

## Light-emission in Tb<sup>3+</sup> and Eu<sup>3+</sup>: PVP polymer films

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Analysis of photoluminescence spectra of PVP and Tb<sup>3+</sup> or Eu<sup>3+</sup>: PVP polymer films has been done. Emission spectrum of the host matrix poly (vinyl pyrrolidone) (PVP) has shown an intense blue emission at 424 nm [ $\pi_{0\rightarrow n_1\pi_2}$ ]. By using a solution cast method, more clear and transparent PVP polymer films have been developed for analysis with the addition of Tb<sup>3+</sup> and Eu<sup>3+</sup> ions separately into PVP polymer matrix; green and red colour emitting polymer films have been developed. Also undoped PVP polymer film has been prepared as a reference film for which XRD, FTIR, Raman and TGA-DTA spectral profiles have been carried out. From the measured emission spectrum of the Tb<sup>3+</sup>: PVP polymer film, an intense green emission at 544 nm ( $^5D_4 \rightarrow ^7F_5$ ) has been observed with an excitation at 311 nm. Under an UV source a bright green emission has been noticed from the surface of the Tb<sup>3+</sup>: PVP polymer film, and a bright red emission has been noticed from the surface of the Eu<sup>3+</sup>: PVP polymer film. The emission spectrum of Eu<sup>3+</sup>: PVP polymer film has also revealed an intense red emission at 612 nm ( $^5D_0 \rightarrow ^7F_2$ ).

**Keywords:** Structural-optical characterization, Luminescent polymers, Polymer films

### 1 Introduction

In recent years, a great deal of interest has been made towards the development of different luminescent polymer films<sup>1</sup>. Among polymers, the polyvinyl pyrrolidone (PVP) has been a water soluble non-ionic polymer material which demonstrates both hydrophilic and hydrophobic natures; it is therefore known to be amphiphilic polymer, which is a vinyl polymer possessing planar and highly polar side group<sup>2</sup>. Chemically PVP has been found to be inert, non-toxic, and interestingly, it displays a strong tendency for complexes formation with several smaller molecules<sup>3,4</sup>.

Rare earth ions containing polymers are actively investigated because of their useful applications. Since PVP polymer is water soluble chemical, it has been considered more convenient to incorporate with certain luminescent ions such as rare earth ions and transition metal ions<sup>5-14</sup>. In the present work, Tb<sup>3+</sup> or Eu<sup>3+</sup>: PVP polymer films have been undertaken to analyze their excitation and emission spectra.

### 2 Experimental Details

PVP (polyvinylpyrrolidone (C<sub>6</sub>H<sub>9</sub>ON)<sub>n</sub>, chemical with a molecular weight [MW] of 13,00,000,) was obtained from Sigma-Aldrich. This PVP chemical was dissolved in a small beaker (50 cc) containing a doubled distilled water and then it was thoroughly mixed by using a magnetic stirrer in a little warm

condition for a homogeneous mixing. Later, this solution was cast into polymer films in flat based Petri dishes under a slow evaporation process. Thus clearer and highly transparent PVP films (undoped) were successfully obtained. Terbium Chloride (99.9%) and Europium Chloride (99.9%) salts were separately dissolved in beaker with double distilled water, PVP was mixed in a double distilled water in another beaker, then by maintaining 1:9 ratio (Weight Percent) of TbCl<sub>3</sub>/EuCl<sub>3</sub> and PVP; both the solutions were mixed up again and later stirred up using a magnetic stirrer. Thus Pure PVP, Tb<sup>3+</sup>: PVP and Eu<sup>3+</sup>: PVP Polymer films were obtained and all of them were found to be in the range of 150  $\mu$ m in thickness. All the polymer films were 6 cm in diameter and from such big sized films; required sizes of films were made appropriately for measurement purpose.

