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Dy^{3+} emission in $M_5(PO_4)_3F$ (M = Ca, Ba) phosphor

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Abstract : Ultrafine $M_5(PO_4)_3F:Dy^{3+}$ (M = Ca, Ba) phosphors were prepared *via* combustion process using metal nitrates as precursors. The formation of crystalline phosphate was confirmed by X-ray diffraction pattern. The PL excitation spectra show the excitation peaks observed at 250 to 400 nm due to $f \rightarrow f$ transition of Dy^{3+} ion, which are useful for solid-state lighting purpose (mercury free excitation). The PL emission of Dy^{3+} ion by 348 nm excitation gave an emission at 489 nm (blue), 582 nm (yellow) and 675 nm (red). All the characteristics of BYR emissions like BGR indicate that Dy doped $Ca_5(PO_4)_3F$ and $Ba_5(PO_4)_3F$ phosphors are good candidates that can be applied in solid-state lighting phosphor (mercury free excited lamp phosphor) and white light LED.

Keywords : Photoluminescence (PL), LED, solid state lighting, XRD, phosphor.

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1. Introduction

White light LED is in high demand for the solid-state lighting technology because the most challenging application for white light LED is the replacement of conventional incandescent and fluorescent lamps [1]. A white light LED consists of a UV or near-UV LED chip and blue/yellow or blue/green/red phosphors. Dy^{3+} doped phosphor, $Sr_2MgSi_2O_7$ [2], $Sr_3Gd(PO_4)_3$, $Ba_3Gd_4(PO_4)_3$ [3] useful for white light lightening. A white light LED that combines a blue LED and a $(Y_{1-a}Gd_a)_3(Al_{1-b}Ga_b)_5O_{12}:Ce$ (YAG) phosphor was made available on the market in 1996. The white light of this LED is produced by a combination of the blue emission from InGaN blue LED and the yellow fluorescence from the YAG phosphors excited by the blue LED. Because it is possible to improve the luminous efficiency of white light LEDs excited by near-UV LEDs in the near-UV to blue part of the spectrum [4] around 380–420 nm, researchers worldwide have been investigated other chemical compounds as suitable phosphors for solid-state lighting. One of the white solid-state light sources were obtained by combining three

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phosphors that emit light in narrow wavelength intervals centered at around 450, 550, 610 nm transitions respectively due to BYR emissions like BGR this phosphors is also potential applications to white LED [5]. In this context, a host that can be activated by different ions emitting in different regions of the visible spectrum is a challenge for the solid materials synthesis [6]. It is important to get different regions of the visible spectrum in a matrix in which different activation ions can be structurally substituted for cation sites. There are currently insufficient references on the use of phosphors converting UV-LED as illumination sources. Therefore, it is the most crucial to study phosphors for UV-LED. At present, more and more researchers devoted them to this work with interest.

For white light-emitting LED, one can also obtain by mixing a blue and a yellow light-emitting phosphors as well as the integration of the InGaN blue LED chip and a yellow-emitting phosphor to obtain the white light-emitting diodes (LEDs) [7]. However, it is difficult to fabricate those persistent phosphors (RGB/YB) which have similar emission ratios to ensure the white light-emitting LED all the time. Dy^{3+} ions, which have the luminescence lines in the 470–500 nm region due to $^4F_{9/2}$–$^6H_{15/2}$ transition and in the 570–600 nm region due to the $^4F_{9/2}$–$^6H_{13/2}$ transition, have attracted much attention because of its white light emission [8–11]. In this paper, we report on a novel white light-emitting afterglow phosphor $Sr_{1-x}Dy_xSiO_3$. It was found that long-lasting phosphorescence indirectly came from the luminescence of Dy^{3+} ions.

In, phosphate based system, Dy^{3+} ion activated phosphors have normally been used as high efficiency activators [12,13] and their photoluminescence spectra range from 450 to 700 nm. Here we were concentrate to prepared phosphate based system in this work by low cast conventional method, which have the advantages over the widely investigated silicate and borate system of higher quantum efficiency and the lower sintering temperature.

2. Experimental

The $M_5(PO_4)_3F:Dy^{3+}$ (M = Ca, Ba) : phosphors were prepared *via* combustion technique. The starting AR grade materials (99.99% purity) taken were calcium nitrate ($Ca(NO_3)_2.4H_2O$), barium nitrate ($Ba(NO_3)_2$), di-ammonium hydrogen phosphate ($NH_4H_2(PO_4)$), ammonium fluoride (NH_4F) and dysprosium oxide (Dy_2O_3). Urea (NH_2CONH_2) was used as fuel for combustion. In the present investigation, materials were prepared according to the chemical formula $M_{5-x}(PO_4)_3F:Dy_x$. The reagents were mixed together to obtain a homogeneous solution. Dy^{3+} was introduced in the form of $Dy(NO_3)_3$ solution by dissolving Dy_2O_3 into HNO_3 solution. The molar ratio of rare earth was varied in relation to $Ca_5(PO_4)_3F$ and $Ba_5(PO_4)_3F$ phosphor. For these compositions of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. After stirring for about 15 min, precursor solution was transferred to a furnace preheated to 500–600°C, and the porous products were obtained.

