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Efficient photoluminescence of Dy³⁺-doped β-PbF₂ crystal

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ABSTRACT

The absorption and luminescent properties of the samples with the compositions (2 mol %) Dy³⁺: β-PbF₂ crystals are featured in this work. The white-light under the irradiation of 350 or 387 nm are comprised of the blue light emission and the yellow light emission, originating from the transitions of ⁴F_{9/2} → ⁶H_{15/2}, ⁴F_{9/2} → ⁶H_{13/2} in the 4f⁹ configuration of Dy³⁺. Excitation and photoluminescence spectra are explained in terms of Dy³⁺ ions are substituted mainly at Pb²⁺ sites with high symmetry (O_h or C_{4v}). The spectral characteristics of this new phosphor make it a promising candidate for application on potential laser transitions, optical devices and solid-state lighting for general illumination purposes. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Bridgman;
Dy³⁺ doped;
Luminescent properties.

INTRODUCTION

The Dy³⁺ (4f⁹) ion is capable of emitting several interesting wavelengths between its f-f transitions, depending upon its host, which find potential applications in diverse fields. Fluorescence at 1.32 μm originating from the ⁶F_{11/2} – ⁶H_{9/2} level of the Dy³⁺ ion is interesting for the application to the fiber amplifiers in the optical transmission system^[1]. Further, the energy levels of Dy³⁺ ion are capable of emitting mid-IR fluorescence at 2.9, 4.4 and 5.5 μm wavelengths, which are may due to the ⁶H_{13/2} → ⁶H_{15/2}, ⁶H_{11/2} → ⁶H_{13/2} and ⁶F_{11/2} + ⁶H_{9/2} – ⁶H_{11/2} transitions, respectively^[2-5]. In addition, the visible luminescence of trivalent dysprosium Dy³⁺ mainly consists of narrow lines in the blue (470–500 nm, ⁴F_{9/2} → ⁶H_{15/2}) and yellow (⁴F_{9/2} → ⁶H_{13/2}, 570–600 nm)

wavelength region^[6]. The intense yellow emissions have been observed in some crystal hosts, and can be utilized as a visible solid-state laser^[7-9]. At a suitable yellow to blue intensity ratio, Dy³⁺ will emit white light, which are necessary for the development of white light emission and are very useful in high resolution optical display systems^[10,11].

Among various host matrices, fluoride possess a series of interesting properties such as low phonon energy, which makes them particularly suitable for IR transitions; longer fluorescence lifetime with improved energy storage; lower upconversion losses; reduced thermal lensing; and extremely low beam depolarization under strong pumping, being that the natural birefringence is larger than that induced by thermal effects^[12]. To date, fluorides have been investigated as host mate-

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rials for the dysprosium ion to develop NIR laser and visible-emitting media^[13,14].

In this work we present the luminescence characterization of Dy³⁺-doped PbF₂ crystal prepared by the Bridgman method in a nonvacuum atmosphere. This study mainly includes growth, absorption, emission measurements of Dy³⁺-doped PbF₂ crystal, and some preliminary results on the white-light phosphorescence from are reported.

EXPERIMENTAL SECTION

At low pressures, PbF₂ is found to exist in two structural phases, namely orthorhombic (α) and cubic (β). Although the cubic phase is the most stable in ambient conditions, the orthorhombic phase is stable at high pressure and low temperature^[15]. The Dy³⁺-doped β -PbF₂ crystals were grown in our crystal research laboratory using the conventional technique modified Bridgman method under non-vacuum conditions. The details procedure of crystal growth can be found in our previous work^[16].

X-ray diffraction analysis of the grown crystal was performed with a Rigaku D/max 2550V diffractometer, using monochromatic Cu K α radiation with a working voltage of 40 kV and current of 100 mA. Room temperature absorption spectrum in the range of 300–800 nm was carried out with a resolution of 2 nm using a JASCO V-570 UV/VIS spectrophotometer. Emission and excitation spectra were measured using a fluorescence spectrophotometer (Hitachi 850) with a Xe lamp as excitation source, and the lifetimes were measured with a phosphorimeter attachment to the main system with a Xe- λ ash lamp (25W power).