The XRD profile of a pure PVP polymer film was measured on a Shimadzu - XD 3A diffractometer with a Ni-filter and CuK $\alpha$  (1.542Å) radiation with an operating voltage of 30 KV and current of 20 mA with a Si detector by changing the 2 $\theta$  values at the rate of 2°/min. FTIR spectrum of this sample was carried out on a Nicolet IR-200 spectrophotometer using the KBr pellet technique in the range 4000-400 cm<sup>-1</sup>. Raman spectrum was recorded on a high resolution Jobin Yvon Model HR800UV system attached with a He-Ne laser (633 nm) as the excitation source having an output power of 15 mW with a laser

beam spot size of 100  $\mu\text{m}$  from an appropriate lens system. Thermogravimetry (TG) and differential thermal analysis (DTA) were simultaneously obtained for the prepared host PVP polymer film in an  $\text{N}_2$  atmosphere at the heating rate of  $10^\circ\text{C}/\text{min}$  on a Netzsch STA 409 simultaneous thermal analyzer. Both excitation and emission spectra of pure PVP,  $\text{Tb}^{3+}$ : PVP and  $\text{Eu}^{3+}$ : PVP polymer films were recorded on a SPEX Fluorolog-2 Fluorimeter (Model-II) attached with a Xe-arc lamp (150W).

### 3 Results and Discussion

The measured X-ray diffraction (XRD) profile of the PVP film is shown in Fig. 1, which confirms the amorphous nature of the prepared polymer film that is in conformity with the earlier reported data<sup>15</sup>. Figure 2 shows the FTIR spectrum of the PVP polymer film. A broad and strong band at  $3100\text{--}2500\text{ cm}^{-1}$  is ascribed to the stretching vibration of the associated hydroxyl group. Bands at  $2900\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  are

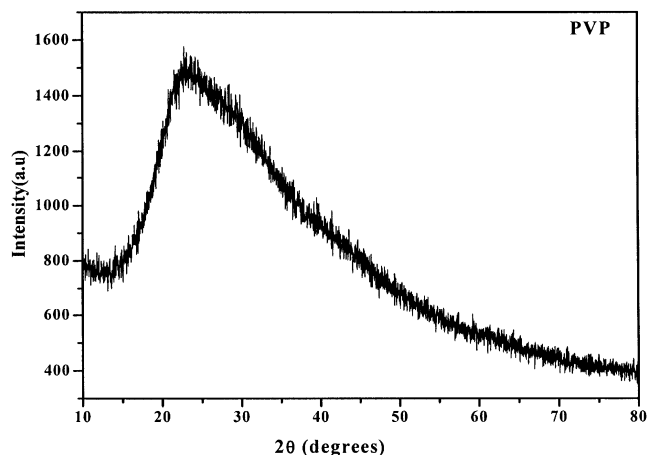


Fig. 1 — XRD profile of PVP polymer film

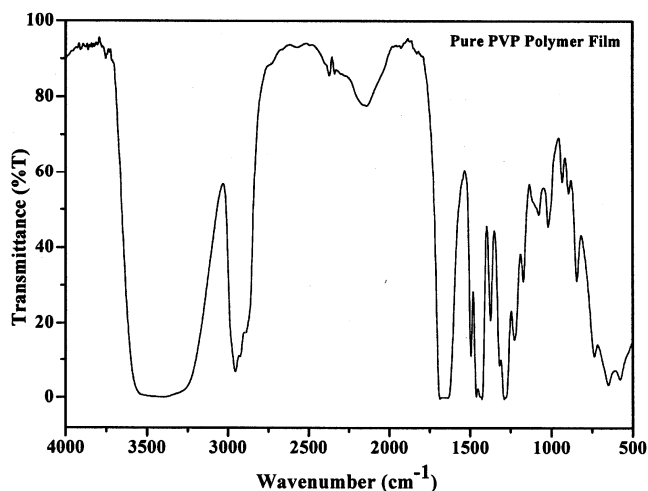


Fig. 2 — FTIR feature of PVP polymer film

attributed to the characteristic stretching vibrations of C-H respectively. A broad peak at  $918\text{ cm}^{-1}$  is due to the outer face vibration oscillation of the hydroxyl group  $\delta$  (O-H), and strong peaks at  $1447\text{ cm}^{-1}$  and  $1286\text{ cm}^{-1}$  are assigned to the inner face of the bending vibrations of the hydroxyl group. We have observed a broad band at  $3400\text{ cm}^{-1}$  in the spectrum of PVP, and the vibration band of C=O group at  $1665\text{ cm}^{-1}$  suggesting the existence of some H-bonding carbonyl groups in PVP. A blue-shift of the C=O group in PVP can be attributed to the change of  $p$ - $\pi$  conjugation associated with the amide group of PVP arising from disassociation of PVP chains due to the incorporation of other species. It is possible that an interaction between the complexes and PVP leads to the disassociation of the aggregated PVP chains, resulting in a blue-shift of the C=O vibration band. The obtained FTIR properties of PVP polymer film is in good agreement with the earlier reported results<sup>16-22</sup>.

