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Synthesis and Photoluminescence Study of Dy, Sm and Eu Doped $Sr_5(PO_4)_3F$ Phosphor Ions for Light Based Applications

Arati Duragkar
Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur 440024, India
aratimduragkar@gmail.com

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ABSTRACT:
Compound $Sr_5(PO_4)F$ doped with various concentrations as 0.1, 0.5, 1, 1.5 and 2 mol% of rare earth dopant Sm & Dy and 0.1, 0.3, 0.5, 0.7,1 mol% of dopant Eu. These phosphors were synthesized by using combustion method. Photoluminescence (PL) emission spectra show highest intensity emission peak at 563nm and 598nm for 2 mol% Sm doped phosphors, 574nm for 2mol% Dy doped phosphor and shows highest intensity emission peak at 591nm and 612 nm for 1mol% dopant Eu. The studies showed that these phosphors are promising candidate for the light application. Commission International deI'Eclairage (CIE) chromaticity colour coordinates of these phosphors were calculated. CIE-Chromaticity colour coordinates of this phosphor shows orange-red emission.

Keywords:- Phosphors, Synthesis, CIE, Combustion method.

INTRODUCTION :

White light- emitting diods (w- LED) are considered to be the next generation of solid-state lighting sources due to their extraordinary optical properties, their extended lifetime, as well as mercury-free excitation. The concept of electroluminescence was the basis for the development of LED lights, and was first observed in 1907 by Henry Josep in silicon carbide, although the yellow light emitted by this phosphor was too faint for real use[E.N. Harvey,1957]. In 1994, Shuji Nakamura presented a fundamental investigation on ultrbright blue LEDs using gallium nitride. These ultrabright blue LEDs headed the foundation of w-LED, Later, in 1997, Nakamura also reported the production of white LEDs. Later, in 1997, Nakamura also reported the production of white LEDs by arranging basic RCB coloured LEDs. At this time, research interest in investigating and developing efficient phosphors for the generation of LED-based solid-state lighting has increased tremendously. In this type of research, sulphats, halosulphates, phosphates, borates, and vanadates are the most popular host materials. Furthermore, rare earth ions can be used as activators because they can be stabilised with the host material in their trivalent oxidation state.Trivalent- lanthanide ions doped phosphor materialshave gained massive attention owing to their wide applicatin in the field of fluorescent lighting, white light emitting diodes (W-LED), display devices,bioimaging, photography,radiation dosimetry etc [R. Yu, H.M.et al. (2014), S.R.R. Anishia et al. (2011), J.Wang et al. (2016), Z. Zhang et al.(2016)]. Red, Orange-red emitting phosphor can be used along with green and blue emitting phosphors to enhance the colourrendering indexof the W-LED[S.K. Rautet et,al.(2014), R. Velchuri et,al.(2009)]. Sm^{3+} dopant ion is one of the lanthanide element producing red luminescence.

In this work, different concentrations of Sm^{3+}, Dy^{3+}, Eu^{3+} doped $Sr_5(PO_4)_3F$ phosphors with well chemical and physical stable performance were synthesized. The photoluminescence study of these samples

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revealed that the phosphors can be excited by blue light and emit orange-red light.

SYNTHESIS

Synthesis of $Sr_5(PO_4)_3F$: Doped With Dy_2O_3, Sm_2O_3, Eu_2O_3 by Combustion Method-

The inorganic material $Sr_5(PO_4)_3F$ was synthesized by using combustion method. The A.R. Grade chemicals, Diammonium hydrogen phosphate $(NH_4)_2HPO_4$, Ammonium fluoride (NH_4F), Strontium nitrate $Sr(NO_3)_2$ and urea were used without further purification. All the chemicals weight per stoichiometric ratio were added to china dish and mix then kept in pre-heated vertical muffle furnace at 600°C, where auto combustion took place accompanied with evolution of brown gases. After complete evolution of the brown gases, the white solid material was obtained. After cooling this material crushed it in fine powder using mortal and pestle. In the same manner synthesized Dy, Sm and Eu doped $Sr_5(PO_4)_3F$ phosphors by adding different concentration of Dy, Sm, Eu in the form of Dy_2O_3 (Dysprosium oxide), Sm_2O_3 (Samarium oxide), Eu_2O_3 (Europium oxide) which was dissolved in little amount of conc. nitric acid before use.

