

# STUDY ON THE LUMINESCENT PROPERTIES OF DYSPROSIUM DOPED BARIUM VANADATE PHOSPHOR

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## Abstract

Rare earth elements (RE) display countless applications in several technological fields and are associated with practically all everyday activities of modern society. In the present work Barium Vanadate ( $Ba_2V_2O_7$ ) phosphor doped with rare earth Dysprosium ( $Dy^{3+}$ ) has been prepared via conventional Solid-state reaction method at  $650^\circ C$  for 4 h. The effects of dopant ions on the resulting phase formation, particle morphology, structure, luminescent properties were characterized by X-ray diffraction (XRD), Fourier Transform Infra Red spectroscopy (FTIR), The photoluminescence excitation (PLE) and emission (PL) spectra, and UV-Visible spectra were also investigated. Phosphors show a broad excitation band in the 250–350 nm wavelength regions. From molecular orbital theory, the band at 330 nm is resulted from the electronic transitions from ground state  $^1A_2(^1T_1)$  to excited states  $^1A_1(^1E)$  and  $^1E(^1T_2)$  of  $VO_4^{3-}$  complexes which make them highly suitable for LED.

**Keywords:** Vanadates, phosphors, photoluminescence,

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## 1. INTRODUCTION

Illumination technology has become indispensable in our daily lives and thus considerable efforts are being made to develop excellent luminescent materials for lighting and display applications [1]. Recently the scientific world has been fascinated by vanadium oxide-based materials because of their stunning optical and magnetic, transport and ferroelectric properties which make them shine over all other materials. The phosphors based on vanadate host matrices have become the subject of great interest for extensive investigation due to their wide applications in lighting and displays. Due to structural variations, they have wide applications which are mainly focused in two directions: one as a photocatalyst and the other as optoelectronic materials [2]. There are several reports on vanadium oxide compounds being widely used as multifunctional optical materials: phosphors, luminescent indicators, thermo luminescent detectors, lasing media, scintillators, and so forth [3]. Vanadates usually show a rather short wavelength of optical absorption edge. This makes them appropriate as hosts to accommodate active rare earth ions. Rare earth ions, such as  $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$  and  $Sm^{3+}$  are well-known luminescent activators in a variety of host lattices and the rare earth activated phosphors have been studied extensively because of their high light output, excellent color rendering index, energy efficiency and greater radiation stability due to intra configuration f–f transitions within

the incompletely filled 4f shell, shielded with outer 5s and 5p orbital's, and this gives rise to specific optical features such as narrow emission band widths, long lifetime, better quantum yield, etc[4]. Particularly, RE-doped inorganic nanoparticles display singular luminescent properties that currently find a number of applications, such as the development of excimer lamps for the elimination of Hg in fluorescent tubes, plasma displays with improved resolution, light-emitting diode (LED) lamps, and bio labeling materials [5]. Among them luminescent materials doped with Dy<sup>3+</sup> may be used as potential white phosphors with a single emitting centre because of its two dominant emission bands in the blue region (470–500 nm) and yellow region (560–600 nm). By suitably adjusting the yellow-to-blue intensity ration values, it is possible to obtain near-white emission with Dy<sup>3+</sup>-activated phosphors [6]. Due to the broad band emission spectrum the emission color of most vanadates is almost white.

The present work was undertaken to find a new vanadate as host material for Dy<sup>3+</sup> ions. Here, we chose Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> as the host material. To the best of our knowledge, the luminescence properties of Dy<sup>3+</sup> doped Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> have rarely been reported. Barium orthovanadates, Ba<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> exhibit intense rare-earth activated luminescence and can be used as efficient luminescence phosphors and host materials for lasers because of its emission from the charge-transfer of VO<sub>4</sub><sup>3-</sup> group of high emitting intensity in some species lattice structures that has potential application in illumination devices. In this work, Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>:Dy<sup>3+</sup> was synthesized by conventional solid-state reaction for phosphor WLED by the measurement of their photoluminescence (PL) and structural and optical properties annealing temperature 650°C. All these samples were characterized by XRD, FT-IR and photoluminescence excitation and emission spectra has been studied in detail to explore the best suitable phosphor for light emitting diodes (LEDs) application.

