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## Efficient photoluminescence of Dy<sup>3+</sup>-doped β-PbF<sub>2</sub> crystal

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### ABSTRACT

The absorption and luminescent properties of the samples with the compositions (2 mol %) Dy<sup>3+</sup>: β-PbF<sub>2</sub> 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 <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> in the 4f<sup>9</sup> configuration of Dy<sup>3+</sup>. Excitation and photoluminescence spectra are explained in terms of Dy<sup>3+</sup> ions are substituted mainly at Pb<sup>2+</sup> sites with high symmetry (O<sub>h</sub> or C<sub>4v</sub>). 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;  
Dy<sup>3+</sup> doped;  
Luminescent properties.

### INTRODUCTION

The Dy<sup>3+</sup> (4f<sup>9</sup>) 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 <sup>6</sup>F<sub>11/2</sub> - <sup>6</sup>H<sub>9/2</sub> level of the Dy<sup>3+</sup> ion is interesting for the application to the fiber amplifiers in the optical transmission system<sup>[1]</sup>. Further, the energy levels of Dy<sup>3+</sup> ion are capable of emitting mid-IR fluorescence at 2.9, 4.4 and 5.5 μm wavelengths, which are may due to the <sup>6</sup>H<sub>13/2</sub> → <sup>6</sup>H<sub>15/2</sub>, <sup>6</sup>H<sub>11/2</sub> → <sup>6</sup>H<sub>13/2</sub> and <sup>6</sup>F<sub>11/2</sub> + <sup>6</sup>H<sub>9/2</sub> - <sup>6</sup>H<sub>11/2</sub> transitions, respectively<sup>[2-5]</sup>. In addition, the visible luminescence of trivalent dysprosium Dy<sup>3+</sup> mainly consists of narrow lines in the blue (470–500 nm, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub>) and yellow (<sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub>, 570–600 nm)

wavelength region<sup>[6]</sup>. The intense yellow emissions have been observed in some crystal hosts, and can be utilized as a visible solid-state laser<sup>[7-9]</sup>. At a suitable yellow to blue intensity ratio, Dy<sup>3+</sup> will emit white light, which are necessary for the development of white light emission and are very useful in high resolution optical display systems<sup>[10,11]</sup>.

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<sup>[12]</sup>. 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<sup>[13,14]</sup>.

In this work we present the luminescence characterization of Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal prepared by the Bridgman method in a nonvacuum atmosphere. This study mainly includes growth, absorption, emission measurements of Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal, and some preliminary results on the white-light phosphorescence from are reported.

### EXPERIMENTAL SECTION

At low pressures, PbF<sub>2</sub> is found to exist in two structural phases, namely orthorhombic ( $\alpha$ ) and cubic ( $\beta$ ). Although the cubic phase is the most stable in ambient conditions, the orthorhombic phase is stable at high pressure and low temperature<sup>[15]</sup>. The Dy<sup>3+</sup>-doped  $\beta$ -PbF<sub>2</sub> 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<sup>[16]</sup>.

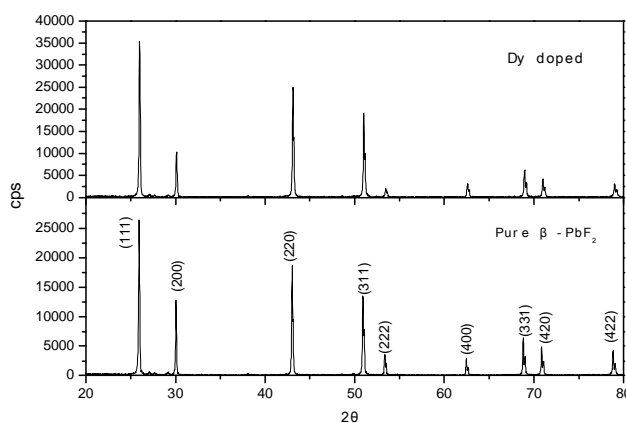
X-ray diffraction analysis of the grown crystal was performed with a Rigaku D/max 2550V diffractometer, using monochromatic Cu K $\alpha$  radiation with a working voltage of 40 kV and current of 100 mA. Room temperature absorption spectrum in the range of 300–800 nm was carried out with a resolution 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- $\lambda$ ash lamp (25W power).