The Proposed Chemical reaction is:

5 Sr $(NO_3)_2$ + 3 $[(NH_4)_2H(PO_4)]$ + NH_4F----> $Sr_5(PO_4)_3$ F + 7 NH_3+ 10 HNO_3

Molecular weight of all the components used for synthesis of phosphors are

1. Diammonium hydrogen phosphate $(NH_4)_2HP_4$ = 132.06 g/mol.
2. Ammonium fluoride (NH_4F) = 37.037 g/mol
3. Strontium nitrate, Sr $(NO_3)_2$ = 211.63 g/mol
4. Urea (NH_2CONH_2) = 60.06 g/mol.
5. Molecule weight of Sm_2O_3 = 348.72 g/mol
6. Molecule weight of Dy_2O_3 = 373.00 g/mol
7. Molecule weight of Eu_2O_3 = 351.93 g/mol

Table of components that are be taken in grams.

Table 1.1 - Stoichiometric weight of chemicals in gram to synthesize $Sr_5(PO_4)_3$ F: Dy (0.1, 0.3, 0.5, 1, 1.5 and 2 mol%) phosphors

%Moles of Dopant	Wt. of $(NH_4)_2H(PO_4)$	Wt. of NH_4F	Wt. of $Sr(NO_3)_2$	Wt. of Urea	Wt. Of Dy_2O_3
Pure	1.3064	0.1402	4.0063	6	-
0.1	1.3064	0.1402	4.0055	6	0.0014
0.5	1.3064	0.1402	4.0023	6	0.0070
1	1.3064	0.1402	3.9983	6	0.0141
1.5	1.3064	0.1402	3.9943	6	0.0211
2	1.3064	0.1402	3.9902	6	0.4830

Table 1.2 - Stoichiometric weight of chemicals in gram to synthesize $Sr_5(PO_4)_3$ F: Sm (0.1, 0.3, 0.5, 1, 1.5 and 2 mol%) phosphors

%Moles of Dopant	Wt. of $(NH_4)_2H(PO_4)$	Wt. of NH_4F	Wt. of $Sr(NO_3)_2$	Wt. of Urea	Wt. Of Sm_2O_3
0.1	1.3064	0.1402	4.0055	6	0.0013
0.5	1.3064	0.1402	4.0023	6	0.0066
1	1.3064	0.1402	3.9983	6	0.0132
1.5	1.3064	0.1402	3.9943	6	0.0198
2	1.3064	0.1402	3.9902	6	0.0264

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Table 1.3 - Stoichiometric weight of chemicals in gram to synthesize $Sr_5(PO_4)_3F$: Eu (0.1, 0.3, 0.5, 0.7, 1 mol%) phosphors

%Moles of Dopant	Wt. of $(NH_4)_2H(PO_4)$	Wt. of NH_4F	Wt. of $Sr(NO_3)_2$	Wt. of Urea	Wt. Of Sm_2O_3
0.1	1.3064	0.1402	4.0055	6	0.0013
0.3	1.3064	0.1402	4.0023	6	0.0066
0.5	1.3064	0.1402	3.9983	6	0.0132
0.7	1.3064	0.1402	3.9943	6	0.0198
1	1.3064	0.1402	3.9902	6	0.0264

RESULTS AND DISCUSSION:

Photoluminescence Study of $Sr_5(PO_4)_3F$ doped with different concentrations of Eu^{3+}-

Excitation and emission spectra of $Sr_5(PO_4)_3F$: Eu (0.1, 0.3, 0.5, 0.7 & 1 mol%) –

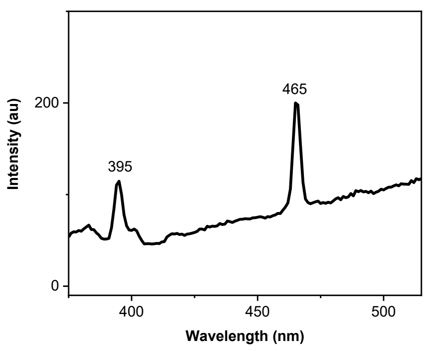

Fig.1.1

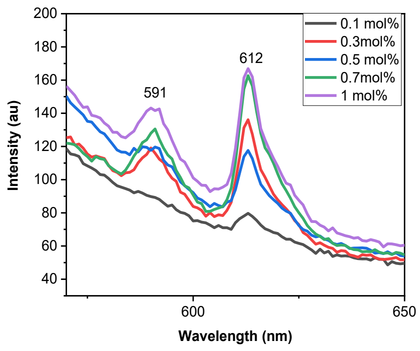

Fig.1.2

Fig.1.1 Excitation of $Sr_5(PO_4)_3F$: Eu at 612 nm emission & **Fig.1.2** Emission of $Sr_5(PO_4)_3F$: Eu at 465 nm excitation wavelength