## **2 EXPERIMENTAL**

Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>:Dy<sup>3+</sup> phosphor has been prepared by using conventional solid state method. The high purity (99.9%) chemicals BaCO<sub>3</sub>(99.6%,Sigma Aldrich),V<sub>2</sub>O<sub>5</sub> (99.2%, Alfa Aesar) and Dy<sub>2</sub>O<sub>3</sub>(99.9%, Alfa Aesar)were taken in stoichiometric ratio and mixed in an agate mortar for two hours using distilled water as the medium and then dried. This dried powder was taken in an alumina crucible and calcined at 650°C for 4 h and cooled down to room temperature to obtain the final white samples(heating and cooling rate was 10 °C/min). The concentration of RE ions was chosen as 0.004mol%.

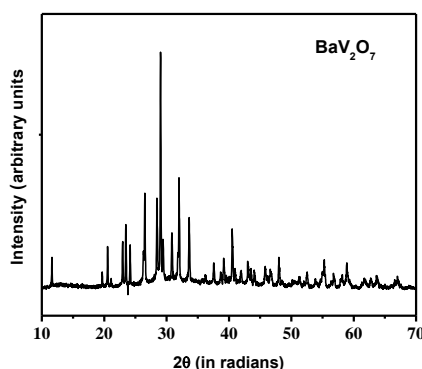
The phase analysis of the phosphors has been done with X-ray diffraction technique on powder samples using a Bruker AXS D8 Advanced using  $\lambda = 1.54 \text{ \AA}$ . The pattern was recorded at a scanning rate of 60 /min<sup>-1</sup> between 20-80 degree and step size was 0.01° and scanning rate 4.0°/min. FT-IR

spectrum of the powder was recorded using a (Perkin Elmer Spectrum 2) with KBr pellet technique from  $4500\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$ . Photoluminescence excitation (PLE) and emission (PL) characteristics were examined by a Fluorescence Spectrophotometer (Horiba Fluoromax 4) equipped with a monochromator and a xenon lamp (150W continuous). All measurements were carried out at room temperature.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 X-RAY DIFFRACTION (XRD)

Fig.1 shows the XRD patterns of the as synthesized  $\text{Ba}_2\text{V}_2\text{O}_7$  phosphor sample at  $650^\circ\text{C}$  compared with the standard JCPDS card no. 76-0612. The d values and  $2\theta$  of our sample seem to be matching with the standard value

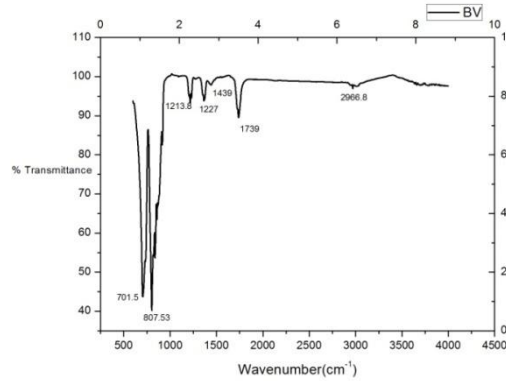


**Fig. 1 The XRD pattern of  $\text{Ba}_2\text{V}_2\text{O}_7$**

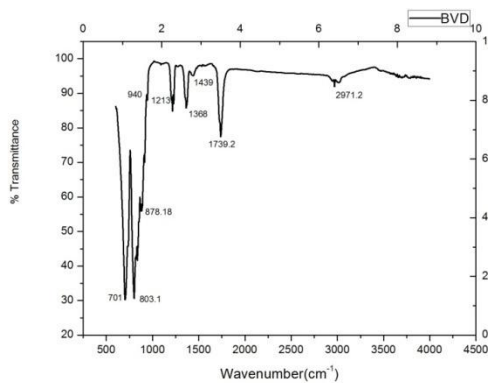
#### 3.2 FOURIER TRANSFORM INFRA RED SPECTRA (FT-IR)

