Indian Journal of Pure & Applied Physics
Vol. 52, September 2014, pp. 588-596

Energy transfer based photoluminescence spectra of Dy^{3+}, Sm^{3+}: PEO+PVP polymer films

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Received 26 August 2013; revised 15 July 2014; accepted 1 August 2014

Dy^{3+}, Sm^{3+} ions doped PEO+PVP polymer films and also a host PEO+PVP polymer films have successfully been synthesized by solution casting method. For the PEO+PVP film, its XRD, FTIR, Raman and TG-DTA profiles have been investigated in order to understand its structural and thermal properties. Dy^{3+} doped film has displayed a *blue* emission under an UV source. Photoluminescence spectra have been measured to study its optical properties. For observed *blue* emission at 480 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) of Dy^{3+} film, its decay curve has been measured in evaluating the lifetime of the blue emission. The Sm^{3+} polymer film has displayed an *orange* emission under an UV source. For this Sm^{3+} film, emission spectra have been measured to evaluate its optical properties. For the orange emission at 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) of Sm^{3+}, the transitions of Sm^{3+} are clearly explained in the form of an energy level diagram. In the co-doped system, an energy transfer between the dopant ions in the host polymer matrix has been explained. These results suggest these films as *blue* and *orange* luminescent optical materials.

Keywords: Dy^{3+}, Sm^{3+}: PEO+PVP polymer films, Analysis, Photoluminescence spectra, Energy transfer

1 Introduction

Polymer blending is an important method towards the development of new polymeric materials for newer potential materials with a wide variety of applications[1]. Polyethylene oxide (PEO) has been an interesting base material because of its high thermal stability and a semi-crystalline natured film exhibiting both amorphous and crystalline phases at the room temperature. Polyvinylpyrrolidone (PVP) has been chosen as the second polymer component for preparing polymer blend with PEO. It has been known that PVP encourages faster ionic mobility compared with other semi-crystalline polymers with a low scattering loss, which makes it an ideal polymer for blending. Due to the presence of carbonyl group(C=O) in the side chains of PVP, it forms a variety of complexes with different inorganic salts in their further development as luminescent materials in order to enable those with applications in optoelectronic industry and signal transmission[2-4]. The luminescence of rare earth complexes as light conversion molecular devices (LCMD) and these could constitute a class of new materials with potential applications possessing commercial importance towards the development of luminescent polymer films[5-7].

2 Experimental Details

2.1 Preparation of polymer films

Blended polymer films were prepared using solution casting method. The chemicals used were polyethylene oxide (PEO) (MW=6×10^5) and polyvinylpyrrolidone (PVP) (MW=13×10^5) from Sigma-Aldrich Company. Films of (thickness ~100 μm) PEO+PVP blended polymers doped with $DyCl_3$ and $SmCl_3$ were obtained in weight percentage ratio of (0.45:0.45:0.1) using triple distilled water as the solvent. PEO, PVP and these rare earth chlorides were dissolved in triple distilled water and stirred at room temperature (~30°C) for 10-12 h to get a homogeneous mixture. The solution was cast onto polypropylene dishes and those solutions were allowed to get evaporated slowly at the room temperature. The final product was dried upon warming up to remove all traces of the solvent. The dried composite polymer films were collected from the polypropylene dishes and stored in a dry vacuum box.

2.2 Measurements

XRD spectra of PEO+PVP polymer blends were measured on SEIFERT 303 TT X-ray diffractometer with CuK_α (1.5405 Å), and it was operated at 40 kV voltage and 50 mA anode current.TG-DTA measurements on the Dy^{3+} and Sm^{3+}: PEO+PVP polymer blended films were carried out on a Thermo-gravimetric analysis and differential scanning calorimetry, Model:-SDTQ600TA Instrument (specimens were scanned in the nitrogen atmosphere from 30-60° at heating rate of 10°C/min) from room temperature to 800°C. FT-IR spectra of RE^{3+}: PEO+PVP were carried out on EO-SXB IR spectrometer in the range 400-4000 cm^{-1}. Raman spectra of RE^{3+}: PEO+PVP were carried out at room temperature in the range 100-2000 cm^{-1} using Horiba Jobin Yvon, Lab Ram HR-800 Confocal Raman Spectrometer, which is having Nd: YAG laser source (1064 nm). The photoluminescence (excitation and emission) spectra of RE^{3+}: PEO+PVP films were recorded on Spex Fluorolog-3 (Model-II) Visible Fluorescence Spectrometer with Xe-arc lamp of 150 W power as an excitation source for a study state emission spectrum measurement on this system while measuring the lifetime of the observed emission transition, the decay curves were plotted to evaluate the lifetimes by attaching a phosphorimeter to the main system with a computer controller and with an attachment of Xe-flash lamp.

3 Results and Discussion

3.1 XRD analysis

The measured XRD profiles of the films are shown in Fig. 1 PEO+PVP polymer blended films exhibit crystalline peaks of PEO, one peak with a maximum intensity at 19.2° (1 2 0), another intense peak at 23.6° (1 1 2) and relatively less intense peak at 27.1°. For the PVP as such there exists no characteristic XRD peak; however for the blended PVP with PEO there exists a small peak at 13°, which suggests its amorphous nature due to addition of PVP. The characteristics peaks of pure PEO+PVP complex show variation in intensity suggesting that the ordering of the PEO polymer crystallinity is disturbed due to the coordination interactions between the RE ions and etheric oxygen. These observations confirm that the present polymer blend systems are possessing both crystalline and amorphous nature. However, with the addition of small amounts of RE ions like dysprosium and samarium to the blended films, thus those could show semi-crystalline nature[8,9].

