Optical Materials 75 (2018) 448–452

Contents lists available at ScienceDirect

Optical Materials

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

$SrAl_2O_4:Eu^{2+}$ (1%) luminescence under UV, VUV and electron beam excitation

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ARTICLE INFO

Article history:
Received 14 September 2017
Received in revised form
24 October 2017
Accepted 1 November 2017

Keywords:
$SrAl_2O_4:Eu^{2+}$
Combustion method
Photoluminescence
Cathodoluminescence
Synchrotron radiation
Thermally stimulated luminescence

ABSTRACT

This paper reports the luminescence properties of nanosized $SrAl_2O_4:Eu^{2+}$ (1%) phosphors. The samples were prepared by combustion method at 600 °C, followed by annealing of the resultant combustion ash at 1000 °C in a reductive (Ar + H_2) atmosphere. X-ray diffraction (XRD), photo luminescence (PL) and cathodoluminescence (CL) analysis and thermal stimulated luminescence (TSL) method were applied to characterize the phosphor. For the first time a peak at 375 nm was observed in CL spectra of $SrAl_2O_4:Eu^{2+}$ (1%) nanophosphors. Luminescence excitation spectra analysis have shown that this peak is related to crystal defects. Also in TSL curve one strong peak was observed in the region above room temperature (T = 325 K), which is attributed to lattice defects, namely oxygen vacancies. A green LED was fabricated by the combination of the $SrAl_2O_4:Eu^{2+}$ (1%) nanosized phosphor and a 365 nm UV InGaN chip.

1. Introduction

Due to high quantum efficiency in the visible spectral region [1], good stability, color purity, excellent physical and chemical properties, $SrAl_2O_4:Eu^{2+}$ alkaline earth aluminates are very useful in preparation of pc LEDs [2,3]. In addition, due to their excellent luminescence properties, they also have potential applications in fluorescent lamps, plasma display panels and also can be utilized as persistent luminescence materials [4–6].

Usually two emission bands at 445 and 520 nm are observed in $SrAl_2O_4:Eu^{2+}$. At room temperature the blue band is quenched and only green band is observed. The origin of these bands has been the subject of discussions for many years. Poort et al. [7] explained these two emission bands with the preferential orientation of d orbitals of Eu^{2+} ion on Sr sites. Clabau et al. [8] explained blue emission band with charge transfer from the ground level of the $4f^7$ configuration of Eu^{2+} to the valence band. More recently, Botterman et al. [9] reported a detailed investigation of the origin of both emission bands in $SrAl_2O_4$:Eu. In spite of the similarity in oxygen coordination, differences in bond lengths to the oxygen ligands for the two sites and in coordination number were used to explain the difference in emission and excitation spectra. Nowadays it is generally accepted that these two bands are attributed to emission from Eu^{2+} ions placed in the two different lattice sites (Sr1, Sr 2) in crystal structure of $SrAl_2O_4$.

In this paper, Eu^{2+} doped $SrAl_2O_4$ nanophosphors were synthesized by energy effective, fast and low-cost combustion method. Homogeneous, high crystallinity and good morphology samples were obtained as a result of the synthesis. In this paper, a photoluminescence (PL) analysis was carried out for Eu^{2+} doped $SrAl_2O_4$ aluminates under UV-VUV excitation. The results of the photoluminescence (PL) and cathodoluminescence (CL) of $SrAl_2O_4:Eu^{2+}$ (1%) nanophosphors were compared and discussed. Experimental results prove that the peak at 375 nm in CL spectrum is related to crystal defects. TSL glow curve peaks at 220 and 325 K are explained by existence of the crystal structure defects, namely oxygen vacancies.

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https://doi.org/10.1016/j.optmat.2017.11.001
0925-3467/

2. Experimental section

For the synthesis, stoichiometric amounts of $Sr(NO_3)_2$ (99,99%), $Al(NO_3)_3 \cdot 9H_2O$ (99,99%), $Eu(NO_3)_3 \cdot 6H_2O$ (99,99%), $CO(NH_2)_2$ (99,3%) and H_3BO_3 (99,9%) were dissolved together in 20 ml of deionized water for obtaining a transparent solution. Small amount of boric acid was used as flux and urea as fuel. The components were mixed together and the solution was stirred using a magnetic bar at 70 °C for 2 h [10,11]. Every 15 min the temperature of the solution was raised by 10 °C up to 130 °C. A white viscous gel was obtained. The gel was placed in a preheated muffle furnace at 600 °C. At this temperature the solution evaporated, generating large amounts of gases, e.g. oxides of carbon and nitrogen. The combustion process lasted for about 5–10 min and white ash was obtained. The size of particles is in the range 50–70 nm [10] (Fig. 1).

At the next step, the obtained white ash was annealed at 1000° C for 1 h under reductive (Ar, 20% H_2) atmosphere for the reduction of Eu^{3+} ions to Eu^{2+}.