### RESULTS AND DISCUSSION

Figure 1 presents the X-ray diffraction pattern of the pure PbF<sub>2</sub> and PbF<sub>2</sub>: 2 mol% Dy crystals. As detected by XRD, all diffraction peaks can be readily indexed to the pure cubic PbF<sub>2</sub> (JCPDS: 06-0251) with space group of Fm3m. No additional peaks of other phases have been found, indicating that the existence of Dy<sup>3+</sup> did not significantly influence the phase and crystallization of the products. The Dy<sup>3+</sup> ions usually occupy a cation substitutional position, but charge com-

ensation is required to maintain the electrical neutrality of the system. The extra positive charge is compensated by an interstitial fluorine ion (F<sub>i</sub><sup>-</sup>). Several cases are possible, according to the position of the interstitial F<sub>i</sub><sup>-</sup>: First, the interstitial F<sub>i</sub><sup>-</sup> is situated in another unit cell than the one containing the Dy ion, preserving the cubic local symmetry (O<sub>h</sub>) 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<sub>4v</sub>) if the interstitial F<sub>i</sub><sup>-</sup> is situated in the [100] direction, or trigonal (C<sub>3v</sub>) if it is situated in the [111] direction<sup>[16]</sup>.

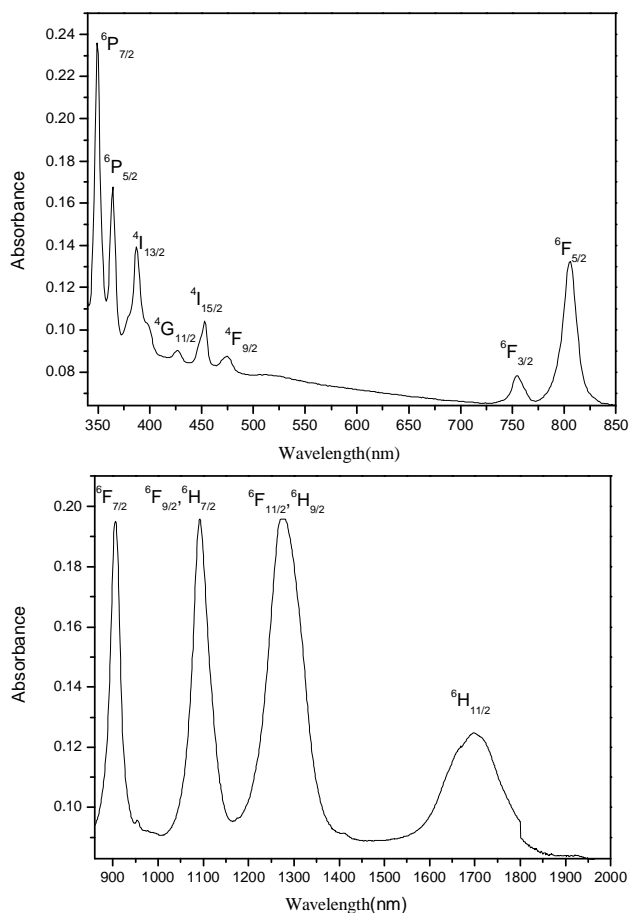
Optical absorption spectra of Dy<sup>3+</sup> (in the wave-



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

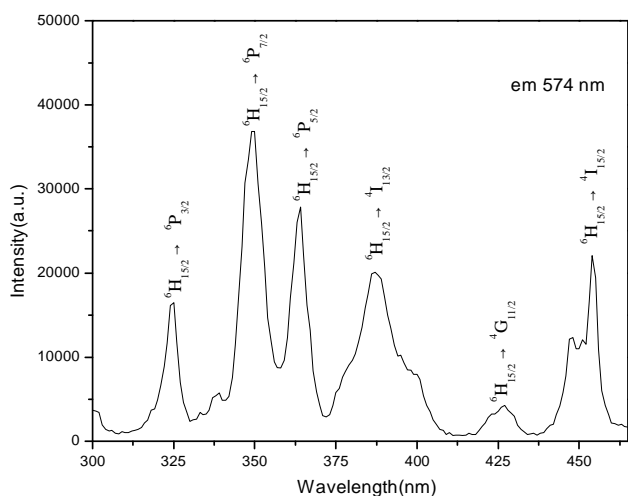
length region 350–2000 nm) ions doped PbF<sub>2</sub> crystal are shown in Figure 2. The characteristic absorption bands of Dy<sup>3+</sup> ions were centered at around 1697, 1275, 1094, 905, 805, 754, 475, 453, 425, 387, 364 and 350 nm. The terminal levels of the corresponding transitions from the <sup>6</sup>H<sub>15/2</sub> 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 Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal. The excitation maxima for the 574 nm emission is located at 350 nm corresponding to the transition from the ground level <sup>6</sup>H<sub>15/2</sub> to the hypersensitive level <sup>6</sup>P<sub>7/2</sub>, from where it relaxes non-radiatively to the <sup>4</sup>F<sub>9/2</sub> metastable level. Four secondary excitation peaks at 325, 364, 387 and 455 nm were assigned and correspond to the transitions from the ground level (<sup>6</sup>H<sub>15/2</sub> → <sup>6</sup>P<sub>3/2</sub>), (<sup>6</sup>H<sub>15/2</sub> → <sup>6</sup>P<sub>5/2</sub>), (<sup>6</sup>H<sub>15/2</sub> → <sup>4</sup>I<sub>13/2</sub>) and (<sup>6</sup>H<sub>15/2</sub> → <sup>4</sup>I<sub>15/2</sub>), respectively. The general observed peaks dis-