3.2 Thermal analysis

Figure 2 shows the profiles of TG/DTA of polymer films, with an occurrence of decomposition at 46°C thus revealing a weight loss of 8% and it could be attributed to the presence of the moisture at the time of loading the samples. The film starts a complete decomposition at 330°C, which indicates the film is stable up to 330°C. The DTA traces show an exothermic peaks at 83°, 300°, 430°C, among them one at 300°C indicates the decomposition of PEO+PVP polymer blended film as is evidenced by a rapid weight loss observed in the TG curve. From this discussion, the thermal stability limit of the polymer blend[10] is about 330°C.

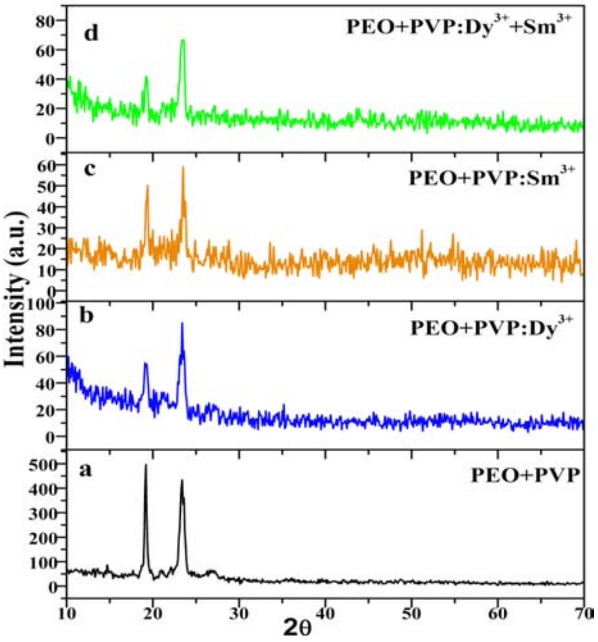


Fig. 1 — XRD profiles of (a) host PEO+PVP (b) Dy^{3+}:PEO+PVP (c) Sm^{3+}: PEO+PVP (d) Dy^{3+} & Sm^{3+} co-doped PEO+PVP polymer films

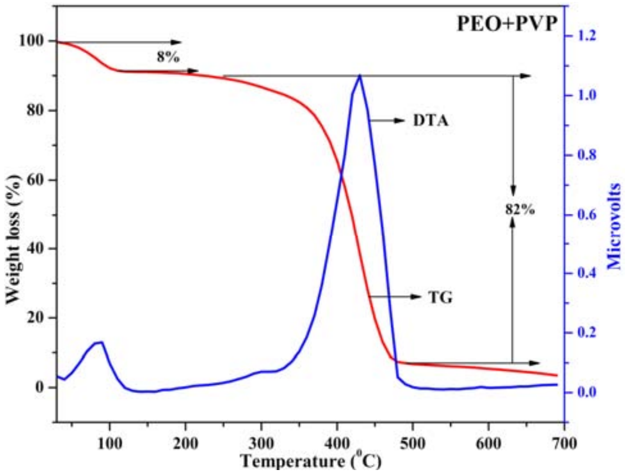


Fig. 2 — TG and DTA profiles of the host PEO+PVP polymer film

3.3 FT-IR analysis

Figure 3 shows the FTIR spectra of the host polymer film and RE doped and co-doped PEO+PVP films in the wavenumber range 400-4000 cm^{-1}. A broad band between 2975-2814 cm^{-1} and two narrow and weak bands at 2585 and 2518 cm^{-1} are the inherent bands of asymmetric (CH) stretching[11] of CH_2 of PEO. The characteristic PEO bands at 2378, 2238, 2161 and 1964 cm^{-1} are noticed. The band region in the range 1480-1410 cm^{-1} is for CH_2 scissoring mode of PEO with in this region. CH_2 bending mode at 1465 cm^{-1}, the CH_2 wagging doublet at 1367 cm^{-1} and 1341 cm^{-1}, the CH_2 twisting modes at 1282 and 1241 cm^{-1}. The band at 1489 cm^{-1} represents the C-H bending of CH_2, respectively which are characteristic of PEO. The relatively weak band at 1255 cm^{-1} is assigned to CH_2 symmetric twisting of PEO, and the vibrational bands at 1101 cm^{-1} because of C-O-C stretching[12,13] of PEO. These bands are more sensitive to macromolecular conformations and hence provide an evidence of crystalline nature due to the presence of PEO. The factors supporting this assignment and the two bands near 945 and 846 cm^{-1} are assigned to CH_2 rocking vibrations of methylene groups and these bands[14] are related to PEO.

The band region between 1346-1246 cm^{-1} and 1281 cm^{-1} indicates the –CH-wagging motion of PVP. The bands at 1242-1297 cm^{-1} correspond to CH_2 twisting or wagging of both PEO and PVP. The characteristic bands of PEO at 1146, 1275, 1352, 1466 cm^{-1} are observed and a vibrational band at 2904 cm^{-1} is due to aliphatic C-H stretching[15] of PVP. Another band at 1700-1610 cm^{-1} is due to symmetric and asymmetric of C=O stretching modes of PVP. The CH_2 wagging of PVP has been observed[16] at 1445 cm^{-1}.

