

Photoluminescence and decay properties of Sm^{3+} and Dy^{3+} in SrAl_4O_7 phosphor

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Received: 19 July 2015, Revised: 28 October 2015 and Accepted: 06 November 2015

ABSTRACT

In this study, Sm^{3+} - and Dy^{3+} -doped SrAl_4O_7 phosphors were synthesized by combustion method. X-ray diffraction (XRD) measurement confirmed the monoclinic crystal structure of SrAl_4O_7 . Sr-O and Al-O bonds were identified by Fourier transform infrared (FTIR) spectroscopy. Under 352 nm excitation, the SrAl_4O_7 : Dy^{3+} phosphor shown emission bands at 475 nm (blue) and 574 nm (yellow) that are due to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^6\text{H}_{13/2}$ transitions, respectively. Photoluminescence spectra (PL) of SrAl_4O_7 : Sm^{3+} phosphor has shown bright orange red emission at 598 nm with an excitation wavelength of 405 nm. The decay curve of Sm^{3+} and Dy^{3+} single doped SrAl_4O_7 phosphors were well fitted to a bi-exponential function. The obtained results show that the prepared phosphors may be applicable in the field of eco-friendly solid state lighting technology. Copyright © 2015 VBRI Press.

Keywords: Phosphor; SrAl_4O_7 ; X-diffraction; photoluminescence.

Introduction

In recent years, energy crisis and environmental pollution exert great pressure on the sustainable development of the modern society. In response to the ever-increasing energy demands coupled with serious concerns for global warming, there has been an immense interest in new sources of white light that can reduce electrical energy consumption and operating expenses while providing accurate colors [1, 2].

Recently, the department of energy in the USA has announced its goal to reduce energy consumed by lighting to 50 % by 2020 using high efficiency light emitting diodes (LEDs) [3]. The conventional fluorescent lamps were replaced by LED for lighting applications to decrease the worldwide electricity utilization for lighting by at least 50 %. The efficiency of white LEDs have already greater than that of fluorescent lamps, for that reason white LEDs can be considered as the next-generation of lighting system [4-8].

However, the efficiency of the present LEDs are limited and there is need to develop the new energy saving devices by selecting the suitable host and rare-earth ion. It is known to all that dysprosium has been serving as an activator in different host materials for developing full color displays and solid state lighting. In general, the Dy^{3+} ion provides two dominant emission bands in the blue region (470–500 nm) and yellow region (560–600 nm) [9-15]. These two emissions are originated from ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and

${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transition of Dy^{3+} , respectively [16, 17]. Similarly, samarium (Sm^{3+}) is also an important activator for many different hosts like silicate, phosphate and aluminates. Samarium gives reddish orange emission to its ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions [18, 19].

In this paper, we have synthesized SrAl_4O_7 phosphor doped with Dy^{3+} and Sm^{3+} ions by combustion method. The structure, time decay study and luminescent properties of the prepared phosphors have been investigated.

Experimental

Material synthesis

Sm^{3+} - and Dy^{3+} -doped SrAl_4O_7 phosphors were prepared by the combustion method. All the starting materials employed in the experiment are of Merck-analytical grade. The starting materials are $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Dy_2O_3 , Sm_2O_3 and Urea (NH_2CONH_2) was used as fuel.

First, Dy_2O_3 and Sm_2O_3 are converted into nitrate form by mixing of appropriate amount of diluted nitric acid. All the mixtures were mixed according to the stoichiometric ratio. The resulting colorless solution was further heated at 85–90 °C with constant stirring until a highly viscous wet gel was formed. Thereafter, the resulting gel was transferred into a vertical furnace maintained at 550 °C. Flame temperature as high as 1600 °C converts the vapors phase into mixed aluminates. The flame persists for about 30 seconds. The final product obtained was in the fluffy form, which is used for the further investigations.

Characterizations

The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-K α radiation) at a scanning step of 0.010°. The data were recorded in the 2θ range from 10 to 70°. The photoluminescence measurement of excitation and emission were recorded on a Shimadzu RFPC5301 Spectrofluorimeter. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. Luminescence decay curves were measured with a FLSP920 Phosphorescence lifetime spectrometer (Edinburgh Instruments, UK) using a μ s Xe flash lamp.