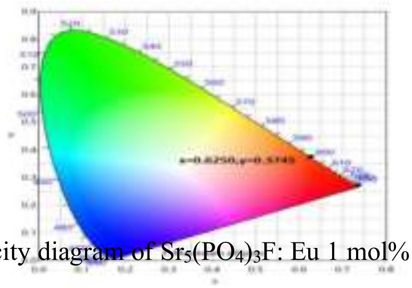

Fig.1.3 CIE chromaticity diagram of $Sr_5(PO_4)_3F$: Eu 1 mol% phosphors

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Irradiation with UV radiation the trivalent europium ion (Eu^{3+}) exhibits an intense red photoluminescence. The Eu^{3+} ion has the great advantage over other lanthanide ions because it contains an even number of 4f electrons hence the starting levels of the transitions in the absorption as well as luminescence spectrum are non-degenerate (J=0) [O.K. Moune et,al.(1983)]. Other than red luminescence, narrow transition in the absorption and luminescence spectra are also the special features of the Eu^{3+} ion. The most important application of europium is the red phosphor Y2O3:Eu^{3+} (YOX) in fluorescent lamps [E. Antic-Fidancev et, al(2002), H.D.Xie et,al. (2014), M.Karbowiak et,al.(2000)].

The PL properties of $Sr_5(PO_4)_3F$: Eu^{3+}(0.1, 0.5, 1, 1.5 & 2 mol %) were further investigated by the PL excitation and emission spectra as shown in Fig.1.1 and 1.2. The excitation spectrum was obtained at emission wavelength 612 nm where various excitation peaks of Eu^{3+} observed between 267 nm and 465 nm. The peak at 267 nm is observed due to the Eu^{3+}-- O^{2-} band charge transfer and is explained by the degree of covalency of the Eu^{3+}- ligand bond, by considering Eu^{3+}--O^{2-}- Sr bonding structure. Since the Sr^{2+} ion is a smaller radius and larger electronegativity cation as compared to Eu^{3+} ion, the electron density clouding around O^{2-} ion decreases when it is bonded to Sr^{2+}ion. In addition to that prominent excitation peaks are observed at 395 nm and 465 nm which are due to the f-f transitions of Eu^{3+}. The highest excitation peak is observed at 396 nm in the UV region due to$^7F_0$--->$^5L_6$ (396 nm) transition. Excitation peak in blue region at 466 nm is also observed due $^7F_0$--->$^5D_2$ transition. Upon excitation at 395 nm, the emission spectra have shown the characteristic transition lines from the excited D0 level of Eu^{3+} ions as shown in Fig.1.1.

On exciting it at 465nm, the PL emission spectra shown the characteristic transition lines from the excited D0 level of Eu^{3+}ions as depicted in Fig. 1.2. Spectral features are observed in two different ranges i.e. 590-603 nm and 603-640 nm due to $^5D_0$--->$^7F_1$ and $^5D_0$--->$^7F_2$ transitions respectively. Transition at 613 nm due to $^5D_0$--->$^7F_2$ is more efficient emission hence is a dominant peak. The CIE chromaticity was plotted by using software, color calculator v7.73 for $Sr_5(PO_4)_3F$: Eu^{3+}(1mol %) phosphor which shows the CIE coordinates located at (x=0.6250) and (y=0.3745). Fig.1.3 shows that the point obtained at CIE chromaticity diagram lies at the orange-red region. The $^5D_0$---> $^7F_2$ transition is observed on Ca^{2+}sites of the apatite structure. PL increases with increasing concentration of $Eu^{3+}$and no significant change in PL emission spectra was observed.

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Photoluminescence Study of $Sr_5(PO_4)_3F$ doped with different concentrations of Dy^{3+}-
Excitation and emission spectra of $Sr_5(PO_4)_3F$: Dy (0.1, 0.5, 1, 1.5 & 2 mol%) –

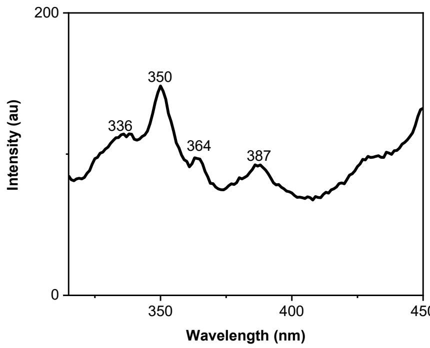

Fig 2.1

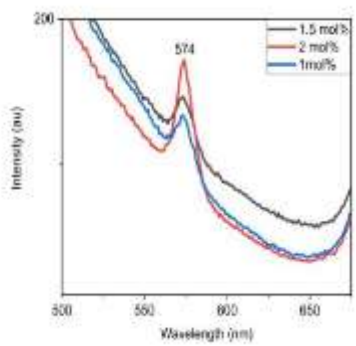

Fig 2.2

Fig.2.1 Excitation of $Sr_5(PO_4)_3F$: Dy at 574 nm emission wavelength& Fig.2.2 Emission of $Sr_5(PO_4)_3F$: Dy at 350 nm emission wavelength