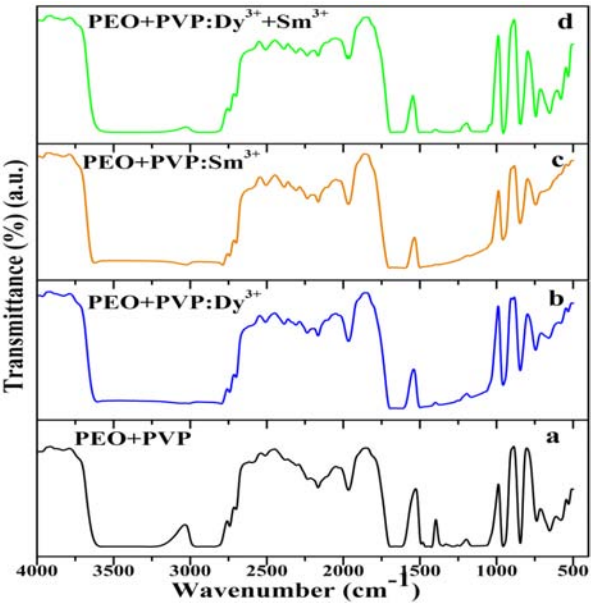


Fig. 3 — FTIR spectra of (a) host PEO+PVP (b) Dy^{3+}:PEO+PVP (c) Sm^{3+}: PEO+PVP and (d) Dy^{3+} and Sm^{3+} co-doped PEO+PVP polymer films

Due to the addition of dopant ions such as Dy^{3+} or Sm^{3+} to the host matrix, the width of the FTIR peak 1100 cm^{-1} becomes slightly broadened and its wave number is slightly decreased. This results from the coordination bonds between Dy^{3+} or Sm^{3+} ions and ether units (–O–) of PEO. In this case, wave number decreases as C–O single bond strength decreases. This leads to the interruption of crystallization so that the fraction of amorphous substance increases. Also a peak by anion appears near 1130 cm^{-1} which broadens this peak. The region 1160-1080 cm^{-1} is the location of C-O-C stretching, due to the interaction of rare earth cations with ether oxygen atoms in PEO. C–H bending of CH_2 in the both PEO and PVP at 1454 cm^{-1} is shifted,gradually, towards 1429 cm^{-1} with the presence of the dopants ions in the host blended film.

The intensity of the peaks in the range 1500-2500 cm^{-1} decreases when dopant is added to blended polymer film, this indicates that the ions are homogeneously distributed in the polymer. The band at 3318 cm^{-1} and a weak one at 657 cm^{-1} corresponds to the O–H stretching. Typically strong hydrogen bonded bands were found in respective region between 3200-3500 cm^{-1}. The bands in the range 3300-2800 cm^{-1} reflect the organization of PVP chains with in the film by hydrogen bonding involving N-H group. The peaks at 3402 cm^{-1} and 2932 cm^{-1} were found which are due to –OH and –CH stretching vibrations[17,18].

The band at 1355 cm^{-1} in pure blend has been shifted to 1360 cm^{-1} in the doped films. The vibrational band at 1069 cm^{-1} of pure blend is due to the C-O stretching of PEO which is shifted gradually to 1090 cm^{-1} when dopant ions are added to the host polymer blend film. Furthermore, C–H bending of CH_2 in both PEO and PVP at 1480 cm^{-1} has also been shifted to 1469 cm^{-1} because of the presence of these dopant ions in the matrix polymer films. A band at 1350 cm^{-1} of host matrix has also been found shifted to 1364 cm^{-1} due to addition of dopant ions in the matrix studied.

3.4 Raman Spectra analysis

Figure 4 shows the Raman spectra of host and RE (Dy^{3+} and Sm^{3+}) ions doped PEO+PVP polymer films. The bands pertaining to PEO in the measured region[19] are 1067, 1040, 932, 861, 829, 846, 535 and 1395 and 365 cm^{-1}. Three bands at 861 cm^{-1}, 829 cm^{-1}, 846 cm^{-1} are active modes of CH_2 rocking and CO stretching modes. The spectral band at 934 cm^{-1} is assigned to CO stretching mixed with CH_2 rocking vibrations[20] of PEO. The bands observed at 1340 cm^{-1} and 1367 cm^{-1} are found to be in good agreement with the earlier reports. In addition to these bands, a new band is noticed at 1343 cm^{-1} and 1445 cm^{-1} and 1464 cm^{-1} due to presence of PEO.

On adding rare earth ions into the PEO+PVP, the intensity of the band at 1063 cm^{-1} that arises due to C−O stretching and/or rocking modes of CH_2 vibrations, is found reduced due to the formation of complexation[21] of PEO+PVP. It has been observed that the intensity of the Raman bands that corresponds to the C-C stretching vibrations at 849 cm^{-1} and 904 cm^{-1} in the pure blended polymer decreases with an increase of rare earth ion content. The significant changes in the C-C vibrational band can be associated with the formation of ionic bond with less polarization. The bands at 1235 cm^{-1}, 1426 cm^{-1} and 1666 cm^{-1} are attributed to C-N stretching, C−H bending and C=O vibrations of PVP, respectively[22]. The intensity of the band at 1665 cm^{-1} attributed to PVP is also found to be diminished with addition of dopant. This variation in intensity might be due to strong interaction taking place between the dissociated salt and the blended polymer. It is well known that the incorporation of larger anion from the salt to the polymer matrix helps to improve semi-crystalline nature of the host polymer because of its role as plasticizer. The semi-crystalline nature has been confirmed by broadening of the Raman modes at 1445 cm^{-1} and 1366 cm^{-1} which are attributed to the mixture of C−H bending and O−H bending vibrations. This has been in good agreement with the XRD results. In Raman spectra of the blended polymer film, the most intense feature band around 936 cm^{-1}, which is associated with the symmetric stretching mode of the anion. This mode is very important and suitable for investigating the ionic association. This is thought to be associated with the formation of ion pairs. In case of PEO+PVP: $RECl_3$, only a single band at 1034 cm^{-1} is seen, which is associated with the presence of the free anions. In the doped systems, symmetric stretching of anion vibration is centered at 1046 cm^{-1}, is obtained. The broadening in Raman spectra is usually an indication of amorphous or semi-crystalline nature of the blended polymer[23]. The semi-crystalline nature of the polymer blend has also been confirmed by XRD analysis.