Figure 3 shows the Raman spectrum of PVP and it has been observed that bands were corresponding to the C-N vibration band at  $758\text{ cm}^{-1}$  and C-C stretching vibration at  $934\text{ cm}^{-1}$ . The bands at  $1228$  and  $1421\text{ cm}^{-1}$  can be attributed to C-N stretching and C-H bends vibrations of pure PVP, respectively. The bands at  $1658$  and  $2920\text{ cm}^{-1}$  can be attributed to C=O and C-H stretching vibrations, respectively. The band broadening in Raman spectrum is usually an indication of amorphous nature of the polymer electrolyte<sup>23</sup>. The amorphous nature of the polymer electrolytes has also been confirmed by XRD analysis.

Figure 4 shows the TG-DTA curves of PVP polymer. The TGA thermograms of weight loss as a function of temperature for pure PVP powder with a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range

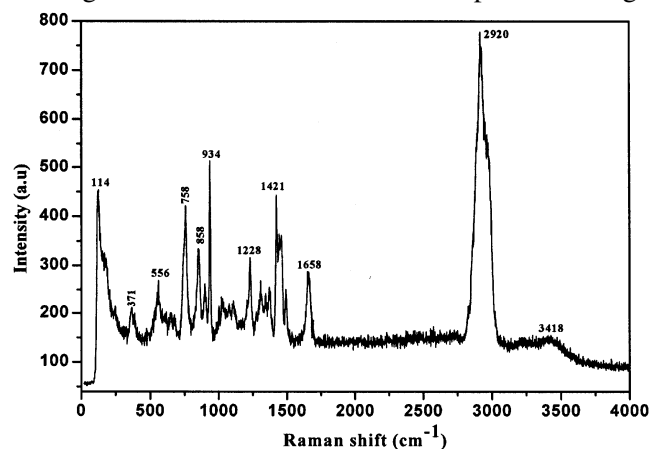


Fig. 3 — Raman spectrum of PVP polymer film

from the room temperature 40 to 700°C. It is clear that the initial weight loss for TG curve is 12% from the temperature of 40 to 103°C, which means the loss of four water molecules. On the DTA curve two exothermic peaks were observed at 433 and 570°C, respectively. A sharp, strong exothermic peak at 433°C confirms the combustion of organic residues, this strong exothermic peak in the DTA curve corresponds to the decomposition temperature of PVP is well above the heating temperature adopted in the present work. Correspondingly the weight loss in TG line is 18% at temperature of 470 to 605°C (Ref. 24).

Figure 5 shows both the excitation and emission spectra of PVP polymer film (undoped). We have observed a broad emission in the blue region at 424 nm. The carbonyl group (>C=O) of PVP, which is one of the most luminescent organic parts due to the conjugation of  $\pi$  electrons, causes the blue emission