Results and discussion

X-ray diffraction (XRD) studies

X-ray The formation of crystalline phase in the host, prepared by the combustion method was confirmed by powder XRD measurements. The XRD peaks are well matched with the standard JCPDS (Joint Committee on Powder Diffraction Standards) file no: 00-025-1208., recently reported by same method [20].

Fourier transform infrared (FTIR) studies

Fig. 1 shows the FTIR spectrum of SrAl₄O₇ phosphor. In the range of 1000 to 600 cm⁻¹, several absorption bands were observed due to the stretching frequencies of metal-oxygen (M-O) such as Al-O, Sr-O and Sr-O-Al bonds [21]. A sharp band at about 1024 cm⁻¹ is assigned to the Al-O stretching vibration [22]. A broad peak near 1453 cm⁻¹ can be ascribed to the Al-O stretching vibration [23, 24]. A weak absorption band at around 1669 cm⁻¹ corresponds to the vibrations of physically absorbed water molecules during the samples preparation for measurements [21].

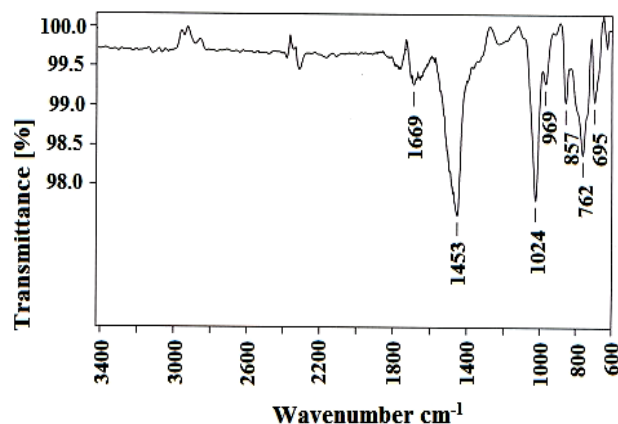


Fig. 1. FTIR spectrum of SrAl₄O₇ phosphor.

Photoluminescence and time decay studies of SrAl₄O₇: Dy³⁺ phosphor

Fig. 2 shows the excitation spectrum of the SrAl₄O₇: Dy³⁺ (Dy³⁺ = 0.5 mol %) by monitoring emission at 475 nm corresponding to ⁴F_{9/2}→⁶H_{15/2} transition of Dy³⁺. The excitation spectrum recorded in the range of 300 to 400 nm that consist of *f-f* transitions of the Dy³⁺ ion. Among the several sharp peaks, the band at 352 nm is predominant

band and is used for further record the emission spectra of SrAl₄O₇: Dy³⁺ phosphors.

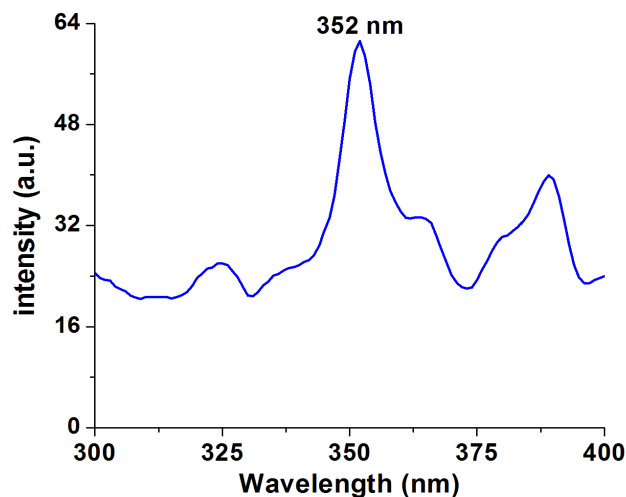


Fig. 2. Excitation spectrum of SrAl₄O₇: Dy³⁺ phosphor (λ_{em} = 475 nm).

