

Wet chemical synthesis and photoluminescence characteristics of $\text{Ca}_5(\text{PO}_4)_3\text{F:Dy}$ phosphor

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Received: 26 August 2013, Revised: 30 October 2013 and Accepted: 24 November 2013

ABSTRACT

$\text{Ca}_5(\text{PO}_4)_3\text{F}$ doped with Dy^{3+} phosphors is synthesized by cost effective and easy wet chemical method and characterized by its luminescence properties. In the emission spectrum of $\text{Ca}_5(\text{PO}_4)_3\text{F:Dy}^{3+}$ phosphor, the two intense bands are centered at 484nm (blue) and 575 nm (yellow) having excitation wavelength 353nm. The emission intensity of 484nm is stronger than that of 575 nm. The emission intensity decreases after 0.5 mole%, of Dy^{3+} ions which may be due to concentration quenching. From the PL results shows that the prepared phosphors could be potentially used as in solid state lighting devices.

Keywords: wet chemical method; photoluminescence; $\text{Ca}_5(\text{PO}_4)_3\text{F}$; phosphor.



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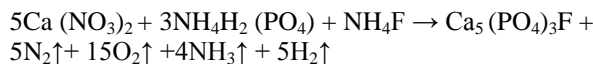
Introduction

In recent years, research on different rare earth activated phosphate based phosphors has received extensive attention due to their structural diversity, higher thermally stable, the large band gap and higher chemical stability [1-3]. Research on phosphate based phosphor materials for the replacement of conventional light source is the important era in the recent years. Phosphate based phosphor materials with different rare earth activated have great interest because phosphate phosphor materials could find many applications in solid state lighting, white LED, display devices and X-ray imaging [4-6]. It is well known that the YAG:Ce³⁺ is commercially used as a white light emitting phosphor and commercial available blue phosphor is BaMgAl₁₀O₁₇:Eu²⁺. But these commercial phosphor materials have the following problems like poor colour rendering index and a less efficiency [7-9]. So it is urgent to develop the single doped phosphor materials by simple synthesis method having high efficiency and less consumption of electricity. For the generation of white light emission, Dy³⁺ ion is used as an activator in many host lattices because it give emission in the blue and yellow region of the visible spectrum. Dysprosium ions which give the emission line in the blue region (470nm-500nm) having ⁴F_{9/2}→⁶H_{15/2} transition and in yellow region (570nm-600nm) having ⁴F_{9/2}→⁶H_{13/2} transition [10, 11]. In this

paper, $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ phosphor were synthesized by wet chemical method and its luminescent properties were also investigated.

Experimental

The phosphor $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ with various concentrations was prepared by wet chemical method. For the preparation of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$, high purity $\text{Ca}(\text{NO}_3)_2$, NH_4F , $\text{NH}_4\text{H}_2(\text{PO}_4) \cdot \text{H}_2\text{O}$ (all AR grade of 99.99% purity) were used as initial raw material. Dy^{3+} was introduced in the form of dysprosium nitrate solution by dissolving Dy_2O_3 into HNO_3 solution. Each initial raw material was weighed using the high precision (0.00001 gm) electronic monopan balance. By taking the raw materials in stoichiometry ratio, they were dissolved separately in distilled water and then mixed together to give desired compound. The compound $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ is prepared by heating at 80°C for 10-12 hrs. The dried samples were then slowly cooled at room temperature. The resultant powder was crushed to fine particle in molten pester. The powder was used for further study. The photoluminescence (PL) emission spectra of the sample were recorded using fluorescence spectrometer (RF -5301). The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The reaction is,



Results & Discussion

The PL excitation spectra $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ phosphors are shown in **Fig. 1**. The excitation spectrum was measured upon the emission wavelength 484nm. The excitation spectra were observed between 220nm to 420 nm ranges. As seen from the figure several narrow peaks observed between 300 to 420 nm are observed, which are 353nm ($6\text{H}_{15/2} \rightarrow 6\text{P}_{7/2}$), 367nm ($6\text{H}_{15/2} \rightarrow 6\text{P}_{5/2}$) and 390nm ($6\text{H}_{15/2} \rightarrow 4\text{K}_{17/2}$). The highest absorption intensity is observed at 353 nm peak, so we choose for this for obtaining the emission spectra.