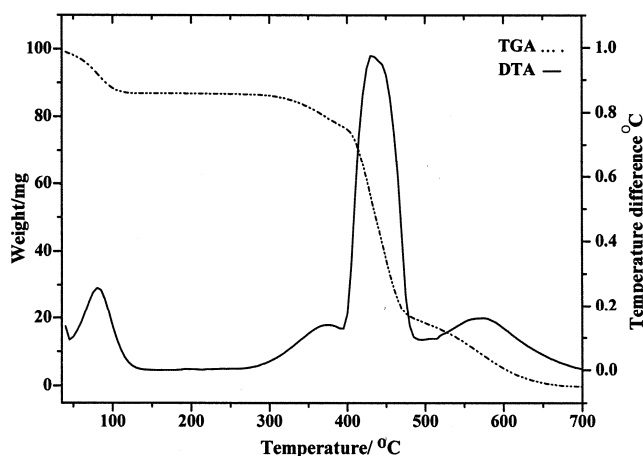


Fig. 4 — TG-DTA curves of PVP polymer film

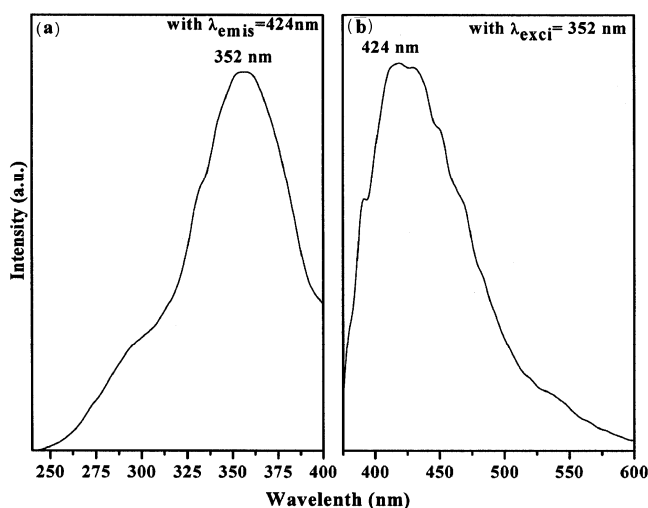


Fig. 5 — (a) Excitation and (b) Emission spectra of PVP polymer film

from the host PVP polymer film<sup>25</sup>. The excitation spectrum (250-500 nm) of the Tb<sup>3+</sup>: PVP polymer film is shown in Figure 6 (a). It consists of an intense broad band from 250 nm to 330 nm having its maximum intensity at 311 nm ( ${}^7F_6 \rightarrow {}^5H_6$ ) which arises due to a combined effect of spin allowed (4f-5d) transitions of Tb<sup>3+</sup> and also due to the energy transfer from carbonyl groups to Tb<sup>3+</sup> ions. Along with it, five other weak bands are also found at 352, 372, 382, 423 and 490 nm which are due to the spin forbidden (4f-5f) transitions which belong to the electronic transitions of  ${}^7F_6 \rightarrow {}^5L_9, {}^5G_4$ ,  ${}^7F_6 \rightarrow {}^5L_{10}$ ,  ${}^7F_6 \rightarrow {}^5D_3$ ,  ${}^7F_6 \rightarrow {}^4G_6$ ,  ${}^5D_5$  and  ${}^7F_6 \rightarrow {}^5D_4$ , respectively<sup>26</sup>. Since the 5d electrons at the excited state have two spin options of either the high spin  ${}^9D$  (4f<sup>7</sup> 5d) or low-spin  ${}^7D$  (4f<sup>7</sup> 5d), the peak at 311 nm comes from the spin allowed  ${}^7F_6 \rightarrow {}^5H_6$  transition. We have observed a bright green emission from the entire surface of Tb<sup>3+</sup>: PVP polymer film.

