

Spectroscopic properties of Ho³⁺: PVA/PVP blend polymer films

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Abstract

This article reports the composite PVA/PVP and various concentrations of Ho³⁺: PVA/PVP blend polymer films were successfully prepared by using the solution casting technique. X-ray diffraction for PVA/PVP and Ho³⁺: PVA/PVP samples were carried out. The XRD shows amorphous nature with increasing Ho³⁺ concentration. The FTIR spectra indicate an interaction between Holmium and PVA/PVP polymer blends at various concentrations. The UV-Vis spectral analysis was studied from the 200 nm to 600 nm wavelength region. The band gap energy (E_g) and refractive index are strongly affected beyond the addition of Ho³⁺ ions in the PVA/PVP blend. The energy band gap reduced from 5.21 eV to 4.7 eV and the refractive index raises from 2.37 to 2.44. The optical edge was initiated to be 5.04 eV for host PVA/PVP and decreased to 4.69 eV for addition of Ho³⁺ in the PVA/PVP polymer. A prominent emission band observed at 440 nm ($^5G_6 \rightarrow ^5I_8$) amongst all the emission at 412 nm ($^5G_5 \rightarrow ^3G_5 \rightarrow ^5I_8$) and 462 nm ($^5F_1 \rightarrow ^5I_8$) respectively. The analysis of photoluminescence reveals that the quenching of luminescence intensity beyond 0.4 wt% of Ho³⁺ concentration. The decay curves of 5I_8 level were studied for various Ho³⁺ ion concentrations in all PVA/PVP blend polymer films and the lifetimes were observed to reduce with increase of Ho³⁺ ion concentration. The concentration quenching is attributed to the energy transfer among the Ho³⁺ excited ions. Further, emission intensities were characterized using a CIE chromaticity diagram and the (x, y) chromaticity coordinates (0.1684, 0.0974) suggests the pure, intense blue emission obtained from the prepared blend polymer films useful for laser applications and optical devices.

Keywords: PVA/PVP, Rare Earth ion and Emission analysis, CIE Chromaticity diagram.

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I. Introduction

At room temperature, light emitting polymer materials incorporate with several rare earth ions have more importance not only in the industry of optoelectronics but also in the scientific research [1] because of their easy refinement and mechanical adaptability. Polymer blend materials doped with rare earth ions have a few applications in applied spectroscopy field. For designing materials blend polymer is a convenient procedure to develop properties with new material [2]. The development cost of blend polymer is low because of using known polymers with fine characterized properties in comparing with co-polymer synthesis. However, the property of blending depends upon miscibility of the components. At a microscopic scale it modifies the structure owing to the polymer blending [3]. Interactions are present in polymer blends, which are hydrogen bonding, dipole and ionic interactions. The most advantages of blend polymers are the properties of definite product can be oriented to the application essentially; they do not attain which by only one polymer.

Polyvinyl alcohol (PVA) has strong transparency, synthetic, water soluble polymer and eminent thermal and mechanical properties. PVA has various internal structures semi-crystalline or amorphous. The physical and chemical properties of PVA depend on a hydroxyl group. PVA has numerous applications on account of the hydroxyl groups and hydrogen bonds [4]. These hydrogen bonds support in the development of blend polymers. PVA hydro gels used for different pharmaceutical and biomedical applications. PVA as a cross-linked gel or linear polymer is being involved in cancer therapy [5].

Polyvinyl Pyrrolidone (PVP) is one of the fascinating polymers having high molecular weight, water soluble and certain polar solvents. It has amorphous internal structure, odourless white powder and tasteless and incorporate the rigid Pyrrolidone group. PVP forms different polymer complexes with another polymer because of capability to sustain hydrogen bonding with polar order and high affinity of the pyridine group [6]. PVP has bounded thermal capability, environmental stability, and effortless process ability [7]. Due to low cytotoxicity PVP has been used in different fields like biomedical and food [8]. Previously the blending of PVP with different polymers has been studied [9-13] because of being high T_g and beneficial hydrophilicity. PVA/PVP blend polymers having dopant dependent properties and good charge storage ability. Y. Shi Y and WH Eisa et al. had discussed PVA/PVP interactions such as hydroxyl group of PVA and carbonyl group of PVP in previous papers due to their attractive properties of the subsequent mix together, which combine both the features of PVA/PVP [14-15]. PVA/PVP hydrogel blends are stable in environment due to its crosslink consisting of

