Journal of Alloys and Compounds 731 (2018) 796–804

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Enhanced luminescence and tunable color of $Sr_8CaSc(PO_4)_7$:Eu^{2+}, Ce^{3+}, Mn^{2+} phosphor by energy transfer between Ce^{3+}-Eu^{2+}-Mn^{2+}

Jingyan Fan [a], Jing Gou [a, *], Yali Chen [a], Binxun Yu [a, **], Shengzhong Frank Liu [a, b, ***]

[a] *Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China*

[b] *Dalian National Laboratory for Clean Energy, iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*

ARTICLE INFO

Article history:
Received 4 September 2017
Received in revised form
12 October 2017
Accepted 13 October 2017
Available online 16 October 2017

Keywords:
Photoluminescence
Energy transfer
LED
Luminescence
Phosphor
White light emission

ABSTRACT

The crystal structure of $Sr_8CaSc(PO_4)_7$:Eu^{2+}, Ce^{3+}, Mn^{2+} phosphor was refined and determined from Rietveld refinement method. The occupation for Eu^{2+}, Ce^{3+} at Ca^{2+} ion site and Mn^{2+} at Sc^{3+} site in $Sr_8CaSc(PO_4)_7$ host material were proved by the XRDs profiles and Van Uitert equation. The designed tri-energy transfer process of $Eu^{2+}\rightarrow Mn^{2+}$, $Ce^{3+}\rightarrow Mn^{2+}$ and $Ce^{3+}\rightarrow Eu^{2+}\rightarrow Mn^{2+}$ occurred in $Sr_8CaSc(PO_4)_7$ phosphor, and furtherly certified by their decay curves. The corresponding calculated energy transfer efficiencies indicated that the energy transfer $Ce^{3+}\rightarrow Mn^{2+}$ made the main contribution on the emission enhancement of Mn^{2+} ion. The chromaticity and color temperature of $Sr_8CaSc(PO_4)_7$:xEu^{2+}, yCe^{3+}, zMn^{2+} phosphors were conveniently adjusted in a broad region by the tri-energy transfer and different excitation energy, which is from (0.2914, 0.3396), 7606 K to (0.4458, 0.3303), 2013 K under 311 nm excitation and (0.2248, 0.5466), 8000 K to (0.3978, 0.4932), 4231 K under 370 nm excitation, respectively. Meanwhile, the corresponding quantum efficiency was improved up to 36.3% in $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5% Ce^{3+}, 2%Mn^{2+} phosphor by tri-energy transfer and high excitation energy 311 nm. The corresponding fabricated 310 SCSPO-LED and 370 SCSPO-LED showed the chromaticity and color temperature as (0.241, 0.345), 10818 K and (0.339, 0.254), 4673 K respectively, that prove $Sr_8CaSc(PO_4)_7$:xEu^{2+}, yCe^{3+}, zMn^{2+} phosphors have potential application value on NUV WLEDs.

1. Introduction

White-light-emitting diodes (WLEDs) are replacing the traditional lighting systems because of their excellent features as high efficiency, high thermal stability, energy-saving, long lifetime, and environmental friendly [1–3]. The commercial methods for WLEDs manufacture are combining blue InGaN chip with yellow-emitting $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce) phosphor or coating three primary red, green and blue-emitting phosphors on the near-UV (NUV) chip. However, in the first method the absence of red-emitting results in cool-white light emitting making this kind of WLEDs not suitable for indoor lighting, and in the second method the energy reabsorption between phosphors lead to the lower luminescence efficiency. Thus how to simply obtain high efficiency warm white light is still a challenge in the field of WLEDs.

Energy transfer (ET) between different luminescent activators is considered as an effective approach to generate warm-white light from single-phase phosphor, that avoid the insufficiency of low correlated color temperature (CCT) and energy reabsorption. How to select appropriate ions and adjust the emission color by energy transfer is valuable to be explored. Because rare earth or transition metal ions have rich energy levels, a rare earth sensitizer and multiactivators (rare earth or transition metal ions) are designed doping into crystalline matrices, such as $Eu^{2+}/Tb^{3+}/Mn^{2+}$ ions in $(Sr_3,Ca,Ba)(PO_4)_3Cl$ phosphor [4], $Ce^{3+}/Tb^{3+}/Mn^{2+}$ ions in $Ca_3Gd_7(PO_4)(SiO_4)_5O_2$ phosphor [5], $Tm^{3+}/Eu^{3+}/Tb^{3+}$ in LaF_3 [6] and $CaW_{1-x}Mo_xO_4$ phosphors [7]. The warm-white-emitting was reported to be directly obtained by efficient energy transfer of

---

* Corresponding author.