Fig 2a.shows the FT-IR spectrum of  $\text{Ba}_2\text{V}_2\text{O}_7$  and fig 2b shows  $\text{Dy}^{3+}$  doped  $\text{Ba}_2\text{V}_2\text{O}_7$  in the spectral region of  $500\text{--}4500\text{ cm}^{-1}$ . The FT-IR spectrum shows three absorption regions. In the first region, the broad band in the range of  $2500\text{--}3500\text{ cm}^{-1}$  with maximum at  $2966\text{ cm}^{-1}$  assigned to the O–H stretching vibration, the second region in the range of  $1300\text{--}1800\text{ cm}^{-1}$ , which originated from the absorption of the H–O–H bending vibrations centered at  $1439\text{ cm}^{-1}$ . These two bands are the characteristic vibrations of water from air; physically absorbed on the sample surface and third region, Modes in the  $700\text{--}1250\text{ cm}^{-1}$  are due to  $(\text{VO}_4)_2$  absorption bands, which are assigned to the O–V–O bending vibrations and V–O stretching vibrations, respectively. It is known that the presence of OH content increases the optical losses and then decreases the quantum efficiency of rare-earth doped materials. However, for the present phosphors, the intensity of the IR band associated to OH group is extremely low, which indicates that these prepared phosphors are suitable for practical applications. The bands associated in the range  $1400\text{--}1600\text{ cm}^{-1}$  is due to asymmetric and symmetric stretching

vibration of CO<sub>2</sub> and 2300-2350 cm<sup>-1</sup> belongs to CH bond stretching. The peak assignments of the FT-IR spectrum of the present phosphors have been compared with the results reported in literature. [7].



**Fig 2a: FT-IR Spectrum of pure Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>**



**Fig 2b: FT-IR spectra of Dy<sup>3+</sup> doped Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>**

### 3.3 UV- VISIBLE SPECTRA

The UV-Visible spectra of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup> was studied using JASCO V 550 Spectrophotometer in the range from 200-700 nm. The well defined absorbance is obtained and indirect band gap of both doped and pure samples are calculated from the graph. The band gap is about 3.345 eV for pure Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and 3.377 eV for Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup>. Slight differences in the absorption band gap of these two samples and the values is matched with reported values. Figure 3a and 3b represent the absorbance spectra of these samples and 3c and 3d corresponds to band gap of our material.

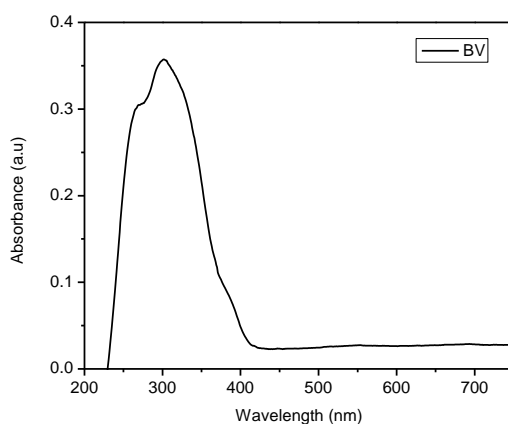


Fig 3a: Absorbance spectrum of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>

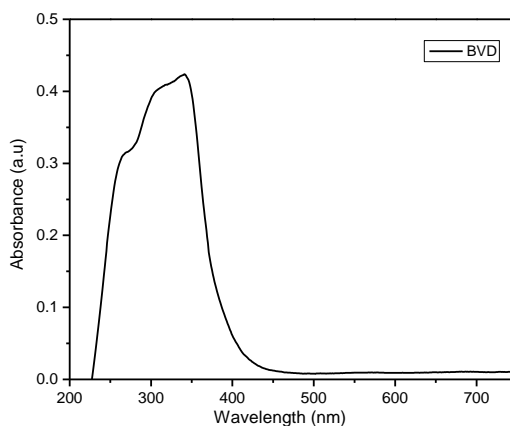


Fig 3b: Absorbance spectrum of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup>