RESULTS AND DISCUSSION

Figure 1 presents the X-ray diffraction pattern of the pure PbF₂ and PbF₂: 2 mol% Dy crystals. As detected by XRD, all diffraction peaks can be readily indexed to the pure cubic PbF₂ (JCPDS: 06-0251) with space group of Fm3m. No additional peaks of other phases have been found, indicating that the existence of Dy³⁺ did not significantly influence the phase and crystallization of the products. The Dy³⁺ ions usually occupy a cation substitutional position, but charge com-

pensation is required to maintain the electrical neutrality of the system. The extra positive charge is compensated by an interstitial fluorine ion (F_i⁻). Several cases are possible, according to the position of the interstitial F_i⁻: First, the interstitial F_i⁻ is situated in another unit cell than the one containing the Dy ion, preserving the cubic local symmetry (O_h) of the Dy ion. Second, the interstitial fluoride is situated in the same unit cell as the Dy ion, inducing a distortion from the cubic symmetry. Hence, the Dy ion symmetry centers are either tetragonal (C_{4v}) if the interstitial F_i⁻ is situated in the [100] direction, or trigonal (C_{3v}) if it is situated in the [111] direction^[16].

Optical absorption spectra of Dy³⁺ (in the wave-

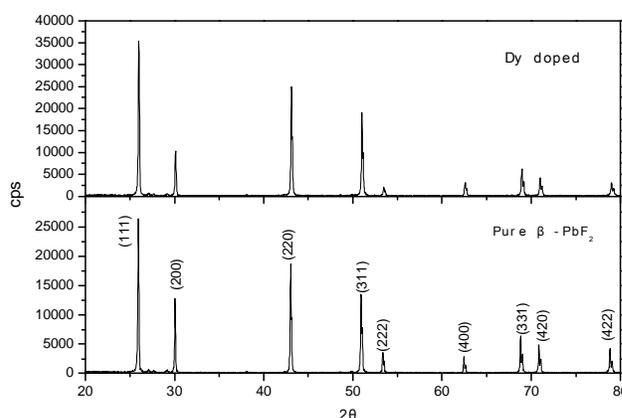


Figure 1 : X-ray diffraction pattern of the grown crystal

length region 350–2000 nm) ions doped PbF₂ crystal are shown in Figure 2. The characteristic absorption bands of Dy³⁺ ions were centered at around 1697, 1275, 1094, 905, 805, 754, 475, 453, 425, 387, 364 and 350 nm. The terminal levels of the corresponding transitions from the ⁶H_{15/2} ground state were assigned as shown in the Figure 2.

The excitation spectrum in Figure 3 is the scanning excited wavelength from 300 to 500 nm when the detection wavelength was set at 574 nm, for Dy³⁺-doped PbF₂ crystal. The excitation maxima for the 574 nm emission is located at 350 nm corresponding to the transition from the ground level ⁶H_{15/2} to the hypersensitive level ⁶P_{7/2}, from where it relaxes non-radiatively to the ⁴F_{9/2} metastable level. Four secondary excitation peaks at 325, 364, 387 and 455 nm were assigned and correspond to the transitions from the ground level (⁶H_{15/2} → ⁶P_{3/2}), (⁶H_{15/2} → ⁶P_{5/2}), (⁶H_{15/2} → ⁴I_{13/2}) and (⁶H_{15/2} → ⁴I_{15/2}), respectively. The general observed peaks dis-