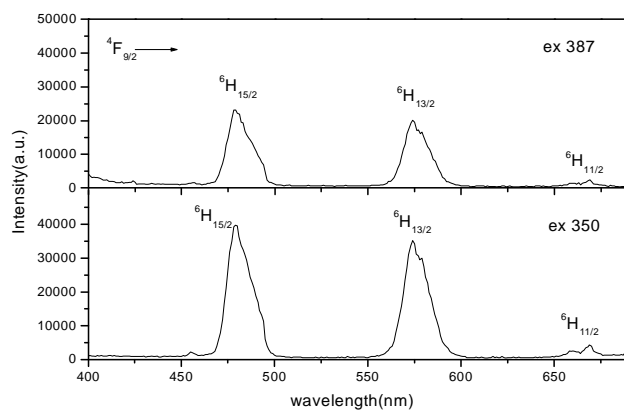


**Figure 2 : Room-temperature absorption spectrum of the Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal**

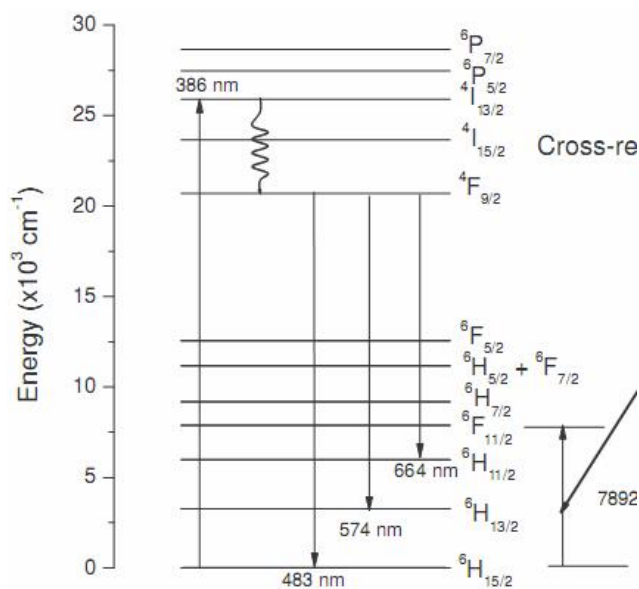
tribution agrees with the reported structure distribution spectra in Ref<sup>[17-20]</sup>. Those broad bands indicate that the Dy<sup>3+</sup> ions are substituted mainly at Pb<sup>2+</sup> sites with low symmetry (C<sub>4v</sub> and C<sub>3v</sub>), arising from the charge compensation processes.



**Figure 3 : Room-temperature excitation spectrum of the Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal**



**Figure 4 : Room-temperature fluorescence spectrum of the Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal in the visible region.**



**Figure 5 : Energy level diagram for Dy<sup>3+</sup> in PbF<sub>2</sub> crystal**

The photoluminescence spectra of Dy<sup>3+</sup>-doped PbF<sub>2</sub> 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 Dy<sup>3+</sup> ions in PbF<sub>2</sub> 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 Dy<sup>3+</sup> can be observed and is well correlated with the Kramer's doublets (2J + 1)/