Rare earth ion doped calcium phosphate phosphors have been prepared by the combustion of respective nitrates along with urea at ~600°C. The stoichiometric amount of redox mixture when heated rapidly at ~600°C boils and undergoes dehydration followed by decomposition generating combustible gases such as oxides of N_2, H_2O and nascent oxygen. The volatile combustible gases ignite and burn with a flame and thus provide conditions for formation of phosphor lattice with dopants. The large amount of escaping gases dissipates heat and thereby prevents the material from sintering and thus provides conditions for formation of nanocrystalline phase. Also, as the gases escape they leave voluminous, foaming and crystalline fine powder occupying the entire volume of the firing container and have no chance of forming agglomerations unlike in the other conventional processes. The combustion reaction can be described as follows :

$$5Ca(NO_3)_2 + 3NH_4H_2(PO_4) + NH_4F + NH_2CONH_2 \\ \rightarrow Ca_5(PO_4)_3F + 8N_2 + CO_2 + 13H_2O \tag{1}$$

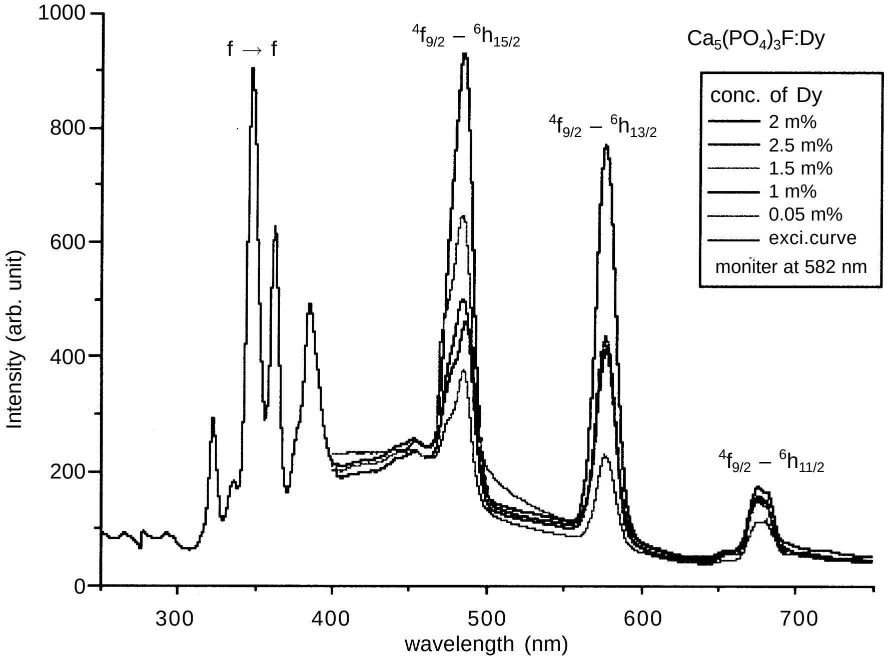
$$5Ba(NO_3)_2 + 3NH_4H_2(PO_4) + NH_4F + NH_2CONH_2 \\ \rightarrow Ba_5(PO_4)_3F + 8N_2 + CO_2 + 13H_2O \tag{2}$$

Several complementary methods were used to characterize the properties of the prepared samples. The as-prepared powder samples were characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.01°, continue time 20 s, in the 2θ range from 10° to 120°; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherer's equation. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer.

