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Research Article

Enhanced Photoluminescence of Mn^{2+} + Tb^{3+} Ions Doped PEO+PVP Blended Polymer Films

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Polymer blended films of PEO+PVP and singly doped and co-doped with Mn^{2+} and Tb^{3+} ions have been synthesized by solution casting method. Structural, thermal and optical properties of these films have been carried out. Thermal stability of these films has been investigated based on the measurement of TG-DTA profiles. Raman analysis demonstrates the complex formation of the polymer with the dopant ions. The optical absoption spectra of Mn^{2+} and Tb^{3+} seperately doped polymers exhibits characteristic bands in octahedral symmetry. From the emission spectrum, two emission bands at 510nm (green) and 614nm (red) are attributed to the $^4T_1 \rightarrow {}^6A_1$, and $^4A_1 \rightarrow {}^6A_1$ transition of Mn^{2+}:PEO+PVP polymer films under 370nm excitation. In Tb^{3+} doped PEO+PVP polymer samples exhibit green emission at 546 nm (green) due to a transition of ($^5D_4 \rightarrow {}^7F_5$) under 370nm excitation. The enhanced *red* emission at 614nm of Mn^{2+} ions is attributed to an effective energy transfer of $Tb^{3+} \rightarrow Mn^{2+}$ ions in the co-doped blended polymer film, which has been evidenced from the measurement of luminescence spectra and emission decay dynamics. These polymeric materials are suggested as bright visible colour luminescent materials.

Key Words: Polymer Films; Energy Transfer Emission

1. Introduction

Light emitting polymeric materials, mainly at room temperature, have great importance not only in the scientific research, but also in the optoelectronic industry (Da Silva *et al.,* 2013). Doping polymers with transition metal halides are considered to be dependent on the chemical nature of the dopants also the way in which those ions could interact with the host matrices. Blended polymer films involving poly (ethyleneoxide) (PEO) and Poly (vinylpyrrolydone) (PVP) have been studied since they enable PEO or PVP block to form coordinative structures with the transition metal salts to evaluate their structural, thermal and optical properties. Polyethylene oxide is a relatively simple structure of which allows semi-crystallization even though it is predominantly atactic in configuration and such polymer optical materials have widely been in use in variety of uses. It is known that PVP is one of the attractive polymers for obtaining the different polymer composites due to the strong affinity of the pyridine group to metals and its ability to undergo hydrogen bonding with polar species (Angesh Chandra *et al.,* 2009).

The blended polymer films are more versatile materials since they can be doped with rare-earth or transition metal ions. Some conjugated polymers can be strongly modified by varying the molecular surroundings as well as dopant and co-dopant concentrations, and these polymeric materials exhibit the predominant optical characteristics. These polymers which have been used to develop a new chemosensory system, amplifiers, fiber and wave guides (Binnemans 2009). The co-doped polymers have showed significant sensitivity enhancements

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(amplification) over single doped polymers. The transition metal (TM) coordinated complexes in polymer hosts are used for numerous practical applications. The fluorescence efficiency of TM complexes which is an important parameter for their use as a photonic device may be improved by variety of methods. Any effort to increase the efficiency by increasing the TM concentration, does not succeed as at higher concentration aggregation of ions takes place and the aggregates acts quenching centres (Gagandeep Kaur *et al.* 2012). Therefore another strategy to enhance the luminescence efficiency of TM coordinated complex through the use of addition of secondary RE dopant is being tried. The fluorescence of the metallic polymeric complex by co-doping with RE ions is significantly enhanced by energy transfer from the rare earth ion to transition metal ion. In co-doped polymeric materials, energy transfer from one ion (sensitizer) to another ion (activator) may occur, in principle, in whole or partly non-radiative and /or radiative processes. Such energy transfer processes have been attracting a significant attention for its practical utility in optical devices, especially $Ce^{3+} \rightarrow Tb^{3+}$, $Ce^{3+} \rightarrow Mn^{2+}$, $Eu^{2+} \rightarrow Mn^{2+}$ and $Pr^{3+} \rightarrow Mn^{2+}$ (Yongchao Jia *et al.* 2013). The emission bands are located in the range from 360nm to 660nm for Tb^{3+} ion, while Mn^{2+} emission bands depending on the surroundings of host, are in the region from 460nm to 700nm. Although the main emission energy of Tb^{3+}ion is lower than that of Mn^{2+} ions in some host, the $^5D_3$ levels of Tb^{3+} ion are higher than the $^4T_1(^4G)$ level of the Mn^{2+} ion. And due to the forbidden $^4T_1$-$^6A_1$ transition of Mn^{2+}, the fluorescence intensity of Mn^{2+} singly doped materials is low under UV excitation. Regarding this information about both the rare earth and transition metal ions such as Mn^{2+} and Tb^{3+} ions, Tb^{3+} represents a suitable sensitizer for photoemission from Mn^{2+}, and has therefore been considered for this purpose on several occasions (Hongpeng You *et. al.* 2008). In the present study, we have studied an energy transfer based emission from Tb^{3+} to Mn^{2+}ions in the blended polymer films.

