/2) characteristic transitions of Sm^{3+}. And the $^4G_{5/2} \rightarrow {}^6H_{7/2}$(603 nm) transitions was more intense than others [37]. According to Dexter theory, the efficient energy transfer is possible when the partial overlap of excitation spectrum of activator and emission spectrum of sensitizer takes place [38,39]. Comparing the Fig. 3(a) and (b), it can be seen that the excitation spectrum of $Sr_3La(BO_3)_3$:0.03Sm had some overlap with the emission spectrum of $Sr_3La(BO_3)_3$:0.03Ce between 350 and 550 nm, which indicated an energy transfer effect in $Sr_3La(BO_3)_3$:

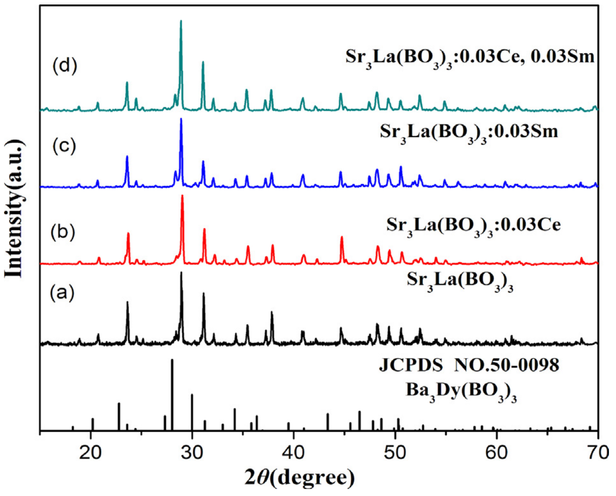

Fig. 1. XRD patterns of samples $Sr_3La(BO_3)_3$ (a), $Sr_3La(BO_3)_3$:0.03Ce (b), $Sr_3La(BO_3)_3$:0.03Sm (c), $Sr_3La(BO_3)_3$:0.03Ce, 0.03Sm (d) and the standard data of $Ba_3Dy(BO_3)_3$(JCPDS NO.50-0098).

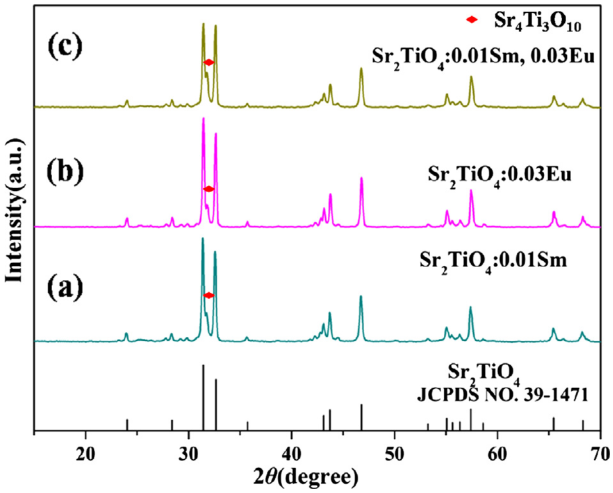

Fig. 2. The XRD patterns of the samples Sr_2TiO_4:0.01Sm (a), Sr_2TiO_4:0.03Eu (b), Sr_2TiO_4:0.01Sm, 0.03Eu (c).