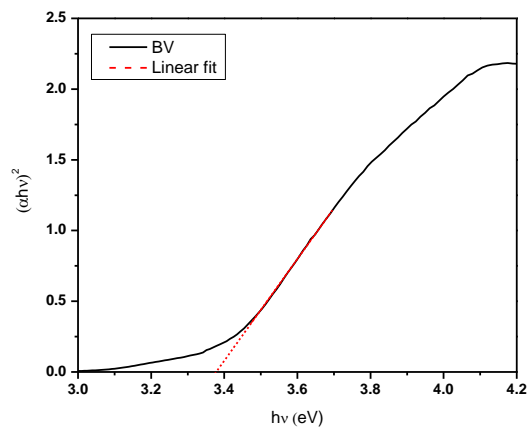
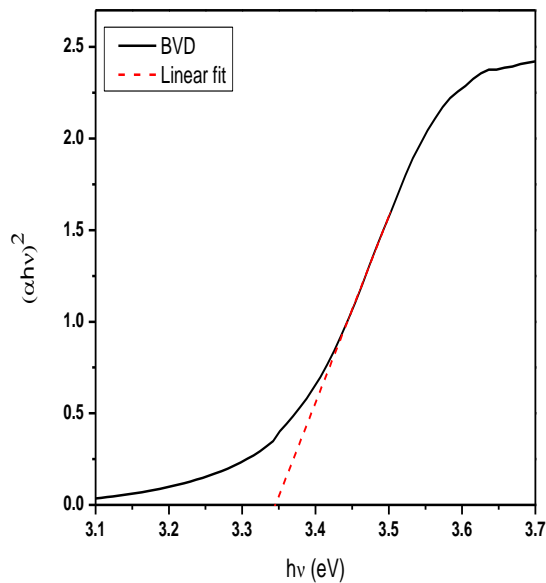


Fig 3c: Tauc plot of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>



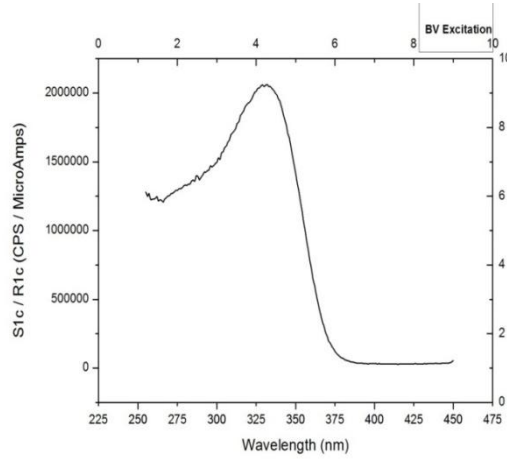
**Fig 3d: Tauc plot of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup>**

### 3.4 PHOTOLUMINESCENCE SPECTRA

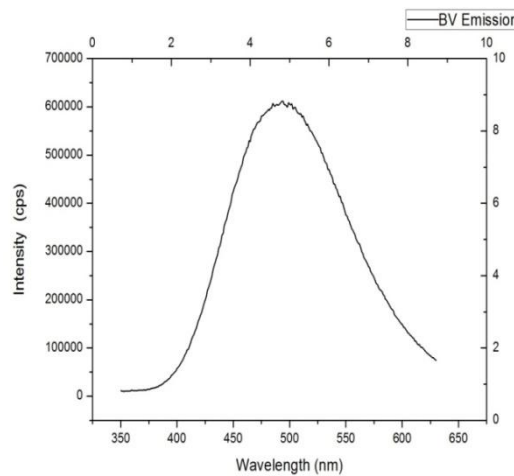
The PL properties of the samples were further characterized by excitation spectra and emission spectra. Figs. 4a- 4d shows the PL excitation and emission spectra of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup> respectively. The excitation spectra (Fig. 3a) consists of abroad, intense band in the ranging from 250 to 350 nm with a maximum at 330 nm. From molecular orbital theory, the band at 330 nm is resulted from the electronic transitions from ground state <sup>1</sup>A<sub>2</sub>(<sup>1</sup>T<sub>1</sub>) to excited states <sup>1</sup>A<sub>1</sub>(<sup>1</sup>E) and <sup>1</sup>E(<sup>1</sup>T<sub>2</sub>) of VO<sub>4</sub><sup>3-</sup> complexes [9] and weak lines in the longer wavelength region due to the absorption edge of host matrix emitted at 493 nm .

The Dy<sup>3+</sup> doped Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> shows peak position corresponding to broad excitation band and the peak positions of the sharp bands remain almost unaltered and it has been attributed to the absorption of excitation energy by the V<sub>2</sub>O<sub>7</sub> host lattice and then transfers the energy to the activator Dy<sup>3+</sup>. Also it may be due to O<sup>2-</sup> → Dy<sup>3+</sup>. Charge transfer band (CTB) which is assigned by electron transfer from filled 2p orbital of O<sup>2-</sup> ions to vacant 4f orbital of Dy<sup>3+</sup>. But there is an emission peak corresponds to 576 nm which is characteristic peak of doped Dy<sup>3+</sup> due to the 4F<sub>9/2</sub>–6H<sub>13/2</sub> electronic transition. It is suppressed by the host matrix and other sharp bands arose from the f–f intra configurational transitions of Dy<sup>3+</sup> ion. The band can be attributed to a charge transfer through the V–O bond overlay the Dy–O charge transfer. When the Dy<sup>3+</sup> ion-doped concentration is excessive, there is non-radiation