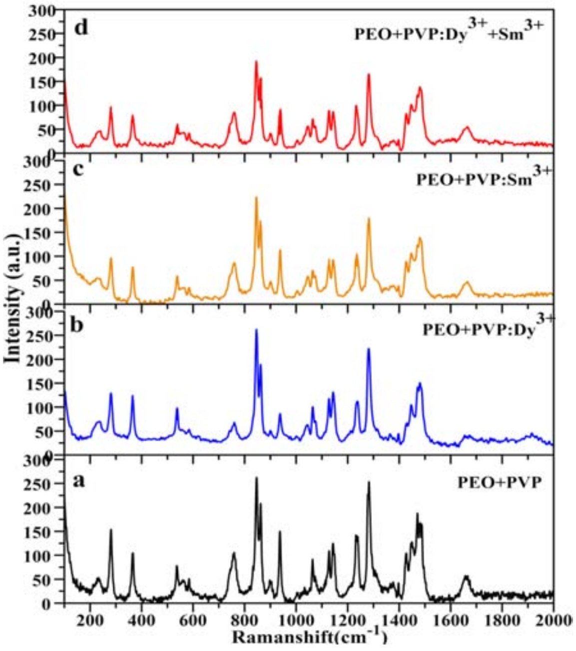


Fig. 4 — Raman spectra of (a) host PEO+PVP (b) Dy^{3+}:PEO+PVP (c) Sm^{3+}: PEO+PVP and (d) Dy^{3+} & Sm^{3+} co-doped PEO+PVP polymer films

3.5 Photoluminescence analysis

Figure 5 shows an emission spectrum of host PEO+PVP polymer film with an inset of an excitation spectrum. The excitation spectrum exhibits two excitation bands at 364 nm and 380 nm. The emission spectrum has been recorded with an excitation at 380 nm. The emission spectrum exhibits the two emissions at 419 nm and 443 nm. These emissions are confirmed as β and α transitions. The active centers of PVP are formed as carbonyl group of double bond and tertiary nitrogen atom (>N-C=O) and thus the charge transfer complexes are formed with the RE in the polymer films of PEO+PVP. This process is highly influenced by the transitional charges of the polymer[24,25].

The excitation spectrum of Dy^{3+}: PEO+PVP polymer film is shown in Fig. 6. The excitation for an