2. Experimental Studies

Highly transparent blended polymer films were prepared using a solvent, by using a solution casting method. Initially polyethylene oxide (PEO) (MW = 6 x 10^5) and polyvinylpyrrolidone (PVP) (MW = 13 x 10^5) were obtained from Sigma-Aldrich. Films of (thickness ~100μm) of PEO+PVP blended polymers doped with transition metal ion such as manganese nitrate and rare earth ion such as terbium nitrate. The precursor materials that are PEO, PVP and $Tb^{3+,}$ Mn^{2+} contained salts were taken in weight percent ratio (0.45:0.45:0.1 wt %), and in co-doped system the precursor materials were taken in the weight percentage ratio (0.40:0.40:0.1:0.1wt %) the triple distilled water taken as solvent. PEO, PVP and dopant salts were dissolved in triple distilled water and stirred at room temperature (~30°C) for 10-12 h to get proper homogeneity. The solution was cast onto polypropylene dishes and allowed to evaporate slowly at room temperature. The dried composite polymer films were obtained from the polypropylene dishes and analyzed.

The XRD spectra of Tb^{3+} & Mn^{2+}: PEO+PVP polymer blended films were measured on SEIFERT 303 TT X-ray diffractometer with CuK_α (1.5405 A^0), and it was operated at 40 KV voltage and 50mA anode current. The TG-DTA measurement for the PEO+PVP polymer blended films by using Thermo-gravimetric analysis and differential scanning calorimetry, Model: - SDTQ600TA Instrument (specimens were scanned in the nitrogen atmosphere from 30-60° at heating rate of 10^0C/min) from room temperature to 800°C. The absorption spectra of Tb^{3+} & Mn^{2+}: PEO+PVP films were measured on a Perkin-Elmer Absorption Spectrophotometer in the range of 250-800 nm. Raman spectra of Tb^{3+}&Mn^{2+}: PEO+PVP were carried out at room temperature in the range of 800 to 1800 cm^{-1} using LabRam HR 800 confocal Raman Spectrometer which is having Nd: YAG laser source (532nm). The Photoluminescence (excitation and emission) spectra of Tb^{3+}&Mn^{2+}: PEO+PVP films were recorded on Perkinelmer fluorimeter with xenon arc lamp of 150W power as an excitation source for a study state emission spectrum measurement on this system while measuring the life time of the observed emission transitions, results of those emission bands 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(a). 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°. No such well defined sharp peaks attributable to PVP, instead a broad peak has been observed at 13°, which suggests the amorphous nature of PVP. The charactacteistic 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 transition metal ions and etheric oxygens. These observations confirm that the present polymer blend systems are possessing both crystalline and amorphous nature. However, with the addition of small amounts of $Tb^{3+}$and Mn^{2+} ions to the blended polymer, thus those could show the amorphous nature (Kiran Kumar *et al.*, 2011; Arup Dey *et al.*, 2011).

3.2. Thermal Analysis

Fig. 1(b) shows TG/DTA profile of pure PEO+PVP blended polymer film, it is observed that the initial decomposition takes place at 46°C with a weight loss of 8% in pure PEO+PVP polymer film due to the presence of moisture at the time of loading the sample. The further decomposition is observed at 330°C, which indicates the film is stable up to 330°C for pure PEO+PVP. The DTA profile shows the endothermic peak at 84° which is corresponds to glass transition temperature of the pure polymer film. And also the exothermic peaks at 330°C, 409°C and 510°C for pure PEO+PVP polymer films. And the peak at 330°C indicates the decomposition of PEO+PVP polymer film as evidenced by a rapid weight loss observed in the TG curves (Sivaiah *et al.*, 2010).

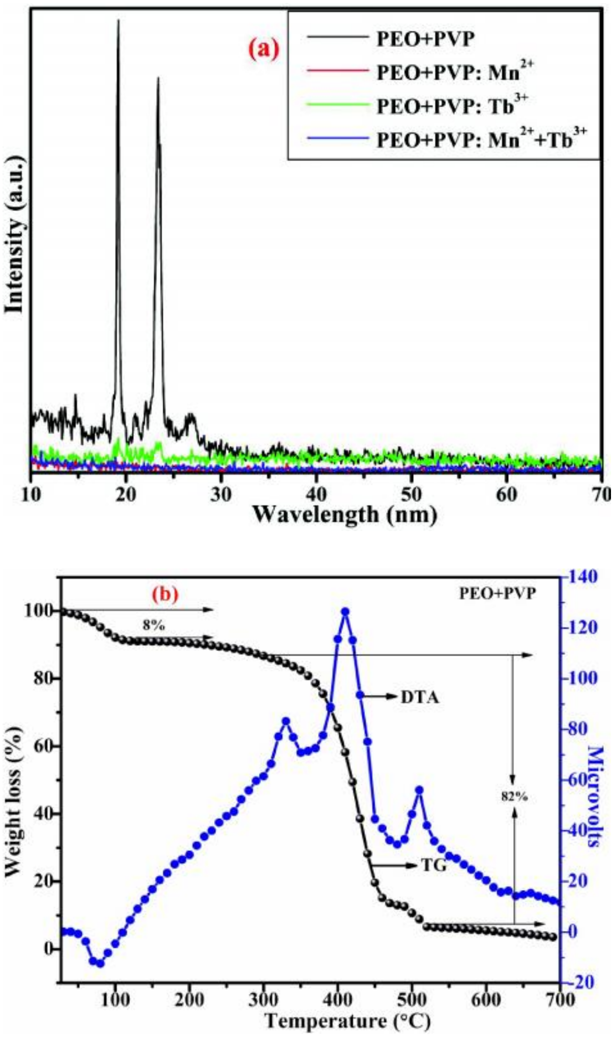

Fig. 1: (a) XRD profiles of pure PEO+PVP, Mn^{2+}(0.1): PEO+PVP, Tb^{3+}(0.1): PEO+PVP and Mn^{2+}(0.1)+ Tb^{3+}(0.1): PEO+PVP polymer films. (b) TG/DTA plots for pure PEO+PVP blended polymer film

