Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 3659–3665

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# An intense red-emitting phosphor $Sr_3Lu(PO_4)_3:Eu^{3+}$ for near ultraviolet light emitting diodes application

Tao Wang, Yihua Hu*, Li Chen, Xiaojuan Wang, Miao He

*School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Waihuan Xi Road, No. 100, Guangzhou 510006, PR China*

Received 24 September 2015; received in revised form 6 November 2015; accepted 6 November 2015
Available online 14 November 2015

**Abstract**

A series of $Sr_3Lu(PO_4)_3:Eu^{3+}$ phosphors were successfully prepared via the solid-state method, and their luminescence properties were investigated. The excitation and emission spectra show that this phosphor can be effectively excited by near ultraviolet (NUV) light, and produces strong and prevailing red emissions at 612 nm belonging to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition. $Eu^{3+}$ ion was heavy doped in $Sr_3Lu(PO_4)_3$ host and the optimal concentration of $Eu^{3+}$ was found as 0.8. The critical transfer distance of $Eu^{3+}$ was determined to be 8.5 Å. The concentration quenching was demonstrated to be caused by the energy transfer among the nearest-neighbor ions in the $Sr_3Lu(PO_4)_3:Eu^{3+}$ phosphor. Under excitation of 394 nm, the integral emission intensity of $Sr_3Lu_{0.2}(PO_4)_3:0.8Eu^{3+}$ is about 6 times that of $Y_2O_3:Eu^{3+}$. The CIE color coordinates of $Sr_3Lu_{0.2}(PO_4)_3:0.8Eu^{3+}$ was (0.636, 0.354) located in red region. In addition, good thermal stability was also identified in $Sr_3Lu_{0.2}(PO_4)_3:0.8Eu^{3+}$ and its emission intensity was reduced to 88% of its initial value at 100 °C and 70% at 200 °C. The current research suggests that $Sr_3Lu(PO_4)_3:Eu^{3+}$ could be a promising red phosphor for white LEDs and display devices.


*Keywords:* Luminescence; $Sr_3Lu(PO_4)_3:Eu^{3+}$; Red phosphor

## 1. Introduction

White light-emitting diodes (W-LEDs) have been considered as a new generation of light source owing to their superior advantages of small size, energy savings, environmental protection, long service life, etc [1–3]. There are many ways to realize W-LEDs, the phosphor conversion technology is growing rapidly because of its mature preparation process, simple control circuit, low cost. Currently, most commercially utilized W-LEDs are composed of a yellow-emitting phosphor ($Y_3Al_5O_{12}:Ce^{3+}$) and a blue LED chip. However, the white light of this combination exhibits poor color rendering index and high color temperature due to the absence of a red spectral component [4,5]. Therefore, a feasible method is to add a highly efficient red phosphor excited by blue light to make up the lack of the red component. The other alternative is to directly use a NUV LED to excite blue, green and red phosphors to create warm-white light. Both two methods above require highly efficient red phosphors with strong absorption from NUV to blue region. At present, the most commonly seen commercial red phosphors are sulfide/oxysulfide (e.g. $CaS:Eu^{2+}$ [6], $Y_2O_2S:Eu^{3+}$ [7]) and nitrogen oxide/nitride (e.g. $M_2Si_5N_8:Eu^{2+}$ (M = Ca, Sr, Ba) [8], β-SiAlON:$Pr^{3+}$ [9]). However, sulfides and oxysulfides are usually not stable enough and decompose at high temperature, whereas (oxy)nitrides are constrained by relatively harsh preparation conditions (required are high temperatures > 1600 °C and $N_2$ atmosphere to prevent oxidation). Therefore, the exploration of high performance, good stability, easily synthesized red emitting phosphors is still necessary and urgent.

For the high efficiency and appropriate CIE chromaticity coordinates of red-emitting phosphors, $Eu^{3+}$ doped materials are preferred due to their intense NUV absorption and excellent pure red emissions corresponding to the $^5D_0 \rightarrow {}^7F_J$ $_{(J=1,2,3,4)}$ transitions of $Eu^{3+}$ [10–13]. In addition, the host material is another key factor to determine the performance of phosphors. Among various kinds of host materials, phosphates are

*Corresponding author. Tel.: +86 20 39322262; fax: +86 20 39322265.
*E-mail address:* huyh@gdut.edu.cn (Y. Hu).

http://dx.doi.org/10.1016/j.ceramint.2015.11.033
0272-8842/

considered to be one type of promising luminescence materials for their easy-synthesis, low-cost and chemical/thermal-stabilities in a wide temperature range. The eulytite-type orthophosphate with the general formula of $A_3M(PO_4)_3$ (A=Ca, Sr, Ba, M=La–Lu, Y, Sc, Bi) has been extensively studied as appropriate matrix for various inorganic luminescent materials. For example, the luminescence properties of activators in $Ba_3Y(PO_4)_3:Sm^{3+}$ [14], $Sr_3Y(PO_4)_3:Dy^{3+}$ [15], $Sr_3Bi(PO_4)_3:Tb^{3+}$ [16] are reported. The energy transfer of activators in $Sr_3La(PO_4)_3:Sm^{3+}$, $Eu^{3+}$ [2], $Sr_3Sc(PO_4)_3$: $Eu^{2+}$, $Mn^{2+}$ [17], $Ba_3La(PO_4)_3:Eu^{3+}$, $Tb^{3+}$ [18], $Ba_3Lu(PO_4)_3:Ce^{3+}$, $Tb^{3+}$ [19] were also investigated. However, to the best of our knowledge, the luminescence properties of $Sr_3Lu(PO_4)_3:Eu^{3+}$ red phosphors have not been recorded before. Herein, we synthesized a series of $Sr_3Lu(PO_4)_3:Eu^{3+}$ samples via a solid-state reaction and the photoluminescence (PL) properties were investigated in detail.