The emission spectra of SrAl₄O₇: Dy³⁺ phosphor are shown in **Fig. 3**. Under 352 nm excitation, the spectra consist of two broad bands at blue and yellow regions. The two bands are located at about 475 and 574 nm correspond to the transitions of ⁴F_{9/2}→⁶H_{15/2} (blue) and ⁴F_{9/2}→⁶H_{13/2} (yellow), respectively. The ⁴F_{9/2}→⁶H_{15/2} (blue) transition is magnetically allowed and hardly varies with the crystal field strength around the Dy³⁺ ions in host, whereas the ⁴F_{9/2}→⁶H_{13/2} (yellow) transition is electric dipole transition and strongly influenced by the chemical environment surrounding the Dy³⁺ ions [25].

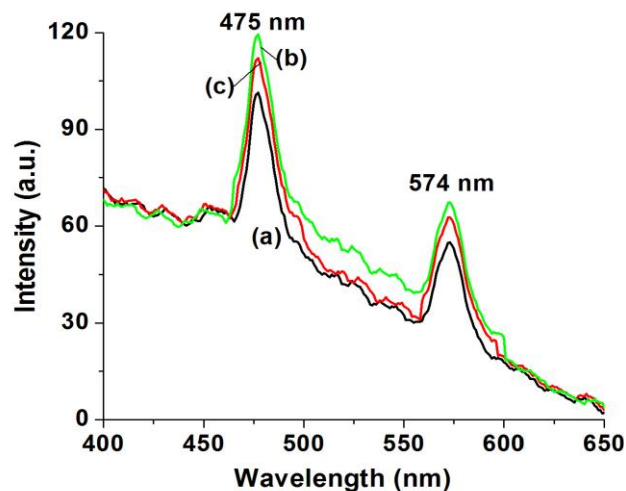


Fig. 3. Emission spectra of SrAl₄O₇: Dy³⁺ phosphor (λ_{ex} = 352 nm), (a) Dy = 0.3 mol %, (b) Dy = 0.5 mol % and (c) Dy = 1 mol %.

The integrated emission intensity of blue emission (475 nm) is higher than yellow emission (574 nm), this indicates that site occupied by Dy³⁺ ions at high inversion symmetries in host [26]. In order to identify the optimum concentration, the Dy³⁺ ions concentration is varied in the host. From the emission spectra, it is clearly observed that the peak positions of the emission bands have not changed by varying the concentration of Dy³⁺ ion.

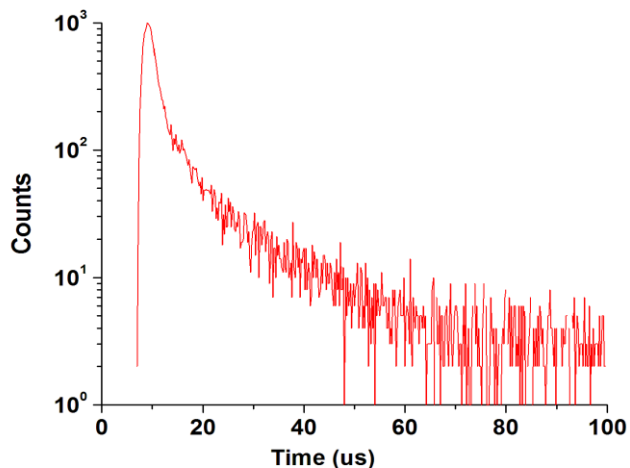


Fig. 4. Luminescence decay curve of SrAl₄O₇: Dy³⁺ phosphor.

The emission intensity increases with an increase in Dy³⁺ concentration up to 0.5 mol %, beyond which the emission intensity tends to decrease. This is due to the concentration quenching effect. At higher dopant concentration, the non-radiation transitions will increase leading to the decrease in emission intensity within the dopant ions [27]. Further, the decay curves were recorded for 475 nm emission. The decay curve of SrAl₄O₇: Dy³⁺ (Dy³⁺ = 0.5 mol %) is shown in Fig. 4. The decay curves were well fitted by a second order exponential function as

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

where, A₁ and A₂ are fitting parameters, τ₁ and τ₂ are the lifetimes. The average lifetimes could be calculated using the relation [28];

$$\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \quad (2)$$

and for SrAl₄O₇: Dy³⁺ phosphor the average lifetime is found to be 2.1 ms.