3.3. Raman Spectra Analysis

Fig. 2(a) shows the Raman spectra of pure, Mn^{2+}, Tb^{3+} and also Mn^{2+}+Tb^{3+} doped PEO+PVP polymer films. The Raman bands at 1234 cm^{-1}, 1425 cm^{-1} and 1666 cm^{-1} are attributed to C-N stretching, C-H bending and C=O vibrations of PVP respectively (Ramya *et al.* 2007). The bands pertaining to PEO in the measured region are 1067 cm^{-1}, 1040 cm^{-1}, 936 cm^{-1}, 862 cm^{-1}, 829 cm^{-1}, 846 cm^{-1} and 1395 cm^{-1} (Christopher *et al.*, 1999). Three bands at 862 cm^{-1}, 846 cm^{-1} are active modes of CH_2 rocking and

CO stretching modes. The spectral band at 932 cm^{-1} is assigned to CO stretching mixed with CH_2 rocking vibrations of PEO (Hiroatsu Matsuura *et al.*1986). The bands observed at 1340 cm^{-1} and 1367 cm^{-1} are in good agreement with the earlier reports (Silva *et al.* 2001). 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 dopant salt to the PEO+PVP, the intensity of band at 1067 cm^{-1} due to C-O stretching and /or rocking modes of CH_2 vibrations is drastically reduced with the addition of rare earth or transition metal salts forming a complexation of PEO+PVP (Yogesh Kumar *et al.* 2011). It has been observed that the intensity of the Raman band corresponding to C-C stretching vibration at 846cm^{-1} and 862cm^{-1} in the pure blended polymer decreases with addition of salt, when the salt concentration increased (in co-doped sample) these band shifts to a higher wavenumber and becomes asymmetric, which is shown in Fig. 2(b) which indicates that the formation of ion pairs. The significant changes in the C-C vibrational band can be associated with the formation of ionic bond with less polarization. The intensity of the band at 1666cm^{-1} attributed to PVP is also found to be diminished in co-doped system. 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 amorphous nature of the host polymer because of its role as plasticizer. The amorphous nature found in co-doping with Tb^{3+} & Mn^{2+} ions has been confirmed by broadening of the Raman modes at 1445cm^{-1} and 1367cm^{-1} which have been attributed to mixture of C-H bending and O-H bending vibrations. This has been in good agreement with the XRD results. In Fig. 2(c), the spectra of the blended polymer film, the most intense feature band around 936cm^{-1}, which is associated with the symmetric stretching mode of the anion. This mode is very important and suitable for investigating ionic association. The intensity of the Raman band 936cm^{-1} decreases and increasing the broadening, with addition of salt. When the salt concentration is increased more (in co-doped sample), the main band shifts to a higher wavenumber and becomes asymmetric, this is shown in Fig. 2(c). This is thought to be associated with the formation of ion pairs. In case of PEO+PVP:Tb^{3+}, only a single band at 1040cm^{-1} is seen, which is associated with the presence of the free anion. The broadening in Raman Spectra is usually an indication of amorphous nature of the blended polymer (Hema M *et. al.* 2010). The amorphous nature of the polymer blend doped with Tb^{3+} and Mn^{2+}has also been confirmed by XRD analysis.