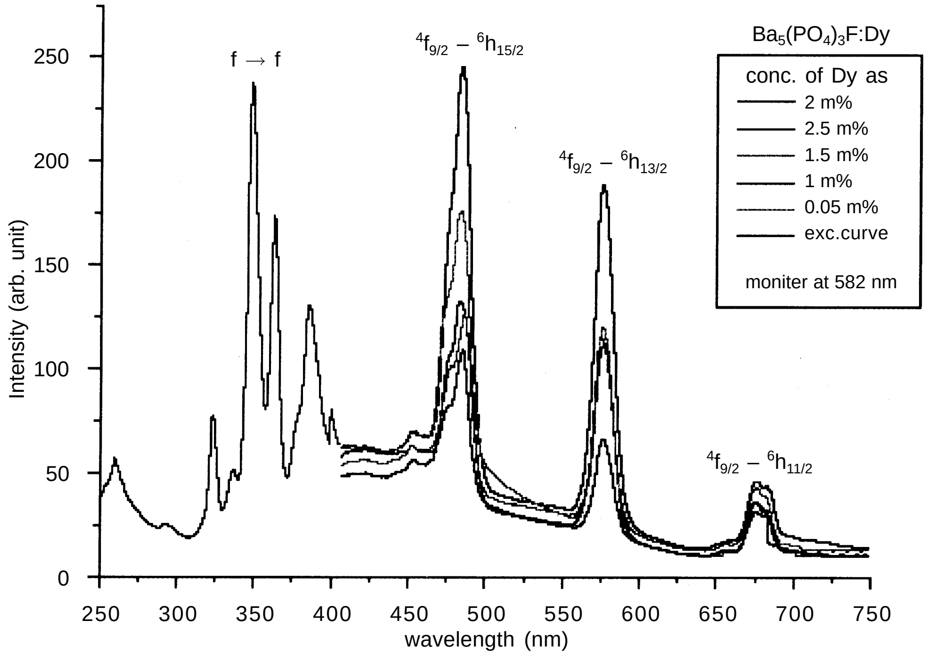
3. Results and discussion

The X-ray diffraction (XRD) patterns of $Ca_5(PO_4)_3F$ and $Ba_5(PO_4)_3F$ phosphors did not indicate presence of the constituents nitrate and traces of ammonia gases, which is an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form.

Monitoring the peak wavelength of the Dy^{3+} emission in the blue, yellow and red emission bands, respectively we made measurements of excitation spectra. Figures 1 and 2 shows the excitation spectra of the Dy activated $Ca_5(PO_4)_3F$ and $Ba_5(PO_4)_3F$. The excitation spectrum monitored at the yellow emission from Dy^{3+} indicates several bands. The excitation spectrum in the range 250–400 nm consists of the $f \rightarrow f$ transition of Dy^{3+} *i.e.* 348 nm ($^6h_{15/2} \rightarrow {}^6m_{21/2}$) are observed.



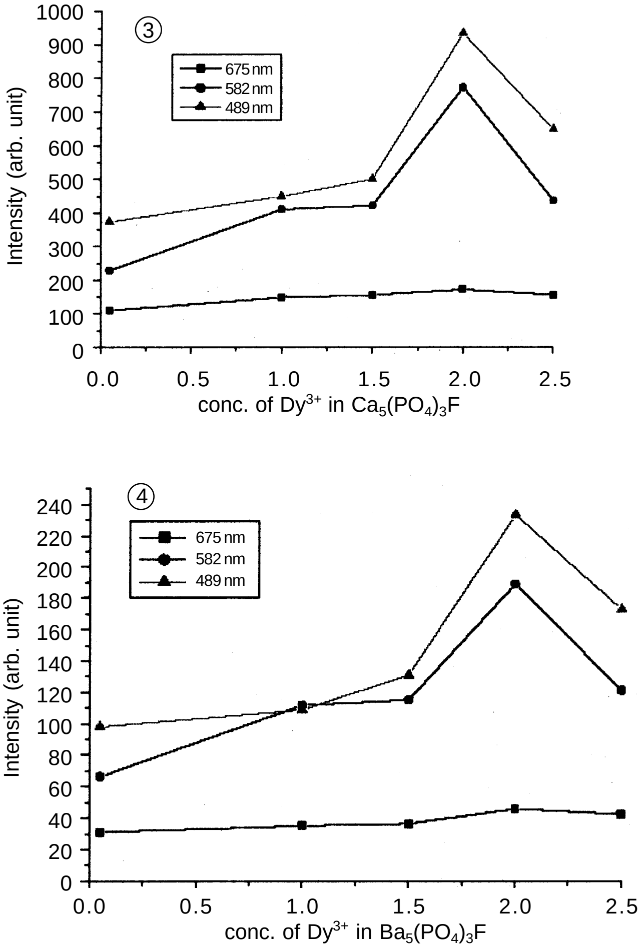
Fgure 1. PL emission spectra of $Ca_5(PO_4)_3F:Dy^{3+}$ phosphor (λ_{ex} = 348 nm).



Fgure 2. PL emission spectra of $Ba_5(PO_4)_3F:Dy^{3+}$ phosphor (λ_{ex} = 348 nm).