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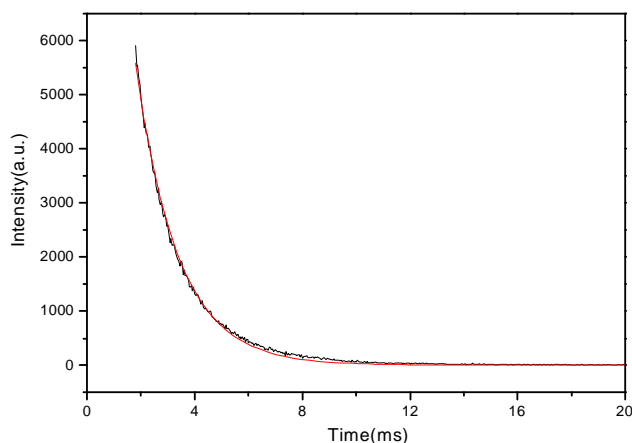


Figure 6 : Decay curves of  ${}^4F_{9/2}$  level of the Dy<sup>3+</sup> in PbF<sub>2</sub> crystal at room-temperature

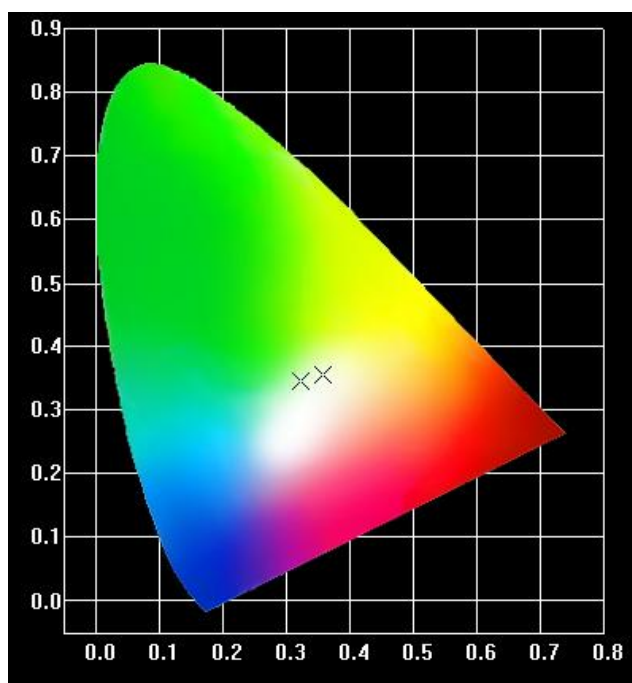


Figure 7 : CIE diagram represented with our obtained chromaticity coordinates

2, where J is the total angular momentum of the electrons<sup>[21, 22]</sup>. It indicates that Dy<sup>3+</sup> ions are well substituted into Pb<sup>2+</sup> sites. In Dy<sup>3+</sup>-doped PbF<sub>2</sub> 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 <sub>2</sub>    | 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)         |                       |

Dy<sup>3+</sup> ion. When Dy<sup>3+</sup> is located at a low symmetry local site (without inversion symmetry), the yellow emission is often dominant in the emission spectrum and when Dy<sup>3+</sup> 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<sup>[23]</sup>. The latter case occurs for Dy<sup>3+</sup>-doped PbF<sub>2</sub> crystal, the Dy<sup>3+</sup> ions are substituted mainly at Pb<sup>2+</sup> sites with high symmetry ( $O_h$  or  $C_{4v}$ ). The decay of  ${}^4F_{9/2}$  level of Dy<sup>3+</sup> ions in PbF<sub>2</sub> 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 Dy<sup>3+</sup> ion in PbF<sub>2</sub> crystal is 1.7 ms.

The Commission International de l'Eclairage (CIE) chromaticity coordinates for Dy<sup>3+</sup>: PbF<sub>2</sub> 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 Dy<sup>3+</sup>: PbF<sub>2</sub> 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 Dy<sup>3+</sup>: PbF<sub>2</sub> 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  $\text{Dy}^{3+}$ :  $\text{PbF}_2$  approaches the National Television System Committee (NTSC). The above observations hint at the promising application of  $\text{Dy}^{3+}$ :  $\text{PbF}_2$  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  $\text{Dy}^{3+}$ -doped  $\beta$ - $\text{PbF}_2$  crystal. The structural and the luminescent properties of  $\text{Dy}^{3+}$ :  $\text{PbF}_2$  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  $\text{Dy}^{3+}$ :  $\text{PbF}_2$  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.

## ACKNOWLEDGMENTS

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