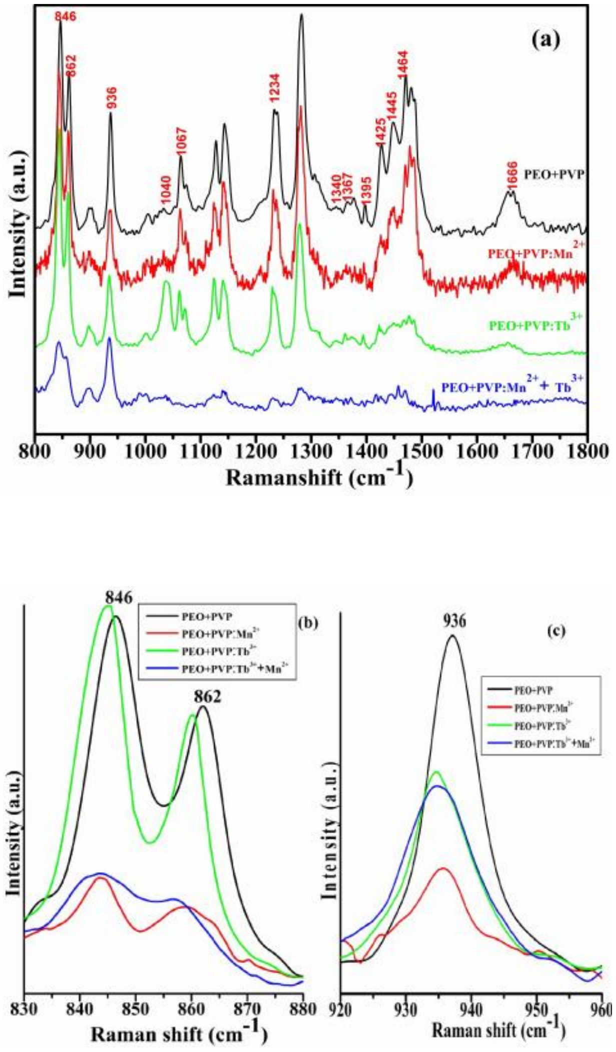

Fig. 2: **Raman Spectra of (a) PEO+PVP, Mn^{2+}(0.1): PEO+PVP, Tb^{3+}(0.1): PEO+PVP and Mn^{2+}(0.1)+ Tb^{3+}(0.1): PEO+PVP polymer films, (b) Raman data in the region of 830-880cm^{-1} and (c) Raman data in the region of 920-960cm^{-1}**

3.4. UV-VIS Characterization

The optical absorption spectrum of Mn^{2+}: PEO+PVP blended polymer films in the wavelength region 300-600nm are shown in Fig. 3(a). The Mn^{2+} ions belong to d^5 configuration, which is having the ground state of $^6S_{5/2}$. These ions occurring in polymeric material in either octahedral or tetrahedral environment. The spectrum exhibits three weak bands centred at 317nm, 379nm and 539nm. These absorption bands are assigned with electronic transition $^6A_{1g}(S) \rightarrow {}^4E_g(D)$ at 317nm, $^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$ at 379nm and $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ at 539nm. These bands are characteristic of the Mn^{2+} ions in the octahedral symmetry. A small absorption band cantered at 480nm. This observed spectrum indicates that the manganese ion seem to retard or interfere with the UV bands while the visible band at about 480nm ($^5E_g \rightarrow {}^5T_{2g}$ (D)) is due to Mn^{3+} ions. It is generally accepted that manganese ions exist in blended polymer in two different ionic states, namely, Mn^{2+} ions with very weak bands, one is in the UV, another one is in visible bands and Mn^{3+} ions with a single spin allowed transition showing a nearly symmetrical band at about 470-520nm, Which are also agreements with the reported values.

Absorption spectra of Tb^{3+}: PEO+PVP blended polymer films are shown in Fig. 3(b), in Tb^{3+} doped polymer film, two weaker absorption bands are observed 377nm, 483nm respectively and these bands have appropriately been assigned to the electronic transitions such as ($^7F_6 \rightarrow {}^5G_6$) at 377 nm and ($^7F_6 \rightarrow {}^5D_4$) 483 nm respectively which are also agreement with the reported values (Seeta Rama Raju *et al.*, 2006; Duan C J *et al.*, 2009).

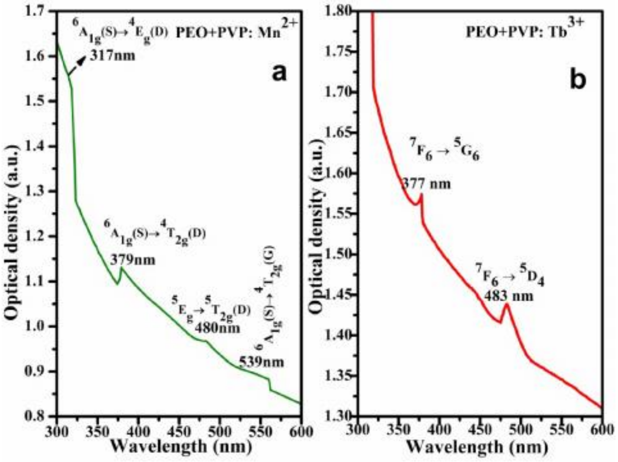

Fig. 3: Optical absorption spectra of the (a) Mn^{2+}(0.1): PEO+PVP. (b) Tb^{3+}(0.1): PEO+PVP polymer films

3.5. Luminescence Analysis

Mn^{2+} doped PEO+PVP blended polymer film excitation spectrum of emission recorded in the 350-500nm wavelength region was inserted shown in Fig. 4(a). It consists of two excitation peaks. The broad peak is likely associated with ligand field transitions of higher energy in Mn^{2+} ions. The larger intensity of the band with respect to the other d-d bands of lower energy can be a consequence of increased mixing with ligand metal charge transfer states. The position of the intense excitation line peaking at 373 nm which corresponds to the $^6A_{1g}$ (^6S) $\rightarrow {}^4E_g$ (^4D) transition and one another peak is obtained at 443nm corresponding electronic transition of $^6A_{1g}$ (^6S) $\rightarrow$ $^4T_2$ (^4G) was found to be temperature independent because it does not depend on the ligand field strength. It consists the several ligand field transitions from the ground level $^6A_1$ (S) to the excited sublevels with in the d^5 electronic configuration of Mn^{2+}ions (Vijay Singh *et al.* 2008). Fig. 4(b) shows emission spectra of PEO+PVP: Mn^{2+} (λ_{exc} = 373nm). Since the transitions of Mn^{2+} are d $\rightarrow$ d spin and parity spin and parity forbidden, the emission intensities are very weak under UV excitation. Two intense broad emission bands are observed at 510nm (green emission) due to the $^4T_1 \rightarrow {}^6A_1$, at 614nm (red emission) can be attributed to the $^4A_1 \rightarrow {}^6A_1$ transition of Mn^{2+} ions. The green emission in the Mn^{2+}: PEO+PVP blended polymer film may be explained as