The PL emission spectrum of Dy^{3+} doped $Ca_5(PO_4)_3F$ is shown in Figure 1 and that of $Ba_5(PO_4)_3F$ phosphor is shown in Figure 2. The PL emission spectrum was taken under excitation at wavelengths between 250 to 400 nm, which is used for the solid state lighting. The optical spectra were taken for the Dy^{3+} ion at 348 nm excitation, which gave an emission at 489 nm (blue) ($^4f_{9/2} \rightarrow {}^6h_{15/2}$), 582 nm (yellow) ($^4f_{9/2} \rightarrow {}^6h_{13/2}$) and weak emission at 675 nm (red). These emission bands are originating from the two origins. The blue and yellow emission band is typical emission of Dy^{3+} ions and emission at 675 nm is due to $^4f_{9/2} \rightarrow {}^6h_{11/2}$. The optical properties of the material are often influenced by the structure of the matrix and synthesis technique. In the present case, due to the rapid combustion process, defects would be produced inevitably because of the partially incomplete crystallization. Besides this, the cation disorder in spinal structure is considerable so that there exist a great number of defects, which can serve as electron and/or hole traps [14]. It is known that Dy^{3+} has two intense peaks at 489 (characteristic blue emission) and 582 nm (characteristic yellow emission) due to fluorescent transitions of $^4f_{9/2} \rightarrow {}^6h_{15/2}$ (magnetic dipole) and $^4f_{9/2} \rightarrow {}^6h_{13/2}$ (electric dipole) and 675 nm due to $^4f_{9/2} \rightarrow {}^6h_{11/2}$ of Dy^{3+} ion, respectively. The $^4f_{9/2} \rightarrow {}^6h_{13/2}$ transition is predominant only when Dy^{3+} ions are located at low-symmetry sites with no inversion centers [15]. Thus, the yellow/blue/red ratio, known as the asymmetry ratio of Dy^{3+} varies in different host lattices. It has been reported that in the Dy^{3+} doped $SrSiO_3$ [16] system, with increase of the calcining temperature, the yellow/blue ratio increases due to the change of the local site symmetry around Dy^{3+} ions.

In our case, the Dy^{3+} ion may enter into the host lattice to substitute Ca^{2+} or locate on surfaces of the crystals due to the porosity of the spinal structure. As the ionic radius of Dy^{3+} is much larger than that of Ba^{2+} and near to Ca^{2+} or phosphate P^{5+} the first possibility is more feasible. Therefore, most of the Dy^{3+} ions are located at the surface of $Ca_5(PO_4)_3F$ as compared to $Ba_5(PO_4)_3F$ phosphors with a few of them entering into the lattice. The low-symmetry location of Dy^{3+} results in the predominant emission of $^4f_{9/2} \rightarrow {}^6h_{15/2}$ transition as shown in Figure 2. Hence $Ca_5(PO_4)_3F$ phosphor shows stronger PL emission as compared to $Ba_5(PO_4)_3F$ phosphor. Doping of activator ions can influence photoluminescence characteristics of a phosphor. Usually, a low doping gives weak luminescence but excess doping perhaps causes quenching of luminescence. The maximum intensity of Dy^{3+} is observed at 2 mol%. Variation of the intensity with respect to change in the concentration of Dy^{3+} ion is shown in Figures 3 and 4. The 300 to 400 nm is Hg free excitation and it is characteristics of solid-state lighting phosphors. Therefore, the entire characteristic indicates that Dy^{3+} doped $Ca_5(PO_4)_3F$ as well as $Ba_5(PO_4)_3F$ phosphors are good candidates for solid state lighting devices (mercury free excited lamp phosphor) and white light LED.



Figures 3 and 4. Variation in the intensity with respect to change in the concentration of Dy.

4. Conclusion

In conclusion, Dy activated $M_5(PO_4)_3F{:}Dy^{3+}$ (M = Ca, Ba) phosphors were synthesized by novel combustion method is reported in this paper. The PL emission of Dy^{3+} ion at the 348 nm excitation gave an emission at 489 nm (blue), 582 nm (yellow) and 675 nm (red). The low-symmetry location of Dy^{3+} results in the predominate emission of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition. The PL revealed the presence of Dy^{3+} ions at asymmetric sites. Hence $Ca_5(PO_4)_3F$ phosphors shows strong PL emission as compare to $Ba_5(PO_4)_3F$ phosphor. Dy^{3+} ion may enter into the host lattice to substitute Ca^{2+} or locate on surfaces of the crystals due to the porosity of the spinal structure due to the Dy^{3+} ions. The BYR emission are important in the context of Dy^{3+} nonequivalent substitution in solid-state lighting phosphor (mercury free excited lamp phosphor) and white light LED.

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