** Corresponding author.

*** Corresponding author. Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China.

E-mail addresses: goujing@snnu.edu.cn (J. Gou), yubx@snnu.edu.cn (B. Yu), liusz@snnu.edu.cn (S.F. Liu).

https://doi.org/10.1016/j.jallcom.2017.10.099
0925-8388/

Eu^{2+}-Mn^{2+} [8–10], however, how to further improve its transfer efficiency is also a challenge. Because of their overlapped PLE spectra, the introduction of Ce^{3+} as a sensitizer to enhance the luminescence efficiency of Eu^{2+} and Mn^{2+} is considered as a good choice.

Whitlockite phosphate $Sr_8MA(PO_4)_7$ ($M = Zn^{2+}$, Mg^{2+}; $A = Gd^{3+}$, Sc^{3+}, La^{3+}) derive from $Sr_9A(PO_4)_7$, which have been developed as the key materials for NUV LEDs applications because of its rigid crystal structure, high chemical and thermal stability [9,11–15]. How to modify its constituents as a stable matrix for luminescent centres is very important. Due to the ionic radius of Ca^{2+} is closed to Sr^{2+}, the incorporation of Ca^{2+} can stabilize original crystal structure, thus $Sr_8CaSc(PO_4)_7$ is chosen as aimed host material. The luminescence properties of the novel $Sr_8CaSc(PO_4)_7$:Ce^{3+}, Eu^{2+}, Mn^{2+} phosphors is firstly explored and reported in this paper.

In our research, the crystal structure and the luminescent properties of $Sr_8CaSc(PO_4)_7$:Ce^{3+}, Eu^{2+}, Mn^{2+} phosphor were detailed investigated. The tunable Commission International de l'Eclairage (CIE) chromaticity coordinates and CCT can be obtained by the increasing incorporation of Mn^{2+} ions and different excitation energy. Furthermore, the mechanism for energy transfer from Ce^{3+} and Eu^{2+} to Mn^{2+} ions was certified by their photoluminescence (PL) spectra, photoluminescence excitation (PLE) spectra and fluorescence decay curves. The EL spectra of fabricated 310 SCSPO-LED and 370 SCSPO-LED proves that $Sr_8CaSc(PO_4)_7$:Eu^{2+}, Ce^{3+}, Mn^{2+} phosphor is potential to be fabricated with NUV (300–420 nm) chip for the warm white-light LEDs application.

2. Experimental

2.1. Materials and synthesis

The polycrystalline phosphors composed of $Sr_8CaSc(PO_4)_7$:xEu^{2+}, yCe^{3+}, zMn^{2+} (SCSPO:xEu^{2+}, yCe^{3+}, zMn^{2+}) ($0 < x \leq 2.5\%$, $0 \leq y \leq 3\%$, $0 \leq z \leq 3\%$) were synthesized by a traditional solid-state reaction, in which the constituent raw materials $SrCO_3$ (A. R., 99%); $CaCO_3$ (A. R., 99.0%); Sc_2O_3 (A. R., 99.99%); $(NH_4)_2HPO_4$ (98.5%); $Ce(NO_3)_3\cdot 6H_2O$ (A. R., 99.95%); Eu_2O_3 (A. R., 99.99%) and $MnCO_3$ (A. R., 99.0%) were weighted in stoichiometric proportions. The mixed powders were sintered at 900 °C for 6 h in air, then reground and calcined at 1450 °C for 24 h under a reducing CO atmosphere. The SCSPO resin is constructed of an epoxy resin well-dispersed with SCSPO:1%Eu^{2+}, 2.5%Ce^{3+}, 1.0%Mn^{2+} and SCSPO:1%Eu^{2+}, 2.5%Ce^{3+}, 2.0%Mn^{2+} phosphors. The epoxy resin was made of Q-203 A and Q-203 B (V_A:V_B = 2:1). The SCSPO-LED was fabricated by combining SCSPO resin on LED chips.

