Journal of Luminescence 184 (2017) 143–149

Contents lists available at ScienceDirect

Journal of Luminescence

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

Enhancing Sm^{3+} red emission via energy transfer from $Bi^{3+} \rightarrow Sm^{3+}$ based on terbium bridge mechanism in $Ca_2Al_2SiO_7$ phosphors

Minhong Li, LiLi Wang, Weiguang Ran, Chunyan Ren, Zeling Song, Jinsheng Shi *

Qingdao Agricultural University, Qingdao 266109, People's Republic of China

A R T I C L E I N F O

Article history:
Received 24 June 2016
Received in revised form
14 November 2016
Accepted 3 December 2016
Available online 13 December 2016

Keywords:
Red phosphor
Novel technical route
Energy transfer
Terbium bridge

A B S T R A C T

Currently, the key change for white-LED is to improve the luminescence efficiency of red phosphor. Sm^{3+} activated phosphor was considered due to suitable emission position of red light. However, the luminescence intensity in the red region is weak. For enhancing red-emitting of Sm^{3+}, Bi^{3+} and Tb^{3+} ions were introduced into $Ca_2Al_2SiO_7:Sm^{3+}$ phosphors based on the concept of energy transfer. For $Ca_2Al_2SiO_7:Bi^{3+}$, Sm^{3+} samples, it can be observed that the energy transfer process was blocked. Hence, Tb^{3+} was introduced into $Ca_2Al_2SiO_7:Bi^{3+}$, Sm^{3+} samples to increase Sm^{3+} luminescence intensity based on $Bi^{3+} \rightarrow Tb^{3+} \rightarrow Sm^{3+}$ energy transfer process. Compared with Sm^{3+} single-doped $Ca_2Al_2SiO_7$ phosphor, the luminescence intensity of Sm^{3+} was enhanced by 2.6 times. It can be found that Tb^{3+} ions play a role of storing the energy or transfer bridge from $Bi^{3+} \rightarrow$ Sm^{3+} by investigating the $Ca_2Al_2SiO_7:Bi^{3+}$, Tb^{3+} and $Ca_2Al_2SiO_7:Tb^{3+}$, Sm^{3+} energy transfer mechanism. All these results suggest that terbium branch mechanism plays an important role on enhancing activators luminescence intensity.

1. Introduction

Inorganic luminescence materials doped with rare-earth and transitional metal ions have attract great attention due to their wide application, such as white light emitting diodes (w-LEDs), filed emission displays (FEDs), plasma display panels (PDPs), lasers and so on [1–5]. In these applications, w-LEDs have caused great interest because of their small size, environmental friendliness, lower energy consumption, and long lifetime compared with traditional incandescent or fluorescence lamps [6–10]. Nowadays, the leading commercial w-LEDs is fabricated by a "blue (InGaN) LED chip+yellow ($YAG:Ce^{3+}$) phosphor" [11]. However, the inherent weaknesses such as the high correlated color temperature ($CCT > 7000$ K) and poor color rendering index ($CRI < 80$) were caused by the absence of red component, which greatly limiting its application [12]. In order to overcome the drawbacks, the new method was explored to enhance red emission for white-LED.

For investigating red-emitting phosphors, Sm^{3+} ions were considered due to suitable emission position. And it can be studied extensively [13]. As reported previous, Ran et al. studied $ZnWO_4:Sm^{3+}$, Bi^{3+}, Li^{+} phosphor, strong red emission from Sm^{3+} was observed excited at UV light. And tunable emissions from blue to white, finally to red were obtained due to energy transfer from WO_6^{6-} to Sm^{3+} and Bi^{3+} to Sm^{3+}[14]. Cao et al. investigated $Sr_2P_2O_7:Sm^{3+}$ phosphor, bright red emission was obtained excited by UV light which can be used for n-UV LED chip [15]. $Ca(WO_4)_2:Sm^{3+}$ phosphor was reported by Maheshwary et al., tunable emissions were realized with changing Sm^{3+} doping concentration [16]. Recently, Shi et al. investigated $LiY_{1-x}SiO_4:Ce^{3+}$, Sm^{3+} phosphor, red luminescence emission was enhanced due to energy transfer from Ce^{3+} to Sm^{3+}[17].