intermolecular hydrogen bonds and intermolecular hydrogen bonds of PVA [16]. During the last years, PVA/PVP blends are utilized in biomedical and industrial applications. Mainly blend PVA/PVP polymers are used in nucleus pulposus replacements, wound dressing, high energy electrochemical devices [17]. PVA and PVP are water-soluble polymers and compoundable in all proportions. Among the rare-earth ions Ho³⁺ ion is the most delightful to study the spectroscopic properties, due to its a few electronic transitions in the visible and IR regions [18-20]. Ho³⁺ ions have been deliberated in different tellurite glasses and ceramics [21-22] numerous transitions are of particularly, the ⁵I₇→⁵I₈ emission close to 2μm wavelength is very useful at room temperature in eye safe potential laser emission with low threshold action and it has a smart applications in LIDAR, atmospheric communication system and medical applications. The main intention of the current work, manufacture of new polymer synthesis blending PVA and PVP polymers with Ho³⁺ ion to make useful in technological applications.

In the present work, Ho³⁺: PVA/PVP blend polymer films were equipped with various concentrations to study the structural and optical properties to understand the appropriateness of these materials for visible luminescence. Band gap and refractive index were calculated from the absorption spectra. The CIE color coordinates were deliberated from the emission spectrum to understand the use of these blend polymer films for blue light applications.

II. Experimental procedure

II.1. Raw materials and films preparation

Polyvinyl alcohol (PVA) (M.W=1, 25,000), Polyvinyl Pyrrolidone (PVP) (M.W=3, 60,000) and Holmium nitrate (M.W=4, 4102) raw materials, purchased from Sigma-Aldrich company with purity 99.9%. Using solution casting method equal amount of PVA/PVP (50/50) was added into distilled water. In this process, the solution was stirred thoroughly with a magnetic stirrer for 7 to 10 hrs at room temperature to get a homogeneous mixture until to complete the decomposition. We left the solution for 24 hrs exclude air bubbles. Finally, we cast the prepared homogeneous solution into petri dishes for 1 week. After drying the film was peeled from the petri dish and used further analysis.

Similarly, we prepared various concentrations of Rare earth ion (0, 0.1, 0.2, 0.3, 0.4 & 0.5 wt%) added to PVA/PVP blend polymers.

II.2 Characterizations

For all the samples of pure PVA/PVP blend polymer film and Ho³⁺: PVA/PVP blend polymer films were investigated by shimadzu model 6000 X-ray diffractometer using CuK_α(1.54 Å) radiation with 2θ range from 10°-80°, FTIR spectra was recorded on Jasco FT-IR 430 spectrometer in the region of 4000-400 cm⁻¹, at room temperature optical absorption spectrum was measured in the spectral region 200 nm to 1000 nm using UV-Vis absorption spectra (V-570, UV-Vis, Jasco). The emission spectra and decay analysis of Ho³⁺:PVA/PVP blend polymer films were carried out using Edin burg UV-Vis –NIR (FLS-980) spectrometer with Xenon arc lamp.

III. Results and Discussions

III.1. XRD analysis

Fig.1(a-f) refers the X-ray diffraction (XRD) patterns of the prepared pure PVA/PVP and various concentrations of Ho³⁺: PVA/PVP blend polymer films. From previous reports, PVP shows two peaks at 12° to 15° and 19° to 24° and Pure PVA shows a wide peak at around 21° [23]. In this present work, fig. 1 shows diffraction peak at 20~15. 2° (belongs to PVP) [24] and 20~22. 3°, which confirm the semi-crystalline nature of synthesized blend polymer films [23]. For the Holmium ion added blend polymer films, it is observed that diminish in intensity of diffraction peaks and width of peak with increasing content. This is caused by the complication of PVA/PVP chains with Ho³⁺ which lead to diminish in intermolecular interaction between the PVA/PVP blend chains and the crystalline degree and for this reason increase in the amorphous province [25]. This confirms the existence of Ho³⁺ within the blend polymer film. After adding diverse concentrations of Ho³⁺ to PVA/PVP blend polymer film new peaks were not appearing.