2.2. Materials characterization

The crystal structure were refined and determined by SmartLab powder X-ray diffractometer. The X-ray diffraction (XRD) data were collected using Cu Kα radiation (DX-2700 powder X-ray diffractometer). The PLE, PL and EL spectra were all recorded by a Hitachi F-7000 fluorescence spectrophotometer with Xe lamp as the light source. All the fluorescence lifetime measurements were investigated by using an Edinburgh FLS980 fluorescence spectrophotometer. The Photoluminescence quantum efficiency (QE) was measured by an Absolute PL quantum yield measurement system Hamamatsu C9920-02G. All the measurements above were performed at room temperature. The thermal quenching measurements were investigated by using the Hitachi F-7000 fluorescence spectrophotometer equipped with a heating accessory (TCB1402C).

3. Results and discussion

3.1. Phase identification and crystal structure

Fig. 1(a) shows the observed (black crosses), calculated (red solid line), and difference (bottom) XRD profiles for the Rietveld refinement of $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+}, 0.5%Mn^{2+} and $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+}, 2.5%Mn^{2+} phosphors at 298 K. The Rietveld refinement results indicate that the incorporation of Eu^{2+}, Ce^{3+} and Mn^{2+} ions in $Sr_8CaSc(PO_4)_7$ host structure didn't cause any impurity. The $Sr_8CaSc(PO_4)_7$:Eu^{2+}, Ce^{3+}, Mn^{2+} phosphors crystallize as a monoclinic structure with space group $I2/a$. For $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+}, 0.5%Mn^{2+}, its lattice parameters were determined as a = 18.0583(1) Å, b = 10.6681(8) Å, c = 18.4782(1) Å, α = 90°, β = 133.0128°, γ = 90°, and V = 2598.05(31) Å^3. Its refinement finally converged to R_P = 5.25%,

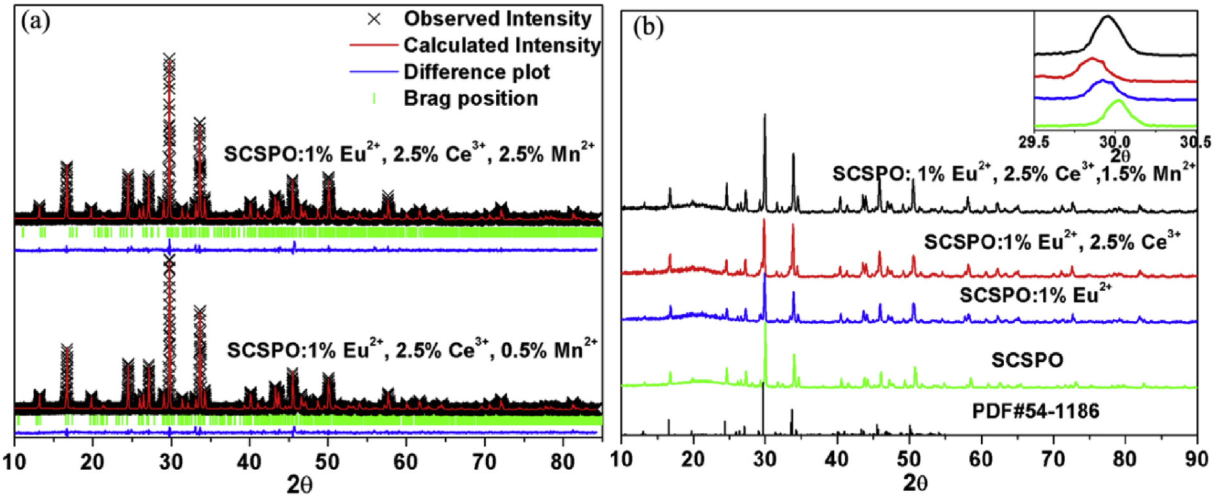

Fig. 1. (a) Observed (black crosses), calculated (red solid line), and difference (bottom) XRD profiles for the Rietveld refinement of $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+}, 0.5%Mn^{2+} (down) and $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+}, 2.5%Mn^{2+} (up) phosphors at 298 K. Bragg reflections are indicated by green tick marks; (b) the XRDs of $Sr_8CaSc(PO_4)_7$, $Sr_8CaSc(PO_4)_7$:1% Eu^{2+}, $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+} and $Sr_8CaSc(PO_4)_7$:1%Eu^{2+}, 2.5%Ce^{3+}, 1.5%Mn^{2+} phosphors. The magnified diffraction peaks at about 30° were inserted in the figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)