Figure 6(b) shows the emission spectra of Tb<sup>3+</sup>: PVP polymer film at two excitations wavelengths and in site of Figure 6 (b) displays a bright green emission from the surface of Tb<sup>3+</sup>: PVP polymer film when it was put under an UV source. Intense green emission ( ${}^5D_4 \rightarrow {}^7F_5$ ) at 544 nm, a medium intense blue emission ( ${}^5D_4 \rightarrow {}^7F_6$ ) at 488 nm, a weak orange emission ( ${}^5D_4 \rightarrow {}^7F_4$ ) at 589 nm, a weak red emission ( ${}^5D_4 \rightarrow {}^7F_3$ ) at 622 nm and a weak reddish-orange emission ( ${}^5D_4 \rightarrow {}^7F_4$ ) at 694 nm are observed at both the excitation wavelengths. Among these four emissions, the green emission band ( ${}^5D_4 \rightarrow {}^7F_5$ ) is a magnetic dipole transition satisfying the selection rule of  $\Delta J \pm 1$  (Ref. 27). Figures 7(a) and (b) represent the excitation and emission spectra of Eu<sup>3+</sup>: PVP polymer film, respectively. The excitation spectrum of Eu<sup>3+</sup>: PVP polymer film has also revealed a broad and intense excitation band in the region of 250 nm to 400 nm which is due to a combined effect of the charge transfer band of the carbonyl groups to Eu<sup>3+</sup> ions and the  ${}^7F_0 \rightarrow {}^5L_9$  and  ${}^7F_0 \rightarrow {}^5L_{10}$  transitions of Eu<sup>3+</sup> ion. Along with this, other low excitation bands such as ( ${}^7F_0 \rightarrow {}^5L_6$ ) at 396 nm, ( ${}^7F_0 \rightarrow {}^5D_3$ ) at 410 nm, ( ${}^7F_0 \rightarrow {}^5D_2$ ) at 461 nm and ( ${}^7F_0 \rightarrow {}^5D_1$ ) at 522 nm have also been observed<sup>28</sup>. Among these bands, prominent excitation bands at 352 nm and 396 nm have been used to record the emission spectra of Eu<sup>3+</sup>: PVP polymer film. Emission spectrum of Eu<sup>3+</sup>: PVP film shows emission bands because of high non-radioactive relaxations from the excited states of energy higher than  ${}^5D_0$  state. The intense emission bands in the range of 575-725 nm are assigned to the electronic transitions of ( ${}^3D_0 \rightarrow {}^7F_{J=1,2,3,4}$ ), and the transitions such as  ${}^5D_0 \rightarrow {}^7F_{2,4,6}$  transitions are

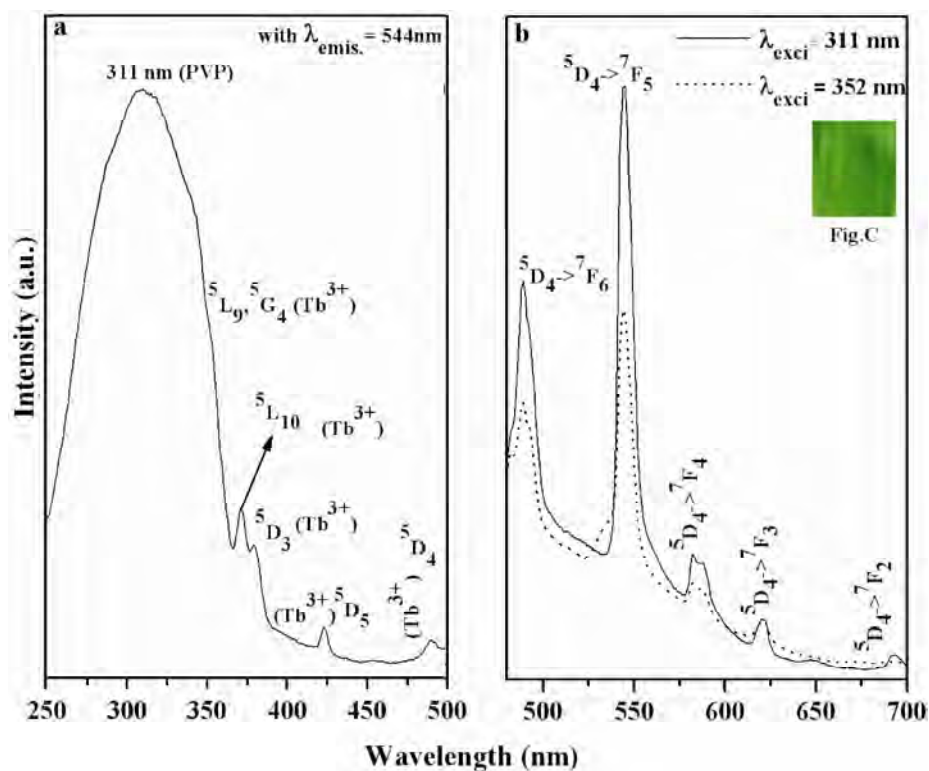


Fig. 6 — (a) Excitation and (b) Emission spectra of  $Tb^{3+}$ : PVP polymer film, (c) Green emission under an UV source from  $Tb^{3+}$ : PVP polymer film