In the research of UV chip activated phosphors with high color rendering index and excellent CIE chromaticity coordinates, bismuth ion was considered because of $^3P_1 \rightarrow {}^1S_0$ transition. As the common activator and sensitizer for inorganic luminescent material, the photoluminescence properties have been investigated extensively [18–21]. Dependent on different matrix environment, Bi^{3+} can display alterable luminescence color from ultraviolet, blue, green or even yellow [22].

In the present work, we synthesized $CASO:Bi^{3+}/Tb^{3+}/Sm^{3+}$ phosphors by conventional solid state reaction. The luminescence properties of Bi^{3+}, Tb^{3+} and Sm^{3+} activated single-phase CASO phosphors were studied by XRD and photoluminescence properties. The luminescence intensity of Sm^{3+} was improved 2.6 times through energy transfer from Bi^{3+} to Sm^{3+} by introduction Tb^{3+} in $CASO:Bi^{3+}$, Sm^{3+} phosphor. By investigating the energy transfer mechanism of $CASO:Bi^{3+}$, Tb^{3+} and $CASO:Tb^{3+}$, Sm^{3+} phosphors, indicating terbium bridge model plays an important role on enhancing Sm^{3+} luminescence intensity. In addition, tunable

---

* Corresponding author at: Institute of Chemistry and Pharmacy, Qingdao Agricultural University, Qingdao 266109 P. R. China.
E-mail address: jsshiqn@aliyun.com (J. Shi).

http://dx.doi.org/10.1016/j.jlumin.2016.12.014
0022-2313/© 2016 Elsevier B.V. All rights reserved.

emissions were obtained in CASO:Bi^{3+}/Tb^{3+}/Sm^{3+} phosphors though controlling energy transfer process and adjusting doping concentration of activators.

2. Experimental

2.1. Sample preparation

The raw materials of $CaCO_3$ (A.R.), Al_2O_3 (A.R.), SiO_2 (A.R.), Bi_2O_3 (99.99%) Tb_4O_7 (99.99%) and Sm_2O_3 (99.99%) were purchased from Sionpharm Chemical Reagent Co., Ltd, and all the chemicals were used directly and no further treatment. In this work, as-prepared phosphors of $Ca_2Al_2SiO_7$:0.04Bi^{3+}, xSm^{3+}, $Ca_2Al_2SiO_7$:0.04Bi^{3+}, yTb^{3+}, $Ca_2Al_2SiO_7$:0.05Tb^{3+}, zSm^{3+} and $Ca_2Al_2SiO_7$:0.04Bi^{3+}, yTb^{3+} and xSm^{3+} (x=0.02, 0.04, 0.06, 0.08 and 0.10, y=0.02, 0.04, 0.06, 0.08, 0.10 and 0.12, z=0.01, 0.02, 0.04, 0.06, 0.08 and 0.10) were prepared by high temperature solid state reaction. The starting materials were weighed according to desired composition and ground for 30 min in agate mortar, then, the powders were moved to aluminum crucible, and calcined for 3 h in air atmosphere at 1400 °C. After the samples were cooled to room temperature, all the powders were reground in agate mortar to obtain final sample for subsequent measurements.

2.2. Measurements and characterization

The XRD patterns of CASO:Ln^{3+} samples are recorded on a D8 Focus diffractmeter (Bruker) at the scanning rate of 10 deg/min over the 2θ range from 10 to 80 deg with graphite monochromatized CuKα radiation (λ=0.15405 nm) and the voltage and current were set as 40 kV and 40 mA, respectively. The structure refinement of CASO host was performed using GSAS (General Structure Analysis System) program. The diffraction pattern was recorded with radiation at a 0.01°(2θ)/0.5 s scanning step. The fluorescence spectra are recorded using a F-4600 device (FL-Spectorphotomet) at excitation voltage 400 V, slit width 0.25 nm and a 150 W xenon lamp as the excitation source.

3. Results and discussion

3.1. Phase and structure analysis

The XRD pattern of CASO:Bi^{3+}, Tb^{3+} and Sm^{3+} samples annealed at 1400 °C in air atmosphere for 3 h was shown in Fig. 1. (the standard card JCPDS: 35–0755 of CASO is provided as a reference). The result shows that all the diffraction peaks of the samples are in accordance well with the reference data JCPDS:35-0755, demonstrating that the obtained samples are single phased and they cannot be changed by inducing a small quantity of Bi^{3+}, Tb^{3+} and Sm^{3+}. This may be attributed to the similar ionic radii (note:R_{Ca}=1.12 Å, R_{Bi}=1.17 Å, R_{Tb}=0.923 Å, R_{Sm}=0.964 Å).