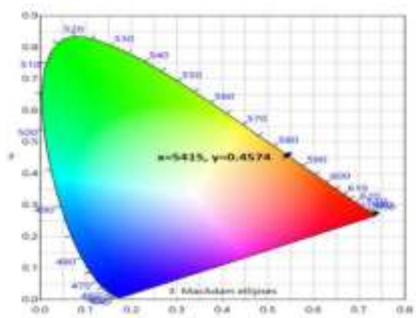

Fig.2.3 CIE chromaticity diagram of $Sr_5(PO_4)_3F$: Dy 2 mol% phosphors

Dy_{3+} is good activator since it exhibits two dominated band in the emission spectra and its position can be determined by the crystal field environment of the host matrices used. One of the wavelength band is blue (480 nm) attributed to $^4F_{9/2}$-->$^6H_{15/2}$transition (magnetic dipole) and the other wavelength band is the yellow (580 nm) ascribed to the $^4F_{9/2}$-->$^6H_{13/2}$ transition (electric dipole). In present investigation analysis of excitation spectra were made by observing the peak wavelength of the Dy^{3+}emission of yellow emission band. Fig.2.1 demonstrates that the excitation spectrum of the $Sr_5(PO_4)_3F$: Dy^{3+} 2mol% phosphor consists of 351 nm, 364 nm and 387 nm excitation wavelength, which is due to $^6H_{15/2}$--->$^6P_{7/2}$, $^6H_{15/2}$--->$^6P_{5/2}$ and $^6H_{15/2}$--->$^4I_{13/2}$respectively. From Fig. 2.1 it has been observed that the intensity of excitation wavelength is maximum when it ismonitored at 574 nm emission wavelength henceforth corresponding excitation wavelength (λ ex = 350 nm) is selected in present investigation. Among the several excitation bands we choose 350 nm because it is suitable for solid-state lighting and UV pumped LED.

In present case $Sr_5(PO_4)_3F$: Dy^{3+} 2mol% have mainly one emission band, i.e., at 574 nm, owing to the transition of $^4F_{9/2}$-$^6H_{13/2}$. Fig. 2.2 shows the emission spectrum of the $Sr_5(PO_4)_3F$: Dy^{3+} 2mol% phosphors. In $Sr_5(PO_4)_3F$: Dy^{3+} 2mol% predominant emission is around 483 nm signifying that ligand field somewhat diverges from its reversal symmetry. A slight marginal shift in the emission peak of Dy^{3+} ions is detected in all synthesized phosphors. Such performance is as predictable for the emission encompassing f-f transitions where ligand field diverges with the host matrix. A series of $Sr_5(PO_4)_3F$: Dy^{3+}

2mol% phosphor with various Dy^{3+} concentrations (x = 0.1 mol % to 2 mol %) are prepared and it has been observed that the maximum photoluminescence intensity is observed for 2 mol % of Dy^{3+}ions. Thus, the best doping concentration for Dy^{3+} ions in $Sr_5(PO_4)_3F$ host lattice is 2 mol %.

In this study, the concentration of Dy^{3+} ions are varied from 0.1 to 2 mol % in $Sr_5(PO_4)_3F$ host lattice and from Fig.2.2 it has been observed that, the maximum photoluminescence intensity is observed for 2 mol % of Dy^{3+} ions. Thus, the best doping concentration for Dy^{3+} ions in $Sr_5(PO_4)_3F$ host lattice is 1 mol%. The representative energy level transitions of Dy^{3+} ions is shown in Fig.2.2.

The CIE diagram for $Sr_5(PO_4)_3F:Dy^{3+}$(2 mol %) phosphor which shows the CIE coordinates located at (x=0.5415) and (y=0.4575). Fig.2.3 shows that the point obtained at CIE diagram lies near white light.