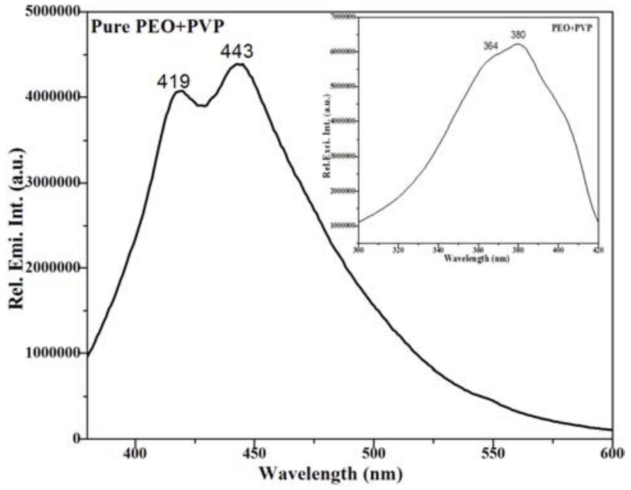


Fig. 5 — Emission spectrum of host PEO+PVP polymer film with excitation spectrum

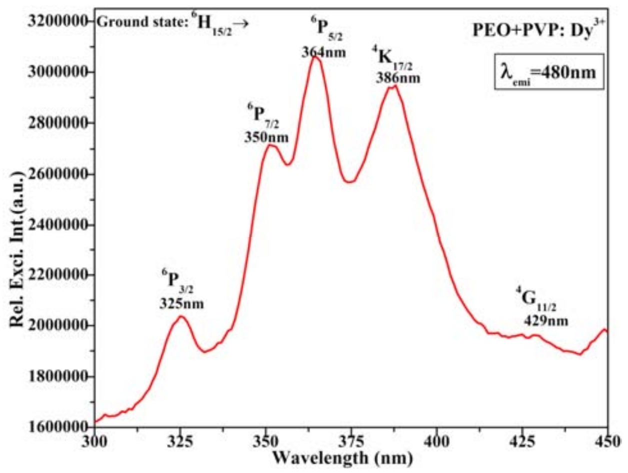


Fig. 6 — Excitation spectrum of Dy^{3+}:PEO+PVP polymer film

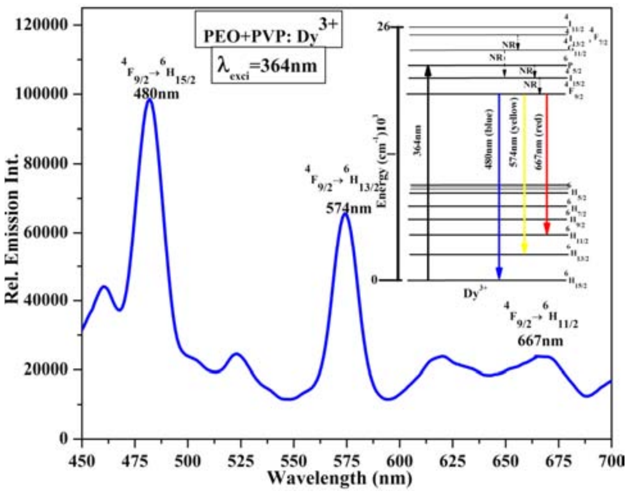


Fig. 7 — Emission spectrum of Dy^{3+}:PEO+PVP polymer film

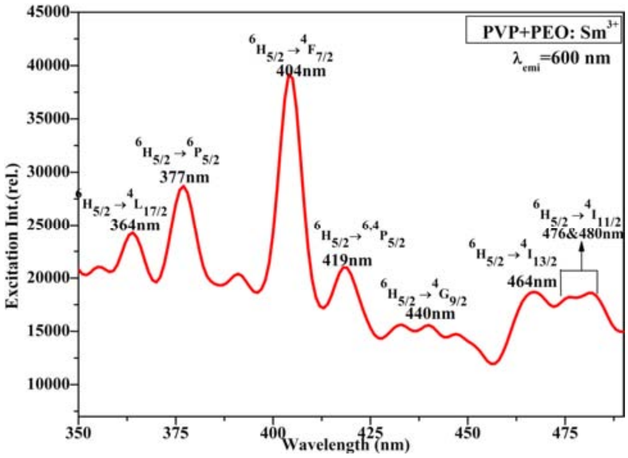


Fig. 8 — Excitation spectrum of Sm^{3+}:PEO+PVP polymer film

emission at 480 nm reveal excitation bands in the range 300-450 nm. The excitation bands at 325, 350, 364 and 386 nm have been assigned to the electronic transitions with the ground state $^6H_{15/2}$ to the higher excitation states ($^6P_{3/2}$ at 325nm, $^6P_{7/2}$ at 350 nm, $^6P_{5/2}$ at 364 nm, $^4K_{17/2}$ at 386 nm and $^4G_{11/2}$ at 429 nm) in the $4f^9$ configurations of Dy^{3+}. Among these transitions, $^6H_{15/2}\rightarrow{}^6P_{5/2}$ at 364 nm is an intense band and by using this, the emission spectrum has been measured as shown in Fig. 7, three emissions at 480 nm (blue), 574 nm (yellow) and 667 nm (red) which correspond to $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$ and $^4F_{9/2}\rightarrow{}^6H_{11/2}$, respectively. Of those, $^4F_{9/2}\rightarrow{}^6H_{15/2}$ is a magnetically allowed and the transition $^4F_{9/2}\rightarrow{}^6H_{13/2}$ is a forced electric dipole transition with $\Delta J=2$, which is strongly influenced by host environment of Dy^{3+} ions[26]. An energy level diagram of Dy^{3+}: PEO+PVP polymer film has been shown in inset of Fig. 7. The decay behaviour emission level of Dy^{3+}: PEO+PVP film strongly depends on the excitation band. Figure 10(a) shows a typical decay curve of Dy^{3+} emission at 480 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) upon excitation at 364 nm ($^6H_{15/2}\rightarrow{}^6P_{5/2}$). The luminescence decay of the transition at 480 nm of Dy^{3+}: PEO+PVP blended polymer film has been studied at the room temperature. The measured lifetime (τ_{meas}) for the ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) transition has been determined from the decay curve as shown in Fig. 10(a) and the lifetime[27] is found to be at 0.90 ms.

Figure 8 shows an excitation spectrum of 0.1 wt% Sm^{3+} doped PEO+PVP polymer film which was measured by monitoring an intense emission at 600nm. In the 350-480 nm wavelength range, seven obvious excitation bands are identified, which are assigned to the electronic transitions of $^6H_{5/2} \rightarrow {}^4L_{17/2}$ at 362 nm, $^6H_{5/2} \rightarrow {}^6P_{5/2}$ at 377 nm, $^6H_{5/2} \rightarrow {}^4F_{7/2}$ at 404 nm, $^6H_{5/2} \rightarrow (^6P, {}^4P)_{5/2}$ at 419 nm, $^6H_{5/2} \rightarrow {}^4G_{9/2}$ at 440nm, $^6H_{5/2} \rightarrow {}^4I_{13/2}$ at 464 nm and $^6H_{5/2} \rightarrow {}^4I_{11/2}$ at 476 and 480 nm, respectively. Sm^{3+} ions will exhibit several overlapped excitation bands from 350-480 nm wavelength due to its several closely spaced energy levels located at these wavelength. We know that RE ions exhibit sharp emission/excitation bands in optical materials, but the sharpness of these bands also depends on the host matrices. Some times, stark splitting may cause broadening of these observed bands. Only the prominent excitation band at 404 nm has been selected for the measurement of emission spectrum of Sm^{3+} ions doped polymer film[28]. Figure 9 shows the photoluminescence spectrum of Sm^{3+}: PEO+PVP polymer film at the room temperature. The fluorescence spectrum exhibits four emission bands at 564, 600, 645 and 705 nm which are assigned to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$, $^4G_{5/2} \rightarrow {}^6H_{11/2}$ transitions, respectively. Among these four transitions $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (600 nm) exhibits an intense orange emission with three more transitions, $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (564 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (645 nm) show moderate luminescence in the visible region and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (705 nm) in NIR region[29]. Figure 9 inserted figure shows the energy level scheme diagram for the reddish orange emission of Sm^{3+}: PEO+PVP polymer film. The measured life time (τ_{means}) for the ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) transition has been determined from the decay curve. Figure 10(b) shows decay curve for Sm^{3+} ion in a PEO+PVP blend which can be fitted to a second order exponential and life time is calculated to be 0.02 ms.