$$Mn^{2+} + h\nu \rightarrow Mn^{3+} + e^-$$

where '$h\nu$' is the energy needed in causing the photo excitation of Mn^{2+} in polymer film. The free electrons in the ground state are excited to the localized states within the forbidden band. From these states there are non radiative decay to $^4T_1$ (G) state and from there a radiative transition decay to the ground state ($^6A_1$). Therefore the green emission line at 510nm in

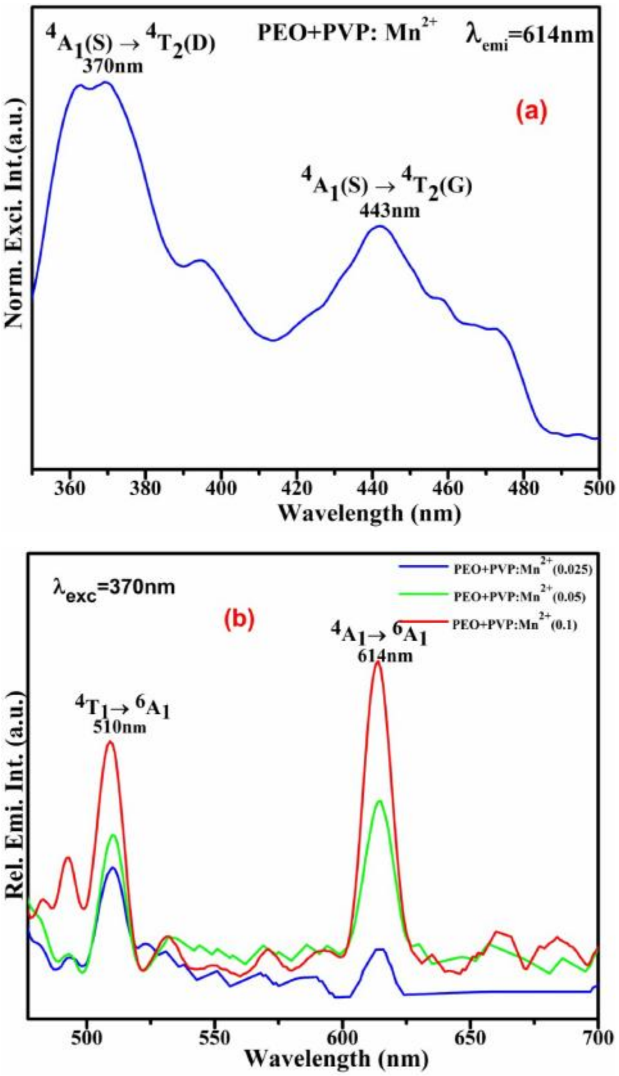

Fig. 4: (a) Excitation & (b) Emission spectrum of Mn^{2+} doped PEO+PVP blended polymer film

PEO+PVP: Mn^{2+} blended polymer film is assigned to a electronic transition from the upper $^4T_{1g}$ to ground $^6A_1$ state of Mn^{2+} ion (Sun kyun Lee *et al.* 2007). It is indicated that the emission intensity of Mn^{2+} is enhanced with the increase of the Mn^{2+} ion concentration and reaches the maximum at 0.1 (wt%) of Mn^{2+} salt (Fuhai Su *et al.* 2001; Yibing Fu *et al.* 2007; Quan Li *et al.* 2006). Fluorescence spectroscopy is a technique for evaluating the physical and chemical properties of a substance by analyzing the intensity and characteristics of light emitted in the form of fluorescence. Inserted Fig. 5(a) shows the excitation spectrum of the Tb^{3+} doped PEO+PVP blended polymer film which has been obtained by monitoring a *green* emission at 546nm. There are several excitation bands between 330nm and 390nm due to f-f transitions of Tb^{3+}, which are assigned to the electronic transitions $^7F_6 \rightarrow {}^5L_6$ at 340nm, $^7F_6 \rightarrow {}^5D_2$ at 353nm, $^7F_6 \rightarrow {}^5L_{10}$ at 370nm and $^7F_6 \rightarrow {}^5G_6$ at 379nm. Among these transitions $^7F_6 \rightarrow {}^5L_{10}$ at 370nm transition has the maximum intensity than other transitions. By using this $^7F_6 \rightarrow {}^5L_{10}$ transition at 370nm, the emission spectra have been recorded and shown in Fig. 5(b). The emission spectra shown a strong green emission between the spectral region from 450nm to 700nm