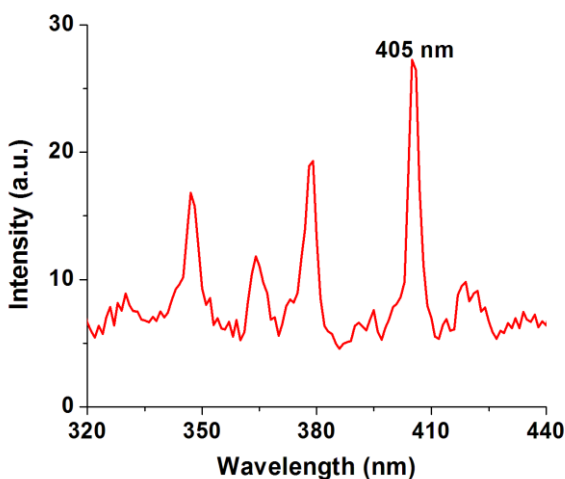


Fig. 5. Excitation spectrum of SrAl₄O₇: Sm³⁺ (λ_{em} = 598 nm).

Fig. 5 shows the excitation spectrum of SrAl₄O₇: Sm³⁺ (Sm³⁺ = 1 mol %) under 598 nm emission wavelength. In the range of 320 to 420 nm, the spectra composed of a

series of sharp peaks at around 347, 364, 379, 405 and 419 nm correspond to the transitions from the ground state to the excited states of Sm³⁺. The intense peak at 405 nm indicates that this phosphor can be effectively excited by near-ultraviolet light-emitting diodes [29].

For measurement of emission spectra, the strongest excitation peak at 405 nm (⁶H_{5/2} → ⁴F_{7/2}) was used. Photoluminescence emission spectra of SrAl₄O₇: Sm³⁺ phosphor is shown in Fig. 6. In the range between 550 and 700 nm, the spectra comprises of several sharp lines, located at 563 nm (⁴G_{5/2} → ⁶H_{5/2}), 598 nm (⁴G_{5/2} → ⁶H_{7/2}) and 645 nm (⁴G_{5/2} → ⁶H_{9/2}). Among them the significant orange emission due to ⁴G_{5/2} → ⁶H_{7/2} transition at 598 nm is the dominant [30, 31]. The most intense emission band at 598 nm is partially magnetic and partially electric dipole transition. Another band located at 562 nm is magnetic dipole transition [32].

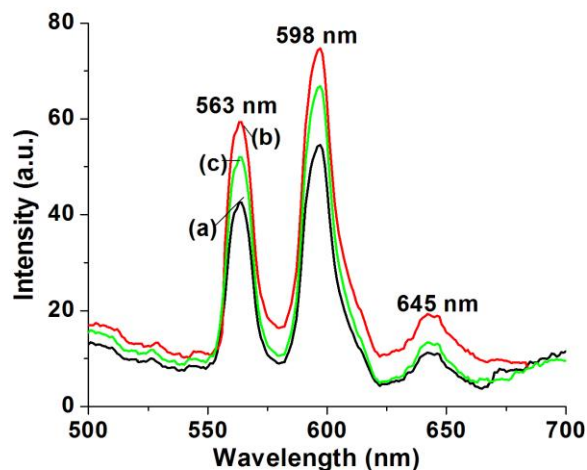


Fig. 6. Emission spectra of SrAl₄O₇: Sm³⁺ phosphor (λ_{exc} = 405 nm) where (a) Sm = 0.5 mol%, (b) Sm = 1.0 mol% and (c) Sm = 2.0 mol %.

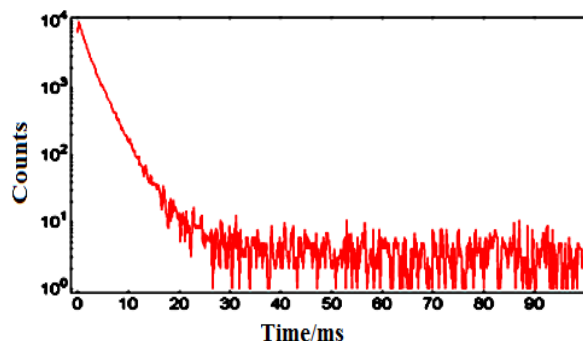


Fig. 7. Luminescence decay curve of SrAl₄O₇: Sm³⁺ phosphor.