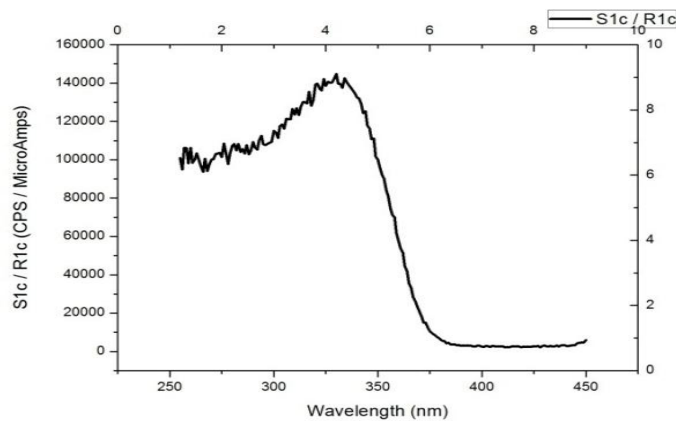
energy transfer between the excited centers [8]. So the excess doping can cause quenching. This broad band excitation of the material makes it highly suitable for LEDs application.



**Fig 4a: Excitation spectrum of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>**

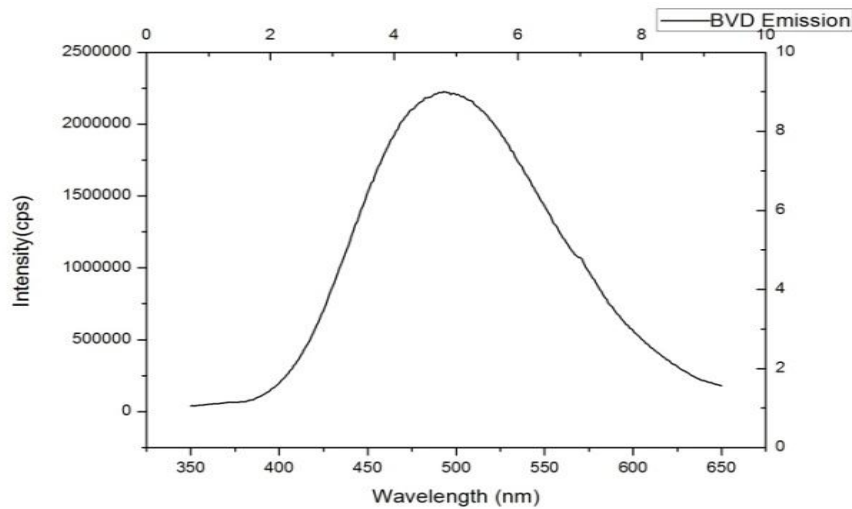


**Fig 4b: Emission spectra of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>**



**Fig 4c: Excitation spectrum of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup>**





**Fig 4d: Emission spectra of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup>**

## V. CONCLUSIONS

Pure and Dy<sup>3+</sup> doped novel Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phosphors have been successfully synthesized using solid state reaction method. Structural, optical and luminescence properties of Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub>: Dy<sup>3+</sup> was investigated. X-ray diffraction analysis confirmed the crystalline phase for synthesized Ba<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phosphor sample prepared at 650 °C by comparing with the standard ICDD card no. 76-0612. FT-IR spectra of pure and Dysprosium doped samples were studied and identify the modes of vibration and organic groups present in it. The role of Dy<sup>3+</sup> ions as mediators in significantly improving the PL emission has been established with PLE, PL spectral analysis. The excitation spectrum exhibits a broad band centered at about 330 nm corresponding to an overlap of the charge transfer transitions of VO<sub>4</sub><sup>3-</sup> and O<sup>2-</sup> to Dy<sup>3+</sup>. Dy<sup>3+</sup> gives PL emission at 576 nm. Absorption spectra and band gap of both these samples were investigated. The band gap of pure and Dysprosium added barium vanadate sample is in the range 3.3- 3.4eV.

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