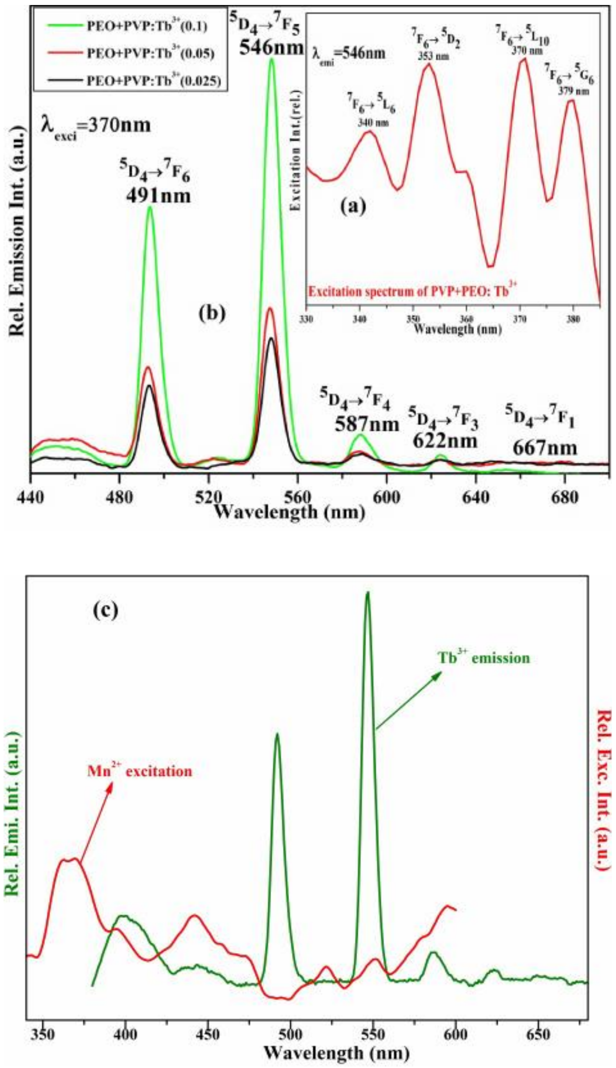

Fig. 5: (a) Excitation (inserted), (b) Emission spectrum of Tb^{3+}: PEO+PVP blended polymer film and (c) Overlapped spectra of Mn^{2+} excitation with Tb^{3+} emission

due to the transitions from $^5D_6$ excited states of Tb^{3+} ions. The emission transitions $^5D_4 \rightarrow {}^7F_6$ at 491 nm, $^5D_4 \rightarrow {}^7F_5$ at 546 nm, $^5D_4 \rightarrow {}^7F_4$ at 587 nm, $^5D_4 \rightarrow {}^7F_3$ at 622 nm and $^5D_4 \rightarrow {}^7F_1$ at 667 nm respectively. Among these transitions the green emission $^5D_4 \rightarrow {}^7F_5$ at 546 nm is intense one owing to the shielding of 4f orbitals from the environment by an outer shell of 5s and 5p orbitals, the f-f absorption bands are very narrow (compared to the broad d-d absorption bands d-block transition metals), which causes mainly perturbed spectral properties of Ln (III) ions by the external field generated by the ligands which is a magnetic dipole transition and which satisfy the Laporte's selection rule $\Delta J = \pm 1$ (Pengpeng Dai *et al.* 2013). 0.1wt% is found to be an optimized content of Tb^{3+}ion.

3.6. Energy Transfer from Tb^{3+} to Mn^{2+}

From the excitation spectrum of (Tb^{3+}+Mn^{2+}): PEO+PVP polymer film as shown in Fig. 6(a), 353nm (UV region) is the chosen excitation wavelength for an energy transfer measurement because relative excitation wavelength of Tb^{3+}. The energy transfer involved in the present host matrix co-doped with Tb^{3+}& Mn^{2+}ions (Mengmeng Shang *et al.* 2012). The emission spectrum of PEO+PVP co-doped with Tb^{3+} and Mn^{2+}ions blended polymer film excited at 353nm ($^7F_6 \rightarrow {}^5L_9$) consists not only the peaks of Tb^{3+} at 546nm ($^5D_4 \rightarrow {}^7F_5$) and 587nm ($^5D_4 \rightarrow {}^7F_4$) but also the peak of Mn^{2+} at 614nm ($^4A_1 \rightarrow {}^6A_1$) as shown in Fig. 6(b).

The energy transfer phenomena from $Tb^{3+}$to Mn^{2+}has been preliminarily justified by the luminescence properties of the obtained samples. In co-doped blended polymer film with Tb^{3+} & Mn^{2+} ions, the emission intensity of the Mn^{2+} ion such as 614nm (red) regarding Mn^{2+} was increased when compared to single Mn^{2+} ion doped PEO+PVP blended polymer film, simultaneously the emission intensity of the Tb^{3+} ion such as 546nm (green) was decreased at the excitation wavelength of 353nm when compared to singly doped polymer films as shown in Fig. 7(a).