The emission band at 645 nm corresponding to the transition ⁴G_{5/2} → ⁶H_{9/2} is electric dipole allowed and is sensitive to the crystal field environment. The integrated emission intensity of the ⁴G_{5/2} → ⁶H_{7/2} transition (598 nm) is higher than that of ⁴G_{5/2} → ⁶H_{9/2} transition (645 nm), indicating that the Sm³⁺ ions are at the symmetric site in host. Moreover, due to the increase in concentration of Sm³⁺ ions, the peak intensity increases and maximum intensity is observed for 1.0 mol% of Sm³⁺ ion. Fig. 7 shows the decay curve of SrAl₄O₇: Sm³⁺ (Sm³⁺ = 1 mol %) for ⁴G_{5/2} → ⁶H_{7/2} (598 nm) emission, excited at 405 nm. The

decay curve is well fitted to the second order exponential function (Equations (1) and (2)) [28] and the average lifetime is found to be 0.38 ms.

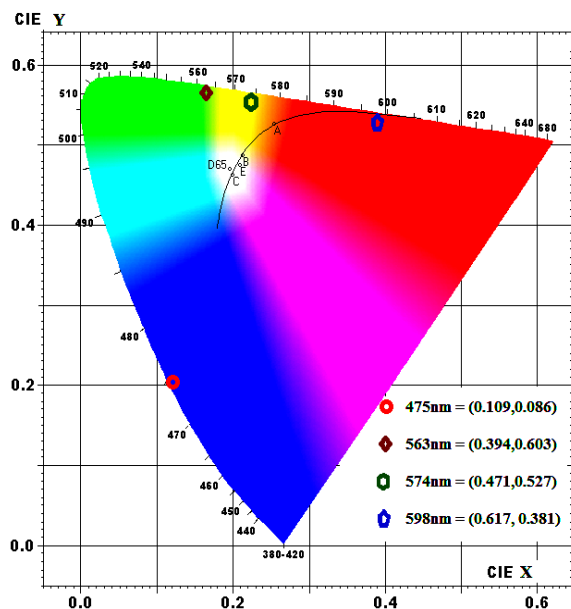


Fig. 8. CIE chromatic diagram showing the chromatic coordinates.

CIE chromatic coordinates of SrAl₄O₇: Dy³⁺ and SrAl₄O₇: Sm³⁺ phosphors

The CIE diagram of Sm³⁺ and Dy³⁺ single doped SrAl₄O₇ phosphors is shown in the Fig. 8. The CIE coordinates of Dy³⁺ doped SrAl₄O₇ phosphor of the colour blue (475 nm) are (x=0.109, y= 0.086) and colour yellow (574nm) are (x=0.471, y= 0.527). The CIE coordinates of SrAl₄O₇: Sm³⁺ phosphor of 563 nm are (x=0.394, y=0.603) and 598 nm are (x=0.617, y=0.381). All the coordinates are indicates that present Sm³⁺ and Dy³⁺ single doped SrAl₄O₇ phosphors are close to the edge of CIE diagram, which indicates the high colour purity of phosphors [33, 34].

Conclusion

In conclusion, the Dy³⁺ and Sm³⁺ single doped SrAl₄O₇ phosphors were synthesized by combustion method. Under the 352 nm excitation, the PL spectra of SrAl₄O₇:Dy³⁺ have shown two broad bands at 475 nm (blue) and 574 nm (yellow) correspond to the transitions, ⁴F_{9/2}→⁶H_{15/2} and ⁴F_{9/2}→⁶H_{13/2}, respectively. The phosphor has shown strong reddish-orange emission at 598 nm corresponding to the ⁴G_{5/2}→⁶H_{7/2} transition of Sm³⁺. The decay times of 2.1ms and 0.38ms were observed for Dy³⁺ and Sm³⁺ ion, respectively.

Acknowledgements

One of the authors, Dr. B. Deva Prasad Raju is grateful to DST, Government of India, New Delhi, for providing financial assistance to carry out this work under the fast track research project scheme (Young Scientist Award SR/FTP/PS-198/2012 dated 14-02-2014).

Author contributions

Conceived the plan: SJD, BDPR; Performed the experiments: ANY, BR; Data analysis: ANY, BR; Wrote the paper: ANY, SJD, BDPR. Authors have no competing financial interests.

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