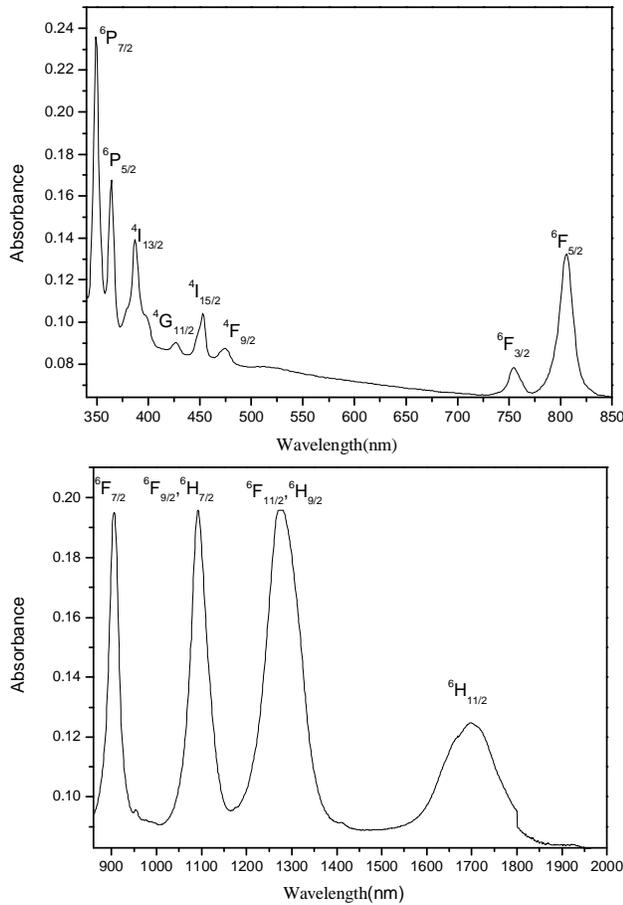


Figure 2 : Room-temperature absorption spectrum of the Dy³⁺-doped PbF₂ crystal

tribution agrees with the reported structure distribution spectra in Ref^[17-20]. Those broad bands indicate that the Dy³⁺ ions are substituted mainly at Pb²⁺ sites with low symmetry (C_{4v} and C_{3v}), arising from the charge compensation processes.

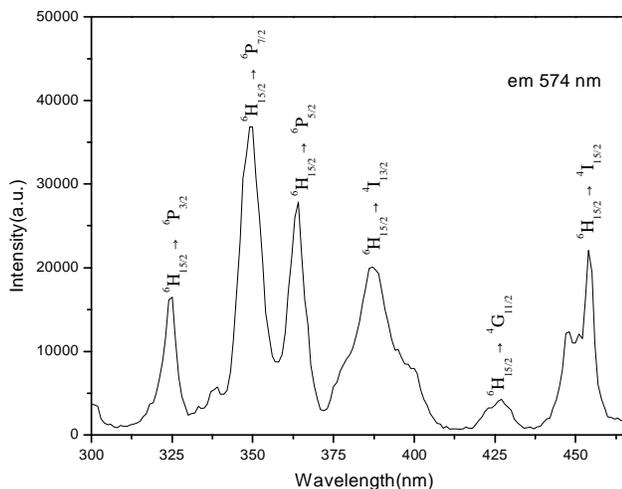


Figure 3 : Room-temperature excitation spectrum of the Dy³⁺-doped PbF₂ crystal

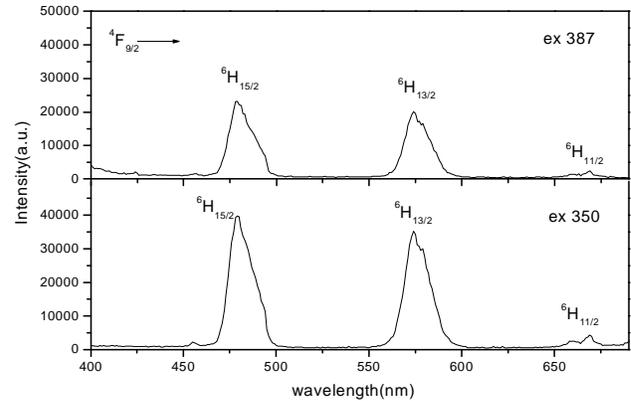


Figure 4 : Room-temperature fluorescence spectrum of the Dy³⁺-doped PbF₂ crystal in the visible region.