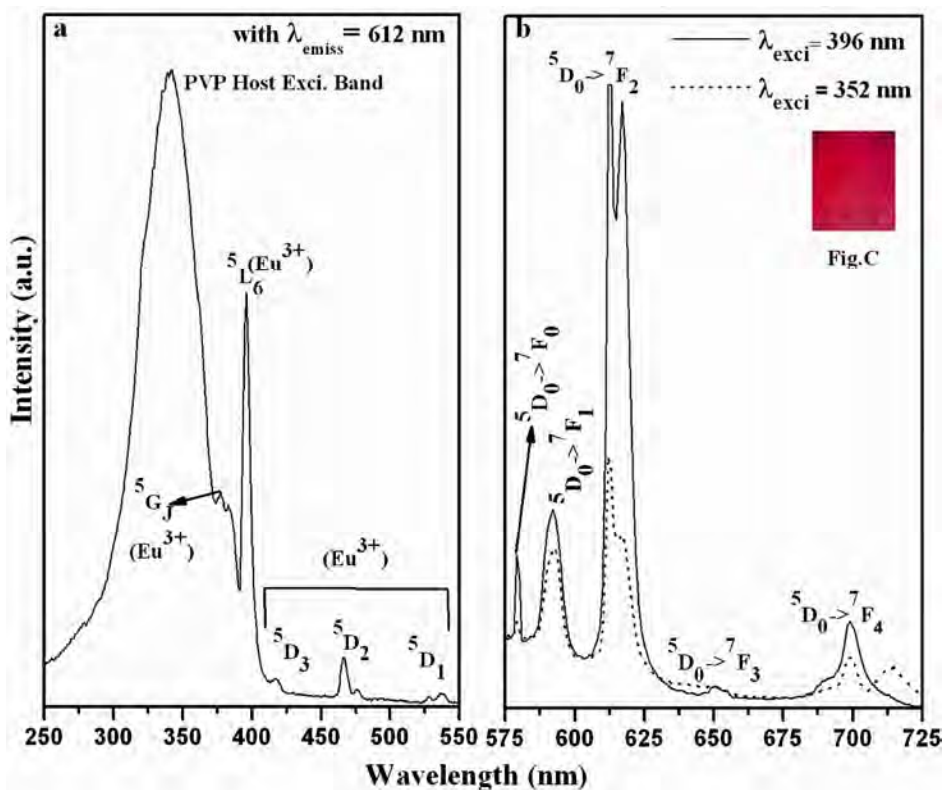


Fig. 7 — (a) Excitation and (b) Emission spectra of  $Eu^{3+}$ : PVP polymer film, (c) Red emission under an UV source from  $Eu^{3+}$ : PVP polymer film

electric dipole (ED) transitions. In particular, the red emission at 613 nm (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>) is considered to be hypersensitive transition that follows the selection rule of  $\Delta J = 2$  and hence demonstrates a very bright emission from Eu<sup>3+</sup>: PVP polymer film<sup>29</sup>. In site of Fig. 7 (b) displays a red emission from Eu<sup>3+</sup>: PVP polymer film under an UV source. Another transition (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>) with  $\Delta J = 1$  has been identified as a magnetic dipole transition (MD), which is a bright orange emission. It is well known that the host matrix environment around the Eu<sup>3+</sup> ions could significantly influence the emission intensity of the hypersensitive transition (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>). The intensities of the electric dipole transitions could be changing based on centre of symmetry variations due to change in the host environment around the luminescent rare earth ion. Conversely, the (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>) emission around 591 nm is allowed by MD consideration; therefore, it is relatively weak in intensity compared to that of the hypersensitive transition.

#### 4 Conclusions

We have successfully developed blue emission showing PVP host polymer film and green (Tb<sup>3+</sup>: PVP) and red (Eu<sup>3+</sup>: PVP) luminescent polymer films. Since dopant rare earth ions, have not modified structural properties of the host PVP polymer film, only for the host PVP film, XRD, FTIR, and Raman spectra have been measured and its structures and thermal (TG, DTA) properties have been analyzed in evaluating their structural and luminescence properties.

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