Photoluminescence Study of $Sr_5(PO_4)_3$ F doped with different concentrations of Sm^{3+}-

Excitation and emission spectra of $Sr_5(PO_4)_3F$: Sm (0.1, 0.5, 1, 1.5 & 2 mol%) –

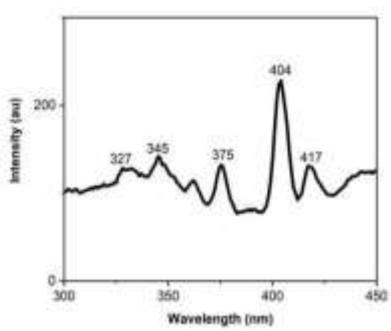

Fig. 3.1

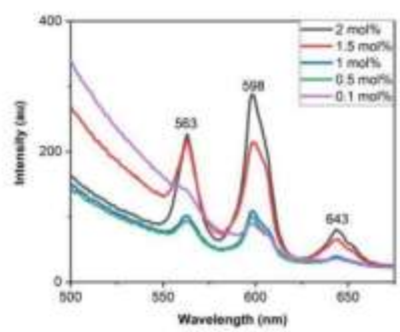

Fig. 3.2

(Fig.3.1 Excitation of $Sr_5(PO_4)_3F$: Sm at 598 nm emission & Fig.3.2 Emission of $Sr_5(PO_4)_3F$: Sm at 404 nm excitation)

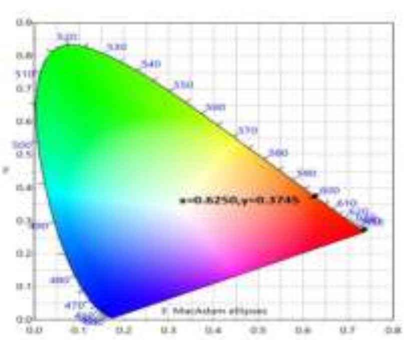

Fig.3.3 CIE chromaticity diagram of $Sr_5(PO_4)_3F$: Sm 2 mol% phosphors

Sm^{3+} ion usually shows orange-red emission and Sm^{3+} ions can be utilized to compensate deficiency of red component in white light-emitting diodes (LEDs). Fig. 3.1 shows the excitation spectra of $Sr_5(PO_4)3F:Sm^{3+}$ monitored at 598 nm emission wavelength which is composed of several sharp peaks in the range of 327-417 nm wavelength. The peaks at 345nm, 362nm, 375nm, 404 and 417nm are allocated to the electronic transitions resulting from $^6H_{5/2}\rightarrow {}^4K_{17/2}$, $^6H_{5/2}\rightarrow {}^4H_{7/2}$, $^6H_{5/2}\rightarrow {}^4P_{7/2}$, $^6H_{5/2}\rightarrow {}^4K_{11/2}$ and $^6H\rightarrow {}^6P_{5/2}$. The strongest peak is centered at

404 nm. Therefore, the emission spectra were monitored at 404 nm excitation wavelength. The emission spectra show three emission peaks at 563nm, 598nm and 643 nm wavelength corresponding to the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transitions of Sm^{3+} ions respectively as shown in Fig.2.3 In this study, the concentration of Sm^{3+} ions is varied from 0.1 to 2 mol% in $Sr_5(PO_4)3F$ host lattice. Fig 3.2 revealed the maximum photoluminescence intensity is at 2 mol% of Sm^{3+} ions. Thus, the best doping concentration for Sm^{3+} ions in $Sr5(PO_4)3F$ host lattice is 2 mol%. The CIE chromaticity diagram for $Sr_5(PO_4)3F:Sm^{3+}$(2mol%) phosphor shows the CIE coordinates located at (x=0.6250) and (y=0.3745). Fig.3.3 shows that the point obtained at CIE chromaticity diagram lies at the orange-red region.

CONCLUSION-

- $Sr_5(PO_4)_3F$ compound doped with different concentrations of Eu^{3+}, $Dy^{3+}$and Sm^{3+} ions were successfully synthesized by combustion synthesis technique.
- **$Sr_5(PO_4)_3F$: Eu^{3+}(2mol%)** phosphor shows strong emission at 613 nm when excited with 465 nm. CIE-chromaticity diagram was plotted which shows orange-red emission.
- **$Sr_5(PO_4)_3F$: Dy^{3+}(2mol%)** phosphor shows strong emission at 574 nm when excited with 350 nm. CIE-chromaticity diagram was plotted which shows yellowish-orange emission. A model was proposed to synthesize white light LED by using this phosphor and combining it with blue LED.
- **$Sr_5(PO_4)_3F$: Sm^{3+}(2mol%)** phosphor shows three strong emission at 563,598 and643 nm when excited with 404 nm. CIE-chromaticity diagram was plotted which shows orange-red emission.

So all prepared phosphors can be served as orange- red phosphor for LED. Out of all the prepared phosphors, $Sr_5(PO_4)_3F$: Sm 2 mol% phosphor was found to be the best phosphor to be used as orange-red component for white LED phosphor.

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