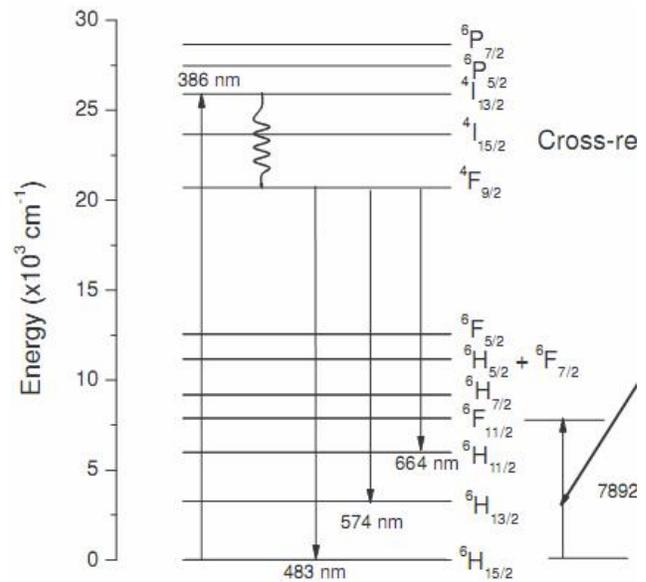


Figure 5 : Energy level diagram for Dy³⁺ in PbF₂ crystal

The photoluminescence spectra of Dy³⁺-doped PbF₂ sample under excitation at 350 and 387 nm are shown in Figure 4. The PL spectra show the two main groups of lines in the blue region (460–500 nm) and yellow region (550–610 nm) and also some weak lines observed in red region. These blue, yellow, and red emissions are assigned to the electronic transitions (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$), (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) and (${}^4F_{9/2} \rightarrow {}^6H_{11/2}$), respectively. All transition of Dy³⁺ ions in PbF₂ are described in the energy diagram from Figure 5. The blue (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) emission corresponding to the magnetic dipole transition and the yellow (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) emission belongs to hypersensitive (forced electric dipole) transition with the selection rule, with $\Delta J = 2$. The crystal field splitting components of Dy³⁺ can be observed and is well correlated with the Kramer's doublets (2J + 1)/

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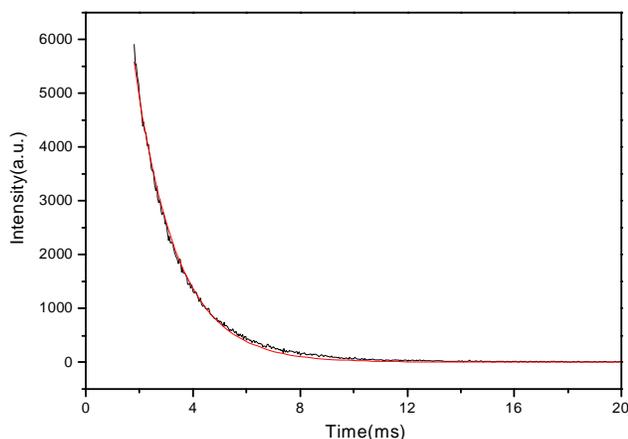


Figure 6 : Decay curves of ${}^4F_{9/2}$ level of the Dy³⁺ in PbF₂ crystal at room-temperature