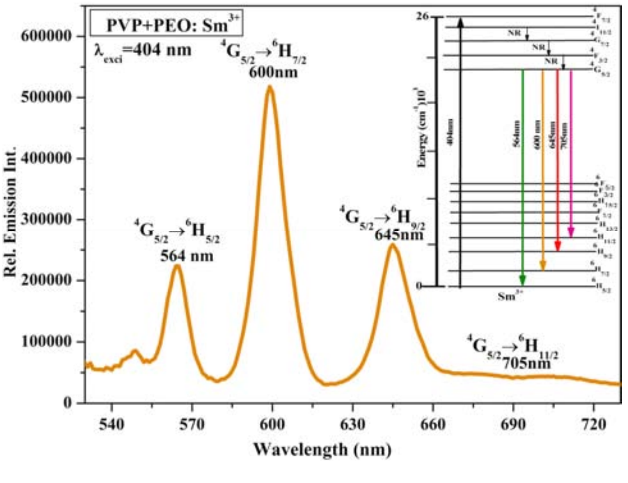
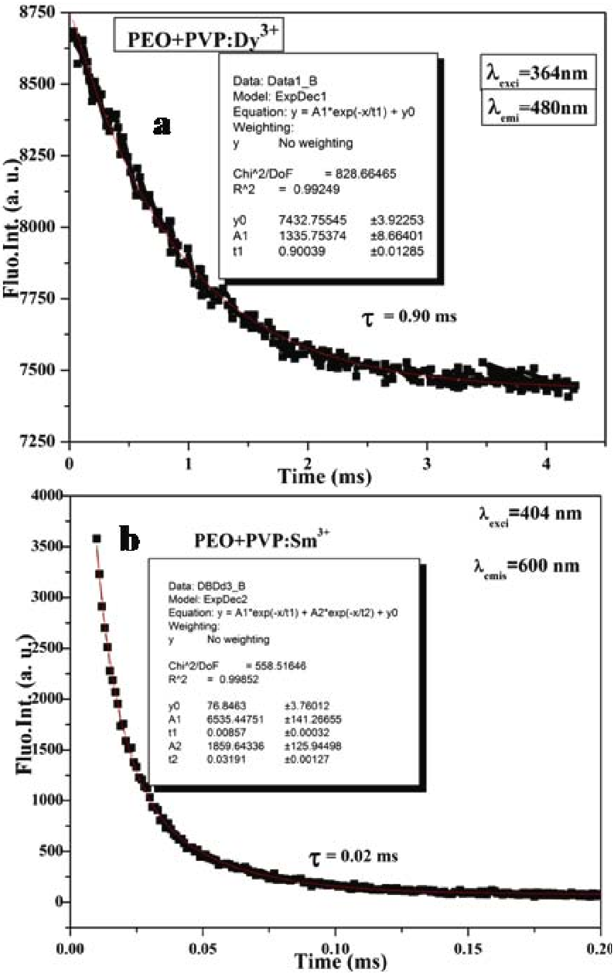


Fig. 9 — Emission spectrum of Sm^{3+}:PEO+PVP polymer film

3.6 Energy transfer from polymer to RE and Dy^{3+} to Sm^{3+} ions in co-doped system

In co-doped blended polymer film with dual rare earth ions (Dy^{3+}, Sm^{3+}), the emission intensities of the both ions such as 480 and 574 nm regarding Dy^{3+} and 600 and 645 nm regarding Sm^{3+} spectral peak intensities were increased at the excitation wavelength of 364 nm when compared to singly doped polymer film. The energy transfer phenomena involved in the present host matrix co-doped with dual rare earth ions are in three stages simultaneously. The emission spectra of PEO+PVP co-doped with Dy^{3+} and Sm^{3+} blended polymer film excited at 364 nm consists not only the peaks of Dy^{3+} at 480 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$), 574 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and 667 nm ($^4F_{9/2} \rightarrow {}^6H_{11/2}$), but also the peak of Sm^{3+} at 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) and 645 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) as shown in Fig. 11. By comparison Fig. 12(a) spectra overlap between emission spectrum of pure PEO+PVP blended polymer film and



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Data: Data1_B
Model: ExpDec1
Equation: y = A1*exp(-x/t1) + y0
Weighting:
y          No weighting

Chi^2/DoF        = 828.66465
R^2       =  0.99249

y0        7432.75545      ±3.92253
A1        1335.75374      ±8.66401
t1        0.90039         ±0.01285
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Data: DBDd3_B
Model: ExpDec2
Equation: y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Weighting:
y          No weighting

Chi^2/DoF        = 558.51646
R^2       =  0.99852

y0        76.8463         ±3.76012
A1        6535.44751      ±141.26655
t1        0.00857         ±0.00032
A2        1859.64336      ±125.94498
t2        0.03191         ±0.00127
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Fig. 10 — (a) Decay curves of blue (480 nm) (Dy^{3+} film) and (b) orange (600 nm) emissions with their lifetime (τ_m) values