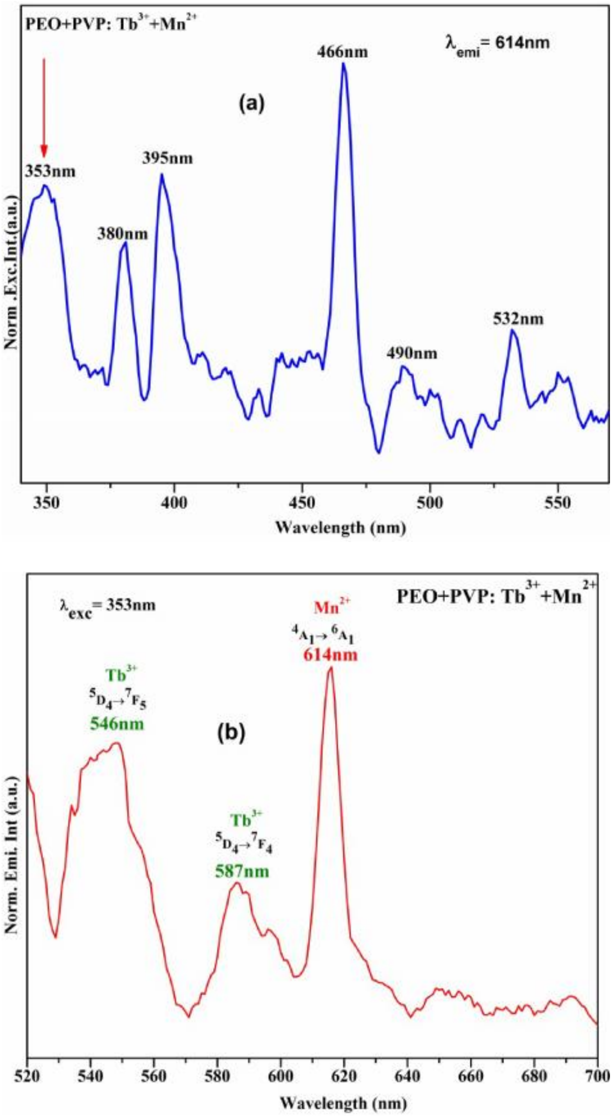

Fig. 6: (a) Excitation and (b) Emission spectra of the co-doped Mn^{2+}+Tb^{3+}: PEO+PVP blended polymer film

By comparison Fig. 5(c) spectra explores the information of overlap between the emission spectrum of Tb^{3+} ion doped PEO+PVP blended polymer film with excitation spectrum of Mn^{2+} doped PEO+PVP blended polymer film has been found. This result indicates that the energy transfer could be occur from the Tb^{3+} ion to Mn^{2+} (Dwivedi *et al.* 2011). Here the Tb^{3+} ion acts as an sensitizer and the Mn^{2+} ion as an activator. These results has been well accepted to be favourable energy transfer takes place through the cross relaxation process from the Tb^{3+} to Mn^{2+} ion. This indicates that efficient emission photons from the Tb^{3+} ion are collectively absorbed by the Mn^{2+}. This is also one of the evidence to energy transfer process involved between Tb^{3+} and Mn^{2+} ion. Finally these results concluded that the energy transfer phenomena takes place within the Tb^{3+} and Mn^{2+} ion with an excitation 353nm. An energy transfer process is shown in Fig. 7(b).

3.7. Decay Analysis

Further to identity of an evidence of Energy Transfer from $Tb^{3+} \rightarrow Mn^{2+}$, the PL decay curves of Tb^{3+} ions in Mn^{2+}:PEO+PVP have been measured with an excitation at 353nm by monitoring an emission at 546nm. The luminescence decay of the transition at 546nm of Tb^{3+} doped PEO+PVP blended polymeric sample has been studied at room temperature. The measured lifetime (τ_{means}) for the $^5D_4 \rightarrow {}^7F_5$ transition has been determined from the decay curve which is represented by the

$$I = I_0 A e^{\left(-\frac{t}{\tau}\right)}$$

where 'A' is the amplitude and 'τ' is the fluorescence life time. Decay curve for Tb^{3+} ion in a PEO+PVP blend can be fitted to a single exponential and life time is calculated to be 0.87ms (Yinyao Liu *et al.* 2010). It is obvious that the decay time of the Tb^{3+} emission in the presence activator Mn^{2+} co-doped PEO+PVP blended polymer film is substantially shorter than that of the absence of Mn^{2+}, and this is in the order of 0.61ms. The increase in the Tb^{3+} emission decay rate on codoping with Mn^{2+} ions can be attributed to the non-radiative transition process from Tb^{3+} to Mn^{2+} ions. It has also been noticed that the emission decay profile of Tb^{3+} have exhibited non-exponential nature in co-doped system. In single Tb^{3+} ion doped blended polymer film, the interaction between the acceptor and donor ions are negligible then decay profiles will exhibit exponential nature,