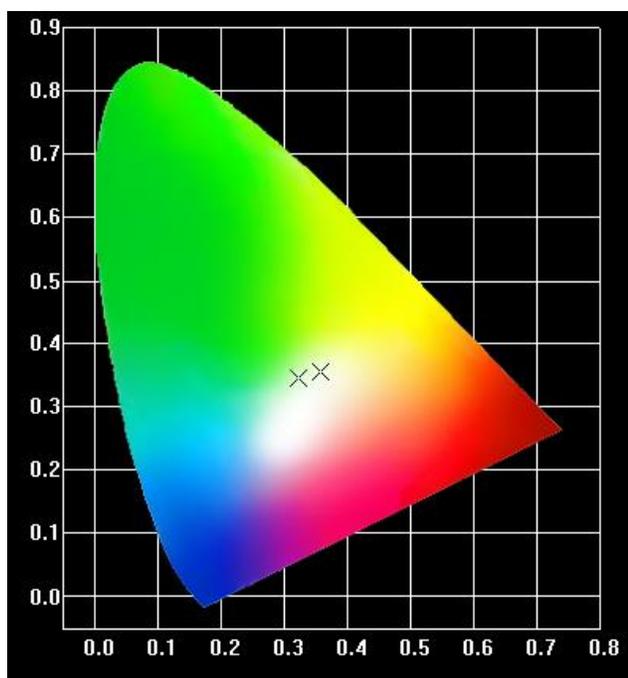


Figure 7 : CIE diagram represented with our obtained chromaticity coordinates

2, where J is the total angular momentum of the electrons^[21, 22]. It indicates that Dy³⁺ ions are well substituted into Pb²⁺ sites. In Dy³⁺-doped PbF₂ sample, the integrated intensity of blue emission is greater than that of the yellow emission, this can be explained according to the following reason: It is well known that the yellow (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) emission belongs to hypersensitive (forced electric dipole) transition with the selection rule, with, which is strongly influenced by the outside surrounding environment. The blue (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) emission corresponding to the magnetic dipole transition hardly varies with the crystal field symmetry around the

TABLE 1 : Chromaticity coordinates and corresponding color temperatures with different excitation wavelength

Sample	Excitation (nm)	Chromaticity coordinates	Color temperature (K)
Dy:PbF ₂	350	(0.357, 0.356)	4574
	387	(0.322, 0.346)	5969
CIE white light point		(0.33, 0.33)	
Pro Photo /Color Match		(0.3457, 0.3585)	
PAL/SECAM /HDTV		(0.3127, 0.329)	
NTSC		(0.3101, 0.3162)	

Dy³⁺ ion. When Dy³⁺ is located at a low symmetry local site (without inversion symmetry), the yellow emission is often dominant in the emission spectrum and when Dy³⁺ is at a high symmetry local site (with inversion symmetry center), and the blue emission is stronger than the yellow emission and is dominant in the emission spectrum^[23]. The latter case occurs for Dy³⁺-doped PbF₂ crystal, the Dy³⁺ ions are substituted mainly at Pb²⁺ sites with high symmetry (O_h or C_{4v}). The decay of ${}^4F_{9/2}$ level of Dy³⁺ ions in PbF₂ crystal has been recorded under excitation at 350 nm (${}^6H_{15/2} \rightarrow {}^5P_{7/2}$), as shown in Figure 6. The measured lifetimes of ${}^4F_{9/2}$ excited state determined by taking the first e-folding times of the decay curves of Dy³⁺ ion in PbF₂ crystal is 1.7 ms.

The Commission International de l'Eclairage (CIE) chromaticity coordinates for Dy³⁺: PbF₂ were calculated and listed in TABLE 1 along with their color temperatures. Some other color systems chromaticity coordinates are presented in table for comparison purpose. The CIE chromaticity coordinates are also represented in Figure 7. We have observed that the Dy³⁺: PbF₂ exhibits excellent CIE coordinates of (0.357, 0.356) and (0.322, 0.346) for 2 mol% under excitation at 350 and 387 nm respectively, which are quite close to that of the CIE white light point (0.33, 0.33) for the National Television Standard Committee (NTSC) system. From the table it is clear that the Dy³⁺: PbF₂ can give cool white light by adjusting the excitation source appropriately. This makes it possible to make a UV-white LED capable of emitting cool white desired for outdoor illumination applications. Also, these

phosphors are useful for optical display systems, because the chromaticity coordinates of Dy^{3+} : PbF_2 approaches the National Television System Committee (NTSC). The above observations hint at the promising application of Dy^{3+} : PbF_2 to produce white-light for UV-LED as well as optical display systems.

CONCLUSION

In this work, we report some preliminary results on the photoluminescence from Dy^{3+} -doped β - PbF_2 crystal. The structural and the luminescent properties of Dy^{3+} : PbF_2 crystal have been studied by the measurement of their XRD, absorption, PLE, PL, spectra along with their lifetimes. The emission spectra show two strong bands in blue (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) and yellow (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) regions. Based on the emission spectral intensities, we could calculate the chromaticity coordinates of Dy^{3+} : PbF_2 phosphors to demonstrate the color stability of the phosphors and which approaches the CIE ideal white light condition. The spectral characteristics of this new phosphor make it a promising candidate for application on optical devices, visible laser and solid-state lighting for general illumination purposes. Investigations of the variation concentration of Dy ions and others (for laser applications) may be taken later.

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