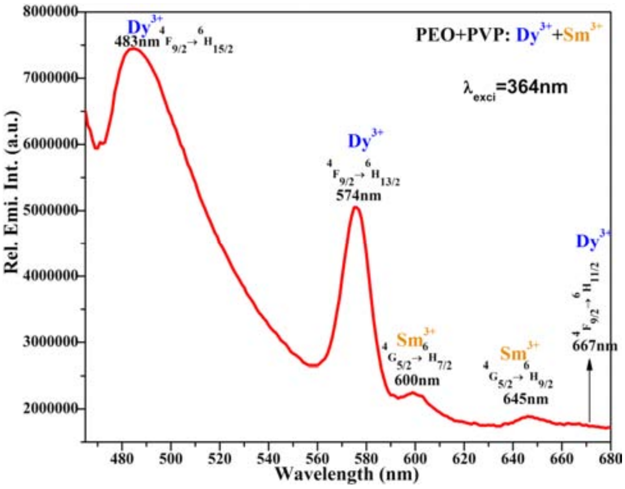

Fig. 11 — Emission spectrum of Dy^{3+} and Sm^{3+}:PEO+PVP polymer film with excitation at 364nm

excitation spectrum of Dy^{3+} ion has been found. These results indicate that energy transfer from pure polymer to Dy^{3+} occurs[30]. Here the pure blended polymer film acts as sensitizer and the dopant ion as activator. In the second case, the emission spectrum of the host matrix is overlapped with an excitation spectrum of Sm^{3+} and also coincides with the emission band of the host at 419 nm which becomes as an excitation band for Sm^{3+}, as shown in Fig. 12(b). The overlap has been well accepted to be favourable energy transfer takes place through the cross relaxation process from pure blended polymer film to Sm^{3+}. Finally, in third part of the energy transfer, the emission spectrum of Dy^{3+} and the excitation spectrum of Sm^{3+} both are overlapped and the emission at 480 nm from Dy^{3+} coincides with an excitation band of Sm^{3+} as shown in Fig. 12(c), which

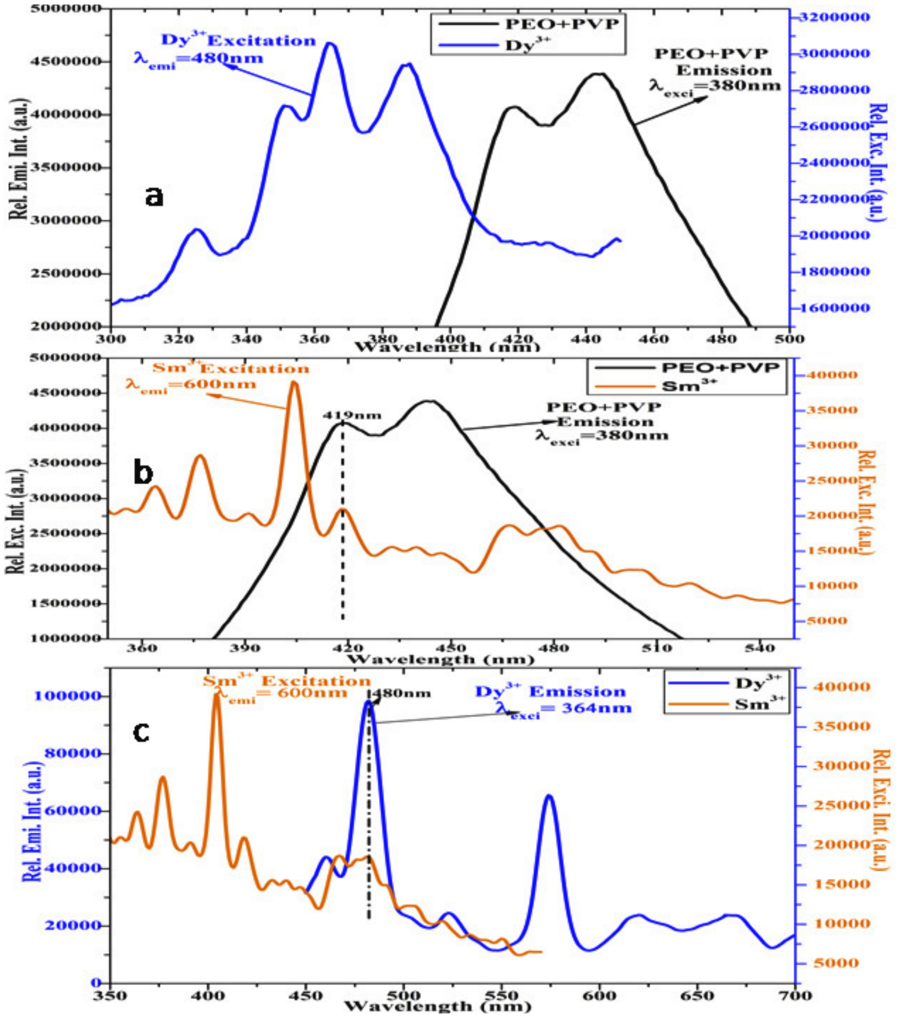

Fig. 12 — Over lapped specta of (a) emission of host PEO+PVP polymer with Dy^{3+} film excitation (b) emission of host PEO+PVP polymer with Sm^{3+} excitation and (c) emission of Dy^{3+}:PEO+PVP polyer with Sm^{3+}:PEO+PVP excitation

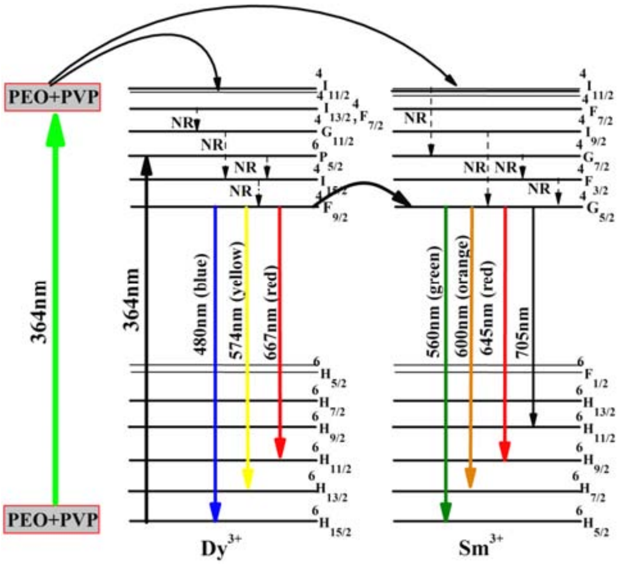

Fig. 13 — Energy level diagram giving energy transfer mechanism involved in dual rare earth ions of Dy^{3+} and Sm^{3+} in PEO+PVP polyer film