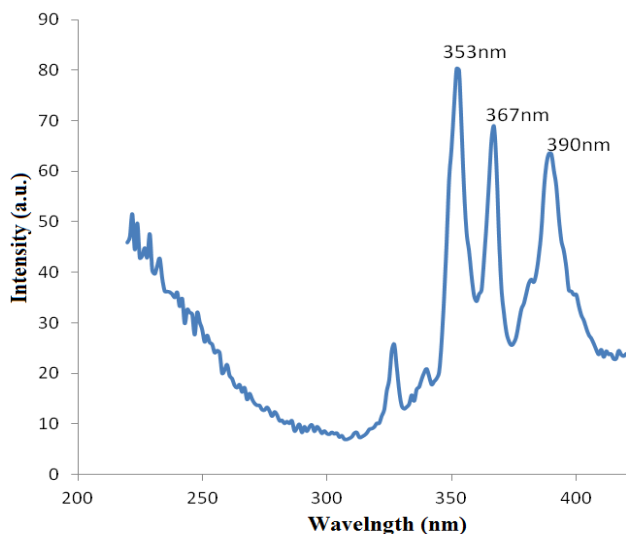


Fig.1. Excitation spectrum of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ monitored at 484 nm.

Fig. 2 shows the PL emission spectra of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ phosphors under excitation wavelength 353nm. The two characteristics emission bands are located at 484nm due to transition $4\text{F}_{9/2} \rightarrow 6\text{H}_{15/2}$ and 575 nm due to transition $4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}$. The emission observed at 484 nm is due to magnetic dipole origin and another emission peak observed at 575 nm is due to electric dipole origin [12]. Strongest emission intensity is observed at 484nm which shows that the Dy^{3+} ions are located in the present host at low-symmetry sites with no inversion centers [13]. It is clear from fig. 3 with increasing concentration of Dy^{3+} , the shape and size of emission spectra does not vary. To find out the critical concentration in $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}^{3+}$ phosphors for that we have prepared a series of samples having concentration of Dy^{3+} ions ranging from 0.05 mole % to 1 mole%.

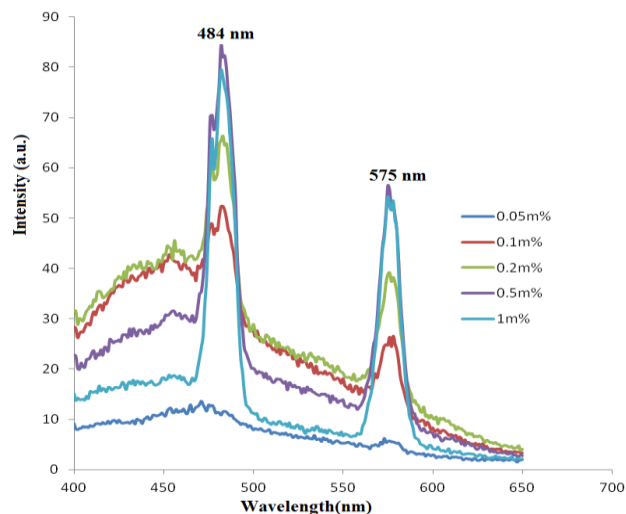


Fig. 2. Emission spectra of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Dy}$ phosphor when excited at 353 nm

Fig. 3 shows the relation between concentrations of Dy^{3+} ion versus 484 peak intensity. With increasing concentration of Dy^{3+} ions from 0.05mole% to 0.5 moles % emission intensity increases after that emission intensity decreases due to concentration quenching [14].