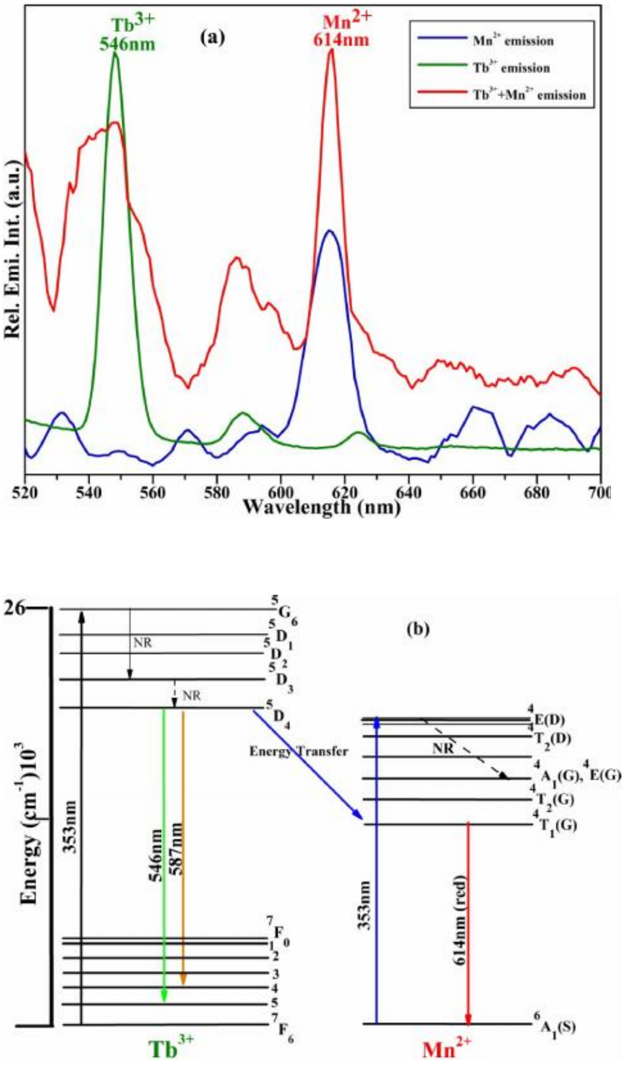

Fig. 7: **(a) Comparison emission profiles of Mn^{2+}, Tb^{3+} singly doped & Mn^{2+}+Tb^{3+} co-doped PEO+PVP polymer films and (b) energy level scheme diagram for energy transfer from Tb^{3+} to Mn^{2+}**

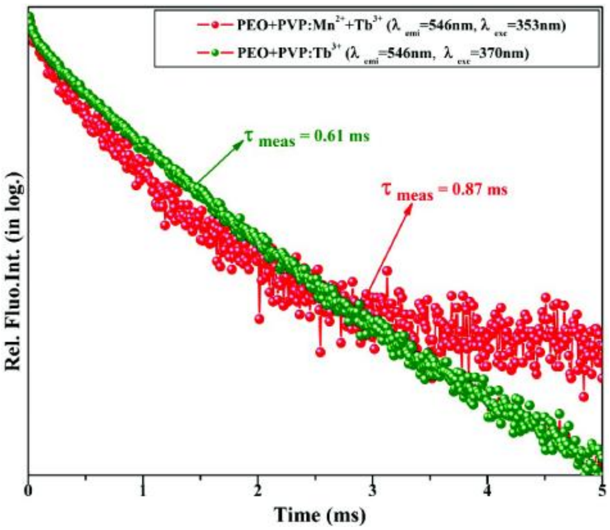

Fig. 8: **Life time profiles of singly doped Tb^{3+}(λ_{emi}=546nm, λ_{emi}=370nm), co-doped Tb^{3+}+Mn^{2+} (λ_{emi}=546nm, λ_{emi}=353nm)**

which is shown in Fig. 8 (green plot). In the case of dual ions Mn^{2+}+Tb^{3+}doped blended polymer film, where as higher concentrations availability of donor ions (Tb^{3+}) per acceptor ion (Mn^{2+}) will be more, therefore the average distance between the acceptor-donor ions will be decreased and electronic multipole-multipole interaction start taking place as a result of this emission decay profiles exhibit non-exponential nature with life time value calculated to be 0.61ms, which is lower lifetime when compared to singled Tb^{3+} doped blended polymer film as shown in Fig. 8 (red plot). Therefore, the above evidences confirms that an energy transfer occurs from Tb^{3+} to Mn^{2+} in the PVP+PEO blended polymer films (Yu-Chun Li *et. al.* 2007).

4. Conclusion

In summary, it could be concluded that polymer films of pure PEO+PVP and with addition of $Mn^{2+}$and Tb^{3+}ions at different concentrations have been synthesized by solution casting method in order to study their structural, thermal and optical properties. The amorphous nature of the polymer films doped with Tb^{3+} & Mn^{2+} has been confirmed from XRD analysis. Thermal stability of pure film has been investigated based on the measurement of TG-DTA profile. Raman analysis confims the complex formation of the polymer with the dopant ions. The optical absoption spectrum of Mn^{2+} doped polymer film exhibits characteristic bands in octahedral symmetry, and also Tb^{3+} doped polymer film has been evaluated. The emission spectra of Mn^{2+}: PEO+PVP polymer film exhibits a predominant emission at 614nm (*red)* at an excitation of 370nm. Tb^{3+}: PEO+PVP polymer film exhibits a prominant green emission at 546nm (*green*) with an excitation at 370nm.. The enhanced *red* emission (614nm) of the Mn^{2+} ions is due to an effective energy transfer from $Tb^{3+}$to Mn^{2+} ions in the blended polymer film, which has been evidenced from the luminescence spectra and decay curve dynamics. These results are found to be more encouraging in suggesting them as visible colour luminescent materials.

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