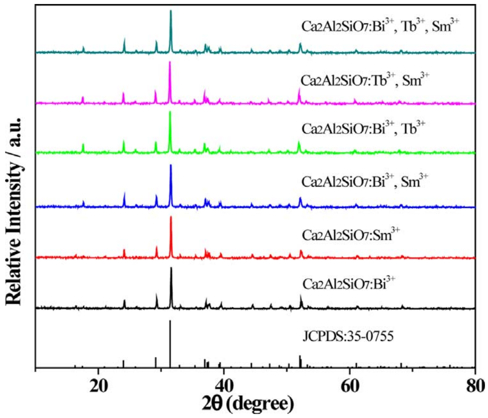

Fig. 1. XRD patterns of Bi^{3+}, Tb^{3+} and Sm^{3+} single-doped or co-doped CASO samples.

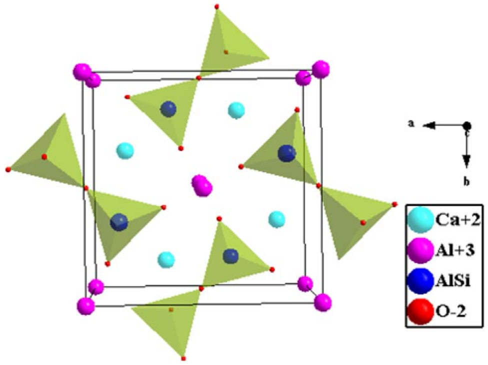

Fig. 2. The crystal structure of CASO.

Fig. 2 shows the crystal structure of CASO host along the c-axis direction from inside to outside. In the compound CASO, Ca^{2+} occupied 2e site surrounded by eight-O atoms. Al1 and Al2 located at 2a and 4e sites respectively. Also, Al2 and Si atoms are both expected to occupy the center of $(Al/Si)O_4$ tetrahedron with the constant composition ratio of 1:1. O atoms are assigned to the 2c, 4e and 8 f sites, expressed as O1, O2 and O3. Besides, two $(Al/Si)O_4$ tetrahedron are connected by sharing O atom to form $(Al/Si)O_7$ group. And these groups connect to each other by Al1 or Ca atoms to form concentrated framework of CASO. Thus, because of similar ionic radii, the Bi^{3+}, Tb^{3+} and Sm^{3+} ions were expected to substitute for Ca^{2+} sites.

The structure refinement of CASO host was performed by the GSAS software and the corresponding pattern was shown in Fig. 3. The pure CASO sample crystallized in space group P-421M (113) with a=b=7.688 Å, c=5.0688 Å, V=300.17 $Å^3$, which in accordance well with standard data [23]. And all atom parameters were refined to convergence and satisfied the reflection conditions well, with Rp=4.85%, Rwp=8.75%, and χ^2=4.214.

3.2. Luminescence properties

CASO:Bi^{3+}, Sm^{3+}phosphor Fig. 4 shows the PLE and PL spectra of Bi^{3+} and Sm^{3+} single-doped or co-doped samples. For CASO:Bi^{3+} sample, the PLE spectrum monitored at 400 nm from Bi^{3+} $^3P_1 \rightarrow {}^1S_0$ transition exhibits that there is a broad absorption band ranging from 200 to 400 nm. The peak at 210 nm is due to host absorption band,

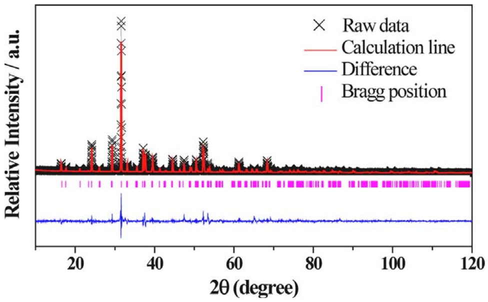

Fig. 3. Experimental (black crosses) and calculated (red solid line) XRD patterns and their difference (blue solid line) for the Le Bail fit of $Ca_2Al_2SiO_7$ host by the GSAS program. The short magenta vertical lines show the position of Bragg reflections of the calculated patterns. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)