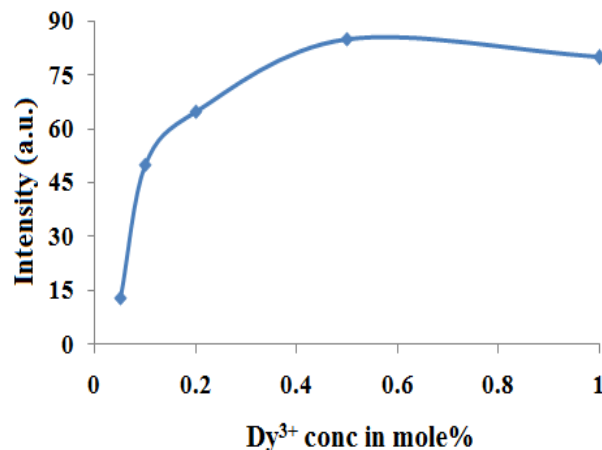


Fig. 3. The relation between emission intensity peaks at 484 nm and Dy^{3+} ion concentration in $\text{Ca}_5(\text{PO}_4)_3\text{F}$ phosphor.

The maximum emission intensity is at 0.5m% of Dy^{3+} ion. The concentration quenching of Dy^{3+} ions at 0.5mole% is mainly due to cross relaxation between Dy^{3+} ions [15]. **Fig. 4** Shows the CIE chromaticity diagram of $Ca_5(PO_4)_3F : Dy^{3+}$ phosphor. The CIE color coordinates of the $Ca_5(PO_4)_3F : Dy^{3+}$ phosphor are, color blue (484nm) ($x = 0.0734, y = 0.185$) and color yellow (575nm) ($x = 0.478, y = 0.520$) phosphor is shown in **Fig. 4**. Obtained results showed that present phosphor have potential applications in the field solid state lighting.

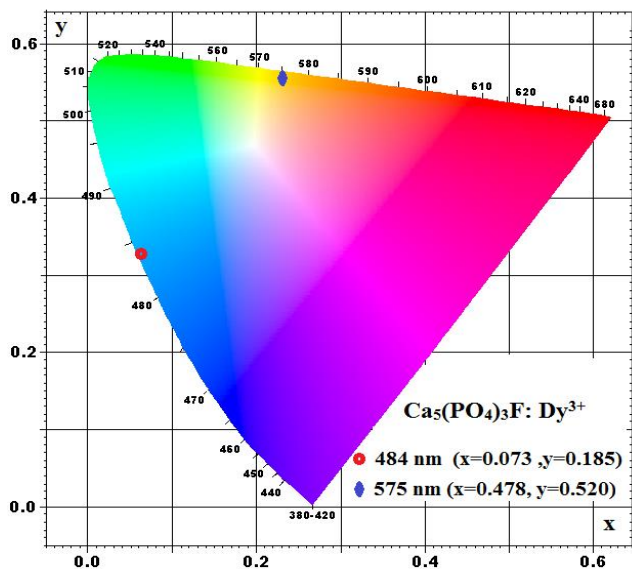


Fig. 4. CIE chromatic diagram showing the chromatic coordinates.

Conclusion

In conclusion, $Ca_5(PO_4)_3F : Dy^{3+}$ phosphor is synthesized by cost effective wet chemical method and there PL characteristics were studied. In Dy^{3+} activated $Ca_5(PO_4)_3F$ phosphor the emission is at 485nm (blue) and 575nm (yellow). The combination of these two emission yielded white-light emission. The strongest emission intensity observed at 0.5 mole% of Dy^{3+} ions. CIE color coordinates and luminescence properties show the $Ca_5(PO_4)_3F : Dy^{3+}$ phosphors may be applicable for solid state lighting.

Acknowledgements

One of the authors, KBG is grateful to UGC, New Delhi for providing financial assistance to carry out of this work under the research project scheme.

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