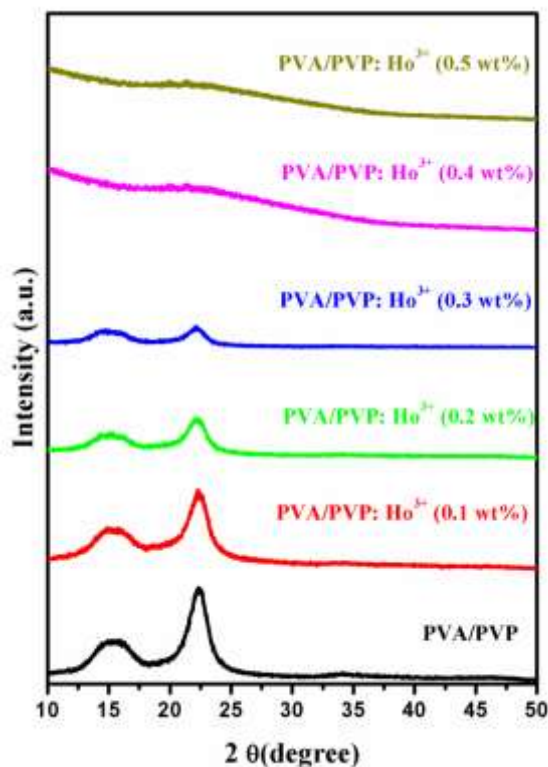


Fig.1 X-ray diffraction pattern of pure PVA/PVP blend and different concentration of Ho^{3+} : PVA/PVP polymer.

Table1

Peak positions and energies along with their assignments of Ho^{3+} : PVA/PVP polymer films

Transition from $^5\text{I}_8$	Peak position λ (nm)	Energy (cm^{-1}) ν_c/ν_a		Nephelauxetic effect $\beta = \nu_c/\nu_a$
$^3\text{H}_6$	359	0	25
$^3\text{G}_5 \rightarrow ^3\text{G}_5$	416	154	63	2.444
$^3\text{G}_6$	450	-17	6	-2.833
$^3\text{F}_3$	485	-30	-73	0.4109
$^3\text{F}_4$	537	-65	-112	0.5803
$^3\text{F}_5$	642	-26	-19	1.3684

III.2. FTIR spectra

FTIR spectrum is used to recognize the interactions between blend polymers and rare earth ion. FTIR spectra of PVA/PVP and 0.1, 0.2, 0.3, 0.4 and 0.5 wt% of Ho^{3+} : PVA/PVP blend polymer films reported in the range of 400-4000 cm^{-1} and presented in Fig. 2.

From Fig. 2, we noticed that an intense band close to 3278 cm^{-1} corresponding to stretching vibrations of the OH hydroxyl group [26]. The band at around 2929 cm^{-1} denoted to the asymmetric stretching vibration of $-\text{CH}_2$ of PVA/PVP polymer blend [26]. The band was assigned to C=O stretching, vibration appears at 1744 cm^{-1} [26]. It is confirmed the semi-crystalline nature of blend polymer film, which is correlated with X-ray diffraction analysis. The noticed band at 1545 cm^{-1} corresponds to vibration of C=N (Pyridine ring) [27]. The band was noticed at 1307 cm^{-1} which is the combination of vibrational of CH_2 twisting (out of plane) [26]. In pure PVA a band at around 1045 cm^{-1} attributes to C-O stretching group present on the PVA back bone [28].

Upon an addition of the rare earth ion Ho^{3+} the FTIR spectra of PVA/PVP was a little variation. This indicated that an interaction between PVA/PVP and Ho^{3+} . From figure. 2, asymmetric stretching CH_2 of PVA/PVP shifts from 2929 cm^{-1} to 2904 cm^{-1} . The shift in bending C=N shifts from 1544 cm^{-1} to 1532 cm^{-1} . The vibration CH_2 twisting mode shifts from 1307 cm^{-1} to 1282 cm^{-1} . The stretching of C-O shifts from 1045 cm^{-1} to 1008 cm^{-1} . This demonstrated the interference of the individual interaction in PVA/PVP blend polymer films and the Ho^{3+} .