X-ray diffraction patterns were recorded using a Bruker 5000 diffractometer in standard (θ-2θ) geometry using Cu Kα radiation.

Elemental analysis was performed on a Peltier cooled dry EDS system (Thermo Scientific Noran System 7, energy resolution of 125 eV).

Photoluminescence (PL) properties were investigated by measuring the excitation and emission spectrum with a FS920 fluorescence spectrometer (Edinburgh Instruments) equipped with a Hamamatsu R928P red-sensitive photomultiplier (wavelength range from 250 to 850 nm) between 100 and 400 K temperature.

The measurements of luminescence and luminescence excitation spectra were also performed using synchrotron radiation in UV - VUV energy regions at the branch-line FINEST (energy region 5–22 eV) at MAX-lab, Lund. The excitation spectra were corrected using sodium salicylate. The luminescence spectra were measured with ARC Spectra Pro 300i monochromator equipped with Hamamatsu H6240-01 photon counting head in the temperature range 5–300 K.

The measurements of cathodoluminescence spectra and TSL curves were performed under irradiation with electrons (5 keV, 0.4 μA, spot ≈ 1 mm^2). TSL was measured with a linear heating rate 0.167 K/s. All measurements were carried out in a liquid helium vacuum cryostat (5–400 K temperature range, $2*10^{-7}$ Torr vacuum) equipped with Lake Shore 331 Temperature Controller. The luminescence was detected using the UV-VIS-NIR (200–1700 nm) monochromator ARC SpectraPro-2300i equipped with Hamamatsu photon counting head H6240.

Green light was obtained by combination of $SrAl_2O_4:Eu^{2+}$ (1%) phosphor silicone epoxy mixture with an UV LED (365 nm) chip with a power of 3 W. Light parameters were measured by using an Everfine PMS-80 integrating sphere at the driving currents 20 mA and 350 mA for comparison of stability of color coordinates of light in different currents. The spectra of the UV LED with and without phosphor coating were recorded on the Horiba Jobin Yvon 1250M monochromator coupled with Andor Newton CCD detector.

Fig. 1. $SrAl_2O_4:Eu^{2+}$ (1%) ash synthesized by combustion method.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was used to identify the crystal structure and phase purity of the undoped and Eu doped $SrAl_2O_4$ phosphors. It is clear from the XRD analysis that the main peaks in the $SrAl_2O_4:Eu^{2+}$ (1%) sample shows good consistence to the data from the standard powder diffraction file (JCPDS-01-024-11-87) of $SrAl_2O_4$. No obvious shift in the diffraction peaks is observed for $SrAl_2O_4:Eu^{2+}$ phosphor, indicating that adding of a small amount of doping Eu^{2+} ions has no strong influence on the structure of the host due to the similar ionic radius of Sr (1,21 Å) and Eu (1,20 Å). However, one of the intensive peaks (32°) does not coincide with the monoclinic $SrAl_2O_4$ ICDD data and corresponds to cubic phase $Sr_3Al_2O_6$ (a = b = c = 15,844 Å). The intensity of this peak (32°) is higher in the undoped $SrAl_2O_4$ crystal structure than in Eu^{2+} doped $SrAl_2O_4$ (Fig. 2).

3.2. Luminescence properties of $SrAl_2O_4:Eu^{2+}$ (1%)

Photoluminescence properties were investigated at 100–400 K temperature range to determine if synthesized phosphors are suitable for use in fabrication of phosphor-converted pc W- LEDs. For instance, measurements of luminescence spectra at high temperatures (up to 400 K) is required to check whether the synthesized nanophosphors are stable at high temperatures for the application in LEDs which are operating at temperatures exceeding the room temperature. As shown in Fig. 3, in the 100–400 K temperature range, there was not observed any considerable shift of

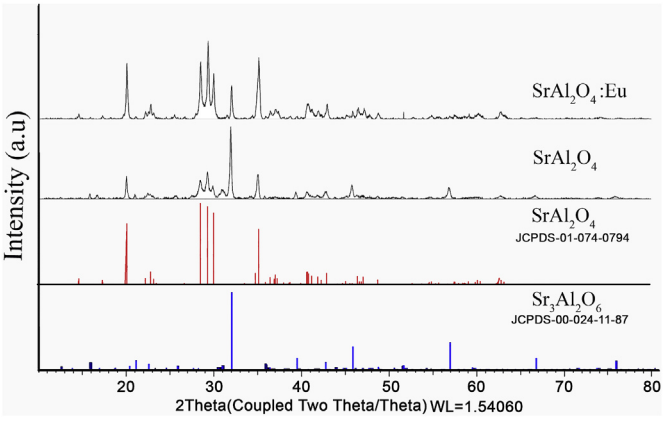

Fig. 2. XRD patterns of $SrAl_2O_4$ and $SrAl_2O_4:Eu^{2+}$ (1%) phosphors and PDF Cards No. JCPDS-01-074-0794, JCPDS-01-024-11-87.