## 2. Experimental

The $Eu^{3+}$ doped $Sr_3Lu(PO_4)_3$ samples were obtained by the solid state reaction as the nominal chemical formula $Sr_3Lu_{1-x}(PO_4)_3:xEu^{3+}$ by varying the $Eu^{3+}$ content $x$ from 0.2 to 1. The reactants were $SrCO_3$ [analytical reagent (A.R.)], $(NH_4)_2HPO_4$ (A.R.), $Lu_2O_3$ (99.9%) and $Eu_2O_3$ (99.9%). The starting raw materials were precisely weighed stoichiometrically and ground in an agate mortar for 1 h for complete mixing. The homogeneous mixture was pre-sintered at 500 °C for 2 h, reground, and finally fired at 1250 °C for 5 h in air. Finally, the products were cooled down slowly to room temperature and then ground to a white powder for characterization.

The phase purity of the final samples was characterized by X-ray powder diffraction (XRD) analysis using an X-ray diffractometer with Cu-Kα irradiation ($\lambda$=1.5406 Å) at 36 kV tube voltage and 20 mA tube current, with a scanning step of 0.02° in the $2\theta$ range from 10° to 70°. The excitation and emission spectra, fluorescence lifetime as well as temperature-dependent PL spectra of the phosphors, were recorded on an EDINBURGH FLS920 Combined Fluorescence lifetime and Steady State Spectrometer and a 450 W xenon lamp was used as excitation source. All measurements were performed at room temperature.

## 3. Results and discussion

### 3.1. XRD patterns of $Sr_3Lu(PO_4)_3$:Eu phosphors

As an eulytite structure compound, $Sr_3Lu(PO_4)_3$ has a cubic crystal structure with a space group of I43d (No. 220) and lattice parameters $a=b=c=10.095$ Å, $Z=4$ and V=1028.77 Å$^3$. The crystal structure of all as-synthesized powders was characterized by XRD. Fig. 1 shows the XRD patterns of $Sr_3Lu_{1-x}(PO_4)_3:xEu$ phosphors with varied doping $Eu^{3+}$ contents ($x$). It can be found that the XRD patterns of all samples are similar to each other, and all detected diffraction peaks for $Sr_3Lu(PO_4)_3$:Eu within the whole range of $Eu^{3+}$ doping contents are well indexed to the standard data of $Sr_3Lu(PO_4)_3$ with JCPDS card No. 33-1344. No extra peaks related to impurity phase are detected when $Eu^{3+}$ were doped into the host matrix, indicating that the samples are complete solid solution at the established reaction condition, no further purification is needed for as-prepared phosphors. Moreover, we can notice that the peaks of samples shift systematically

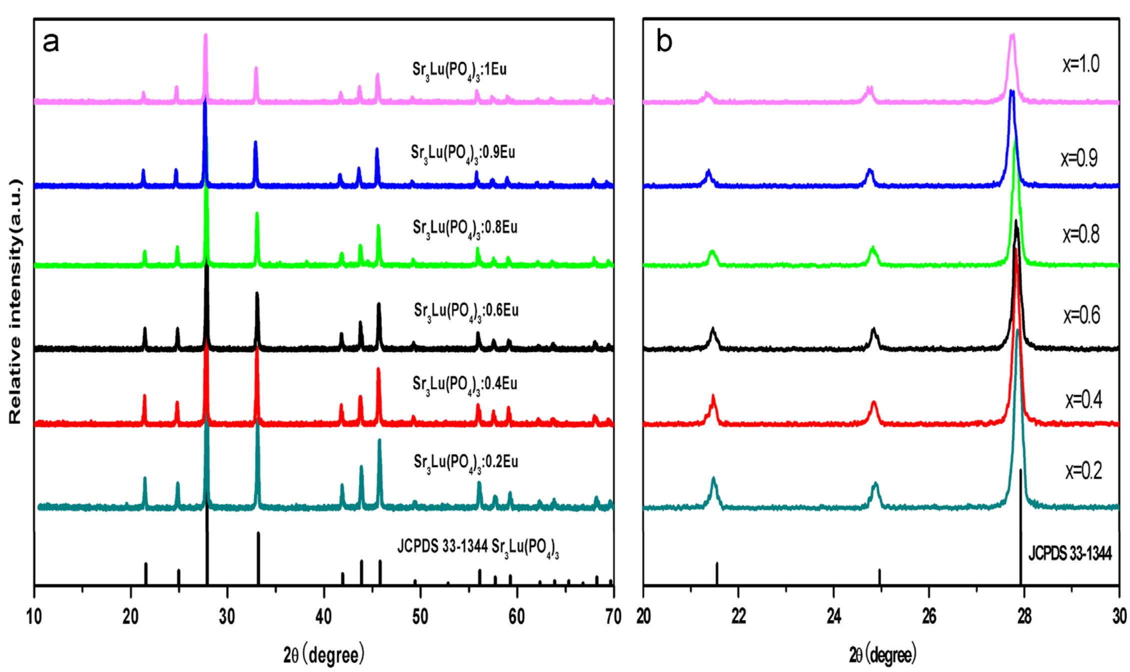


Fig. 1. (a) XRD patterns of $Sr_3Lu_{1-x}(PO_4)_3:xEu^{3+}$ ($x$=0.2, 0.4, 0.6, 0.8, 0.9, 1) phosphors and JCPDS no. 33-1344. (b) The local XRD patterns of $Sr_3Lu_{1-x}(PO_4)_3:xEu^{3+}$ from 20° to 30°.