indicates an energy transfer from Dy^{3+} to Sm^{3+} through a cross relaxation process[31]. These results could be concluded that the energy transfer phenomena take place within the dual rare earth ions doped polymer film in three phases simultaneously with an excitation at 364 nm. Here the host polymer film is acting as efficient sensitizing agent to transfer the energy to the rare earth ions. And also the Dy^{3+} ion is also significantly acting as another sensitizer. The energy transition process from the host polymer film to Dy^{3+}, Sm^{3+} and Dy^{3+} to Sm^{3+} has been given in the form of an energy level diagram as shown in Fig. 13.

3.7 Decay analysis

The lifetime of the Dy^{3+} film emission at 480 nm with an excitation at 364 nm is shown in Fig. 14(a), which is a first order exponential decay curve with an evaluated lifetime is found to be 1.92 ms. Figure 14(b) shows the Sm^{3+} film emission lifetime at the emission with an excitation at 364 nm. The decay curve has been a second order exponential decay curve with a lifetime of 0.027 ms. This lifetime analysis explores that with both Dy^{3+} and Sm^{3+}ions as dopant ions, the blue emission lifetime has been higher than that of the individual ion doped polymer film life time. From these results, we could understand the existence of an effective energy transfer in the rare earth ions together doped in PEO+PVP blended polymer film[32-35].

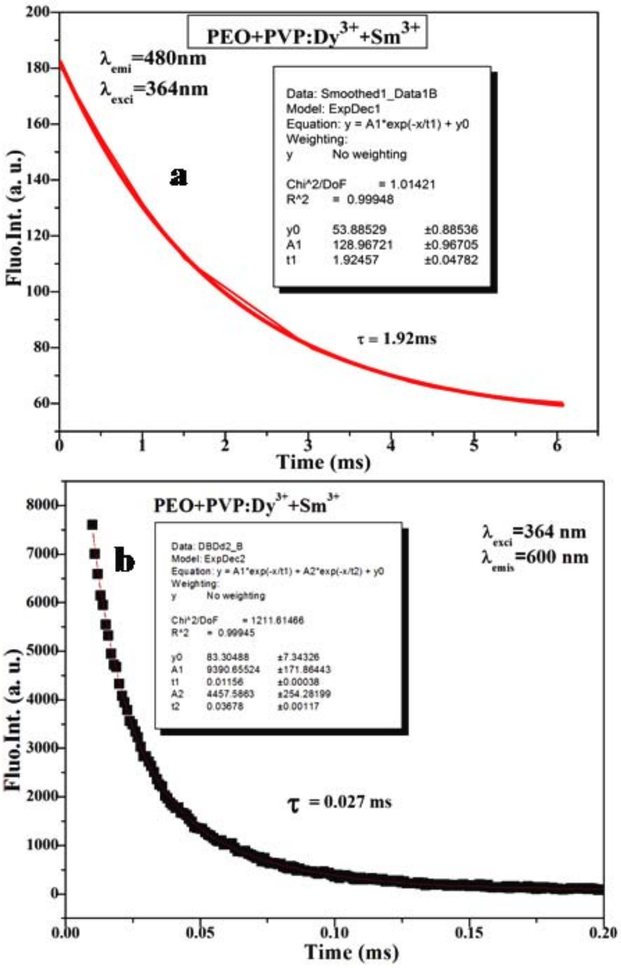

Fig. 14 — (a) Decay curves of blue at 480 nm (Dy^{3+} film) and (b) orange 600 nm (Sm^{3+} film) emissions with 364 nm

4 Conclusions

In summary, it is concluded that we have successfully synthesized transparent host PEO+PVP polymer films and also with dopant ions like Dy^{3+}, Sm^{3+} each separately and also those ions together by using solution casting method. The semi-crystalline nature of the bended polymer films has been confirmed from the XRD features. Thermal properties of these films have been investigated from the measurement of host matrix TG-DTA profiles. Raman analysis confirms the complex formation of the polymers due to the presence of these rare earth ions as the dopant ions. From emission spectrum of Dy^{3+}: PEO+PVP, it is observed that there exists a strong blue emission at 480 nm ($^7F_{9/2} \rightarrow {}^6H_{15/2}$) with an excitation at 364 nm ($^6H_{15/2} \rightarrow {}^6P_{5/2}$), and for this blue emission lifetime has also been measured. In the case of Sm^{3+} film, which has exhibited an orange emission at 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) with an excitation at 404 nm ($^6H_{5/2} \rightarrow {}^4F_{7/2}$) with a decay curve measurement for this emission level lifetime. Regarding the dual (Dy^{3+}, Sm^{3+}) ions together doped films, an energy transfer process has taken place from the host polymer matrix to the dopant dual ions and also an additional energy transfer from Dy^{3+} to Sm^{3+} ion towards the enhancement of blue emission intensity. These results, therefore suggest potentiality of these films, as useful optical materials for their use as blue and orange colours luminescent materials.

Acknowledgement

One of us (KNK), would like to thank the University Grants Commission (UGC), New Delhi, for awarding him with a project fellowship from the UGC-SAP-CAS programme (2009-2014) that has been sanctioned to the Department of Physics, Sri Venkateswara University, Tirupati.

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