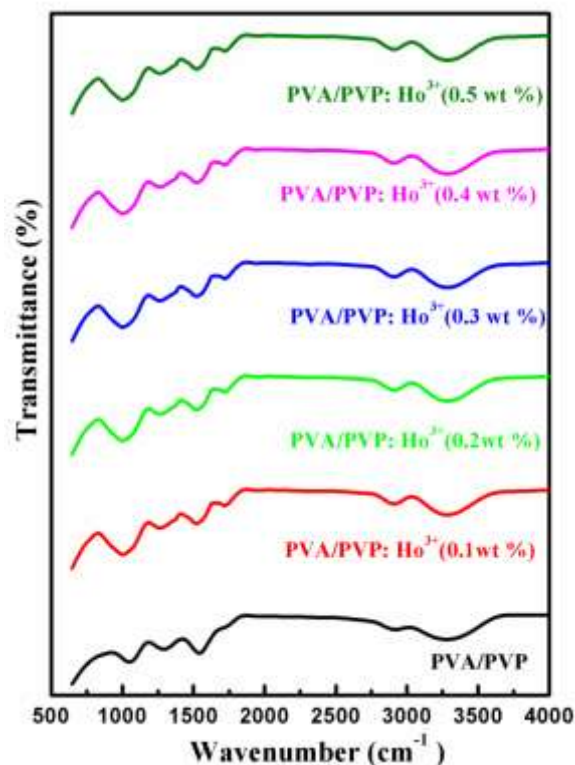


Fig.2 FT-IR spectra of pure PVA/PVP blend and various concentrations of Ho^{3+} : PVA/PVP polymer

III.3. Optical absorption studies

The UV-Vis optical absorption spectra of pure PVA/PVP blend and Ho^{3+} : PVA/PVP blend polymer films are shown in Fig. (3) (a) and (b) in the spectral range of 200 nm to 1000 nm. From the absorption spectra one can study the electronic properties and band structure of the pure PVA/PVP and doped polymer films. The empirical optical absorption edge at 218 nm, it is due to the semi crystalline nature of the samples, which is already confirmed by XRD and observed optical band centred at 285 nm of the pure PVA/PVP blend polymer. This band is ascribed to $\pi \rightarrow \pi^*$ transition which comes from the unsaturated (double) bonds, C=O and/or C=C [29], which is responsible for electrical conduction in the samples which noticed in FTIR at around 1744 cm^{-1} . This absorption edge shifted towards higher wavelength with increasing the Ho^{3+} content, indicating the complication between all used components. They may ascribe this to the change in crystalline due to addition of Ho^{3+} into PVA/PVP polymer film [30].

Various concentrations of (0.1, 0.2, 0.3, 0.4 and 0.5 wt %) Ho^{3+} : PVA/PVP blend polymer films absorption spectra are shown in Fig. (3) (b). For, Ho^{3+} ions the electronic transitions in the optical absorption spectra begin from the ground state of $^5\text{I}_8$ to different excited states. PVA/PVP: Ho^{3+} absorption spectra exhibit six absorption bands at 359 nm, 416 nm, 450 nm, 485 nm, 537 nm and 642 nm corresponding to the $^5\text{I}_8 \rightarrow ^3\text{H}_6$, $^5\text{I}_8 \rightarrow (^3\text{G}, ^3\text{H})_5$, $^5\text{I}_8 \rightarrow ^5\text{G}_6$, $^5\text{I}_8 \rightarrow ^5\text{F}_3$, $^5\text{I}_8 \rightarrow ^5\text{F}_4$ and $^5\text{I}_8 \rightarrow ^5\text{F}_5$ transition respectively [31]. We noticed a absorption peak at 450 nm ($^5\text{I}_8 \rightarrow ^5\text{G}_6$) is identified as hypersensitive transition [32] with the selection rules $\Delta s = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$ is sensitive to the host environment in the PVA/PVP: Ho^{3+} blend polymer films. Ho^{3+} : PVA/PVP polymer films exhibited blue emission under a UV excitation source. There are many theoretical approaches for describing the quantitatively. From the absorption spectra of trivalent rare earth ions in the polymers, the nephelauxetic effect or shift in energy level position (β) and bonding parameter (δ) can be evaluated from the average values of $\bar{\beta}$ using the following relations

$$\beta = \frac{\nu_c}{\nu_a} (1)$$

$$\delta = \frac{1 - \bar{\beta}}{\bar{\beta}} (2)$$

where ν_c and ν_a are the corresponding electronic transitions of energies in the complex and aqua ions are in cm^{-1} . The bonding parameter may be negative and positive representative ionic and covalent bonding depends on the environment field [33]. Here, bonding parameter δ denotes the bonding nature is covalent nature.

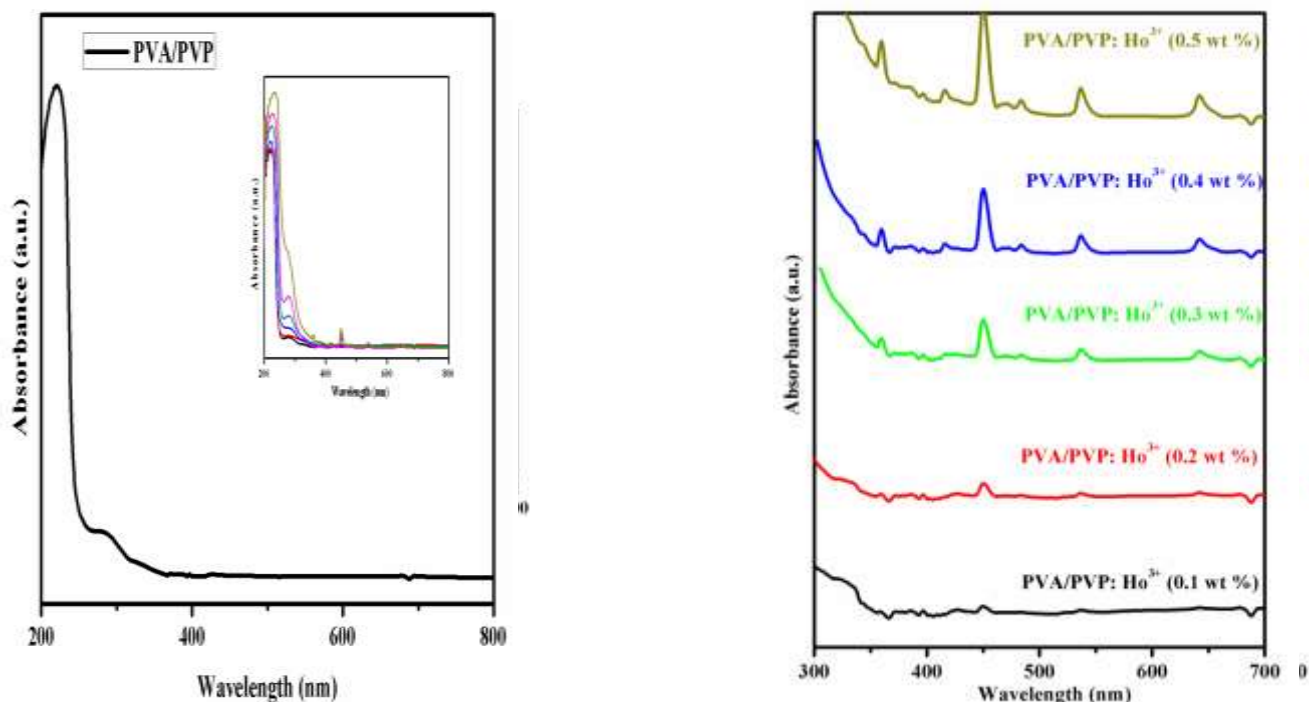


Fig.3. Absorption spectra of (a) Pure PVA/PVP blend polymer film and (b) for various concentrations of Ho^{3+} : PVA/PVP polymer films.

III.4. Optical energy band gap (E_g)

Using the optical absorption data, we evaluated absorption co-efficient in terms of wavelength become [34]

$$\alpha = 2.303 \cdot \frac{A}{d} \quad (3)$$

where d is the thickness of the samples and A is the absorbance of the polymer films. The relation between absorption co-efficient (α) vs $h\nu$ for pure PVA/PVP and Ho^{3+} : PVA/PVP polymer films were shown in Fig. 4(a). It concludes that addition of Ho^{3+} ions to the PVA/PVP films the absorption edge shifts towards lower photon energy. This shifting shows the decrease in the band gap for Ho^{3+} : PVA/PVP samples. We found it the absorbance coefficient (α) increasing with an increase in $h\nu$ along with Ho^{3+} content. For PVA/PVP absorption edge is 5.04 eV. For different content of Ho^{3+} : PVA/PVP. We list the absorption edge values in Table 1. Optical band gap (E_g) calculated for all Ho^{3+} : PVA/PVP samples by using

$$\alpha h\nu = c (h\nu - E_g)^s \quad (4)$$

where c is constant and depends on the transition probability, we use the parameters to define the electronic transitions liable for the absorption. The parameter s has distinct values like $1/2$, $3/2$, 2 or 3 depending on the transition whether it is indirect or direct and forbidden or allowed, in that order [35]. We have predicted the optical energy band gap from the plot between $(\alpha h\nu)^{1/2}$ versus photon energy shown in Fig. 4 (b). We estimated energy gap values by the extrapolation of the linear part of the graph to the $h\nu$ axis. From this plot, we got energy gap values for pure PVA/PVP and various concentrations of Ho^{3+} doped PVA/PVP polymer films. The predicted energy gap value for PVA/PVP is 5.21 eV, while Ho^{3+} added polymer films the optical band gap shifted to lower energy values compared to pure PVA/PVP polymer. With the raise in Ho^{3+} content reduce in E_g values; show that there are charge transfers between PVA/PVP blend polymer and little amounts of Ho^{3+} ions

[36]. All the optical band gaps are overlapping. It shows these overlaps for decreasing the band gap when the Ho^{3+} concentration is increased in the polymer matrix. List of the energy gap values is in a Table 2.

Fig 4(c) shows the band gap energy dependent on the concentration of Ho^{3+} . From the Fig .4(c), it is found to be that energy band gap goes on reducing with a raise in content of Ho^{3+} . Ho^{3+} is accountable for the decrease of E_g . This was caused by the creation of defects in the blend polymer films. These defects generate localized states in the band gap. The content of the defects is proportional to the density of localized states. Increasing in Ho^{3+} concentration can cause the localized states of dissimilar colorcontrast to overlap and extend in the mobility gap [37].The reduce in the band gap reflects the rise in the disorder in the polymer films [38]. Table2. refers the energy band gap values for pure PVA/PVP and different concentrations of Ho^{3+} PVA/PVP polymer films.

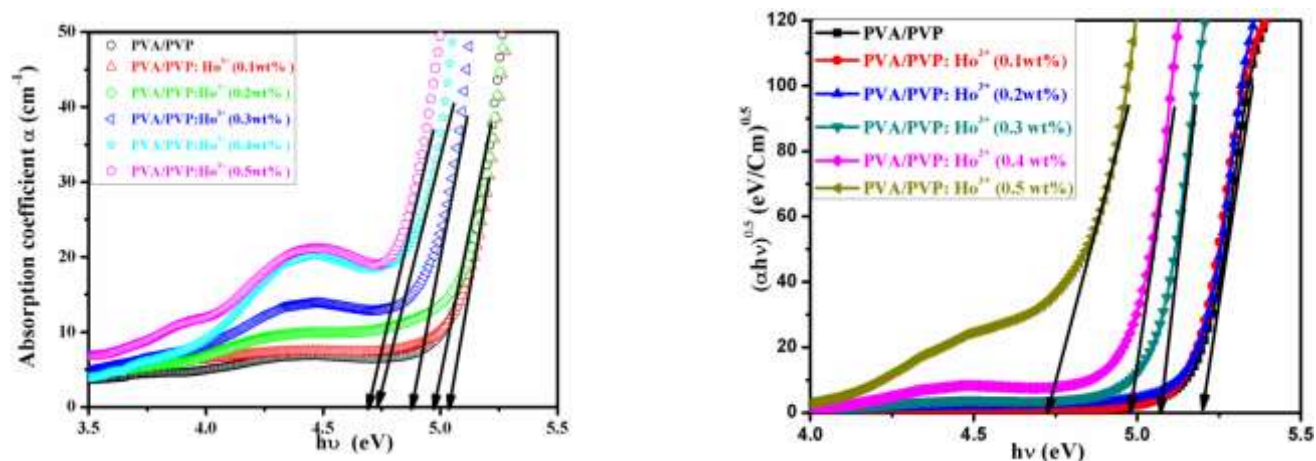


Fig.4 (a) Variation of absorption coefficient (α) with photon energy ($h\nu$) & (b) The indirect band gap plots of pure PVA/PVP and Ho^{3+} : PVA/PVP polymer films

III.5. Refractive index

Optical materials refractive index plays a vital role in designing of optical devices [39].Hence, regulating of the refractive index of polymers makes them suitable for a broad range of medical and industrial applications essentially organic light emitting diodes, polymer lens design, display devices and organic solar cells.

Using band gap values refractive index (n) can be calculated following the equation to various compounds determined by Reddy et al.[39].

$$n = \sqrt{\frac{12.417}{E_g - 0.365}} \quad (5)$$

Pure PVA/PVP and various concentrations Ho^{3+} : PVA/PVP polymer films refractive index values are shown in Table2. From the table2,it is observed that a little bit variation in refractive index for PVA/PVP polymer film compared with different contents of Ho^{3+} : PVA/PVP polymer films. The above- mentioned results may be ascribed to the free carrier effect lead to a raise in the reflection and therefore refractive index increases. Hence, the result playsan important role in optical waveguide fabrication. A strong relationship is noticed between the band gap and refractive index while decreasing the band gap with Ho^{3+} concentration, the refractive index increases. From the table2 it was noticed a big variation between band gap and refractive index of PVA/PVP and different concentrations of Ho^{3+} : PVA/PVP polymer films. This result designates the direct and strong effect of Ho^{3+} ions adding the optical parameters of the PVA/PVP blend polymer film.

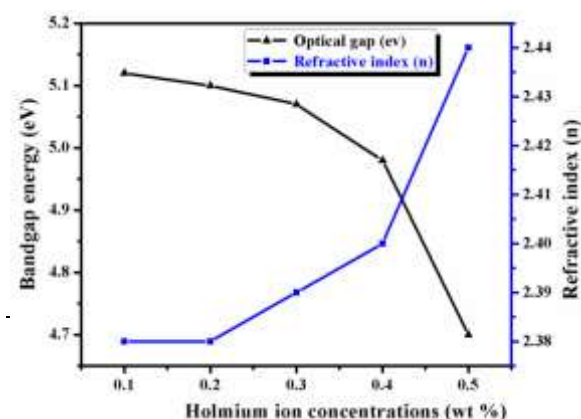


Fig.4 (c) The dependence of E_g and refractive index on Ho^{3+} into PVA/PVP polymer films

Table 2Absorption edge, indirect band gap and refractive index for pure PVA/PVP and Ho^{3+} : PVA/PVP polymer films

Sample	Absorption edge(eV)	Indirect energy gap(eV)	Refractive index (n)
PVA/PVP	5.04	5.21	2.37
PVA/PVP: 0.1 Ho^{3+}	5.04	5.12	2.38
PVA/PVP: 0.2 Ho^{3+}	4.97	5.10	2.38
PVA/PVP: 0.3 Ho^{3+}	4.88	5.07	2.39
PVA/PVP: 0.4 Ho^{3+}	4.74	4.98	2.40
PVA/PVP: 0.5 Ho^{3+}	4.69	4.7	2.44

III.6. Emission analysis

Fig.5 (a) represents the emission spectrum of PVA/PVP with various concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 weight%) of Ho^{3+} polymer films in the range of 400 nm to 500 nm exciting with 370 nm ($^5\text{I}_8 \rightarrow (^5\text{G}_5, ^3\text{H}_5)$) wavelength. The emission spectra reveal the three emission bands at 412 nm, 440 nm and 462 nm corresponding to the electronic transitions ($^3\text{G}_5 + ^3\text{G}_5 \rightarrow ^5\text{I}_8$, $^5\text{G}_6 \rightarrow ^5\text{I}_8$ and $^5\text{F}_1 \rightarrow ^5\text{I}_8$ [31]) respectively. Among these three $^5\text{G}_6 \rightarrow ^5\text{I}_8$ electronic transition has more intensity compared to ($^3\text{G}_5 + ^3\text{G}_5 \rightarrow ^5\text{I}_8$ and $^5\text{F}_1 \rightarrow ^5\text{I}_8$) transition. This variation in intensity is ascribed to inconsistency in the multi phonon relaxation (MPR) rates. The MPR rate increases exponentially with the decrease of an energy gap between the excited state and the nearest lower lying states. The luminescence intensity was notably optimized when the Ho^{3+} ions in the PVA/PVP were increased. The highest emission intensity showing at concentration 0.4wt% of Ho^{3+} ion in PVA/PVP blend polymer. Further increasing the concentration, the emission intensity decreases because of concentration quenching, it shows in **Fig5(b)**. This is due to an excited Ho^{3+} ions and unexcited Ho^{3+} ions and this procedure continues till the energy is dumped non-radioactively in the form of heat.

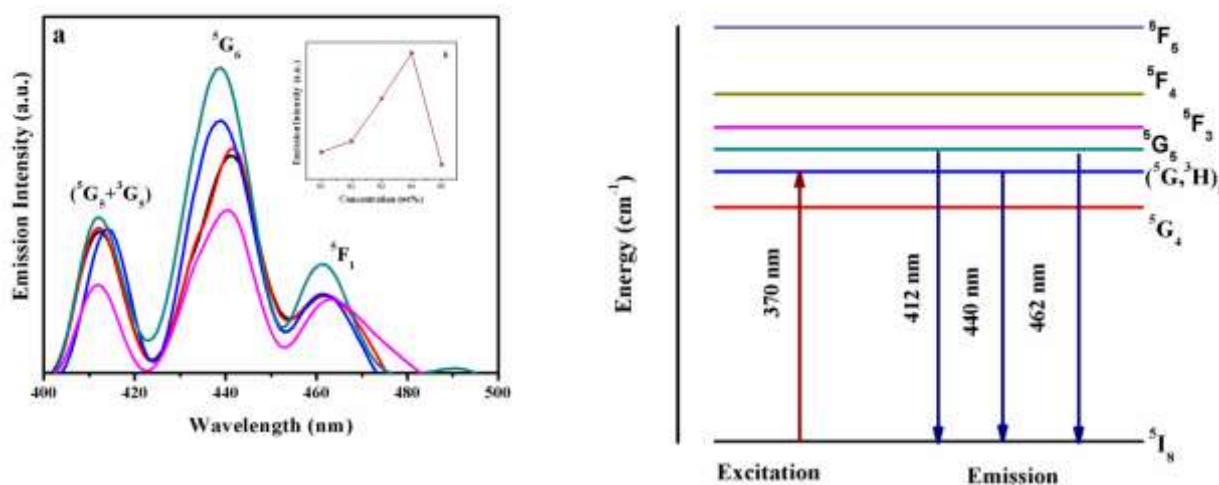


Fig.5 (a) Emission spectra of Ho^{3+} PVA/PVP polymer films at $\lambda_{\text{exci}} = 370$ nm excitation [Fig. 5 (b) the variation of intensity of $^5\text{G}_6 \rightarrow ^5\text{I}_8$ (440 nm) transition as function of Ho^{3+} ion concentration in inset]

Fig.5 (c) Energy level diagram of Ho^{3+} : PVA/PVP polymer film

Fig. 5(c) represents the corresponding energy level diagram of Ho^{3+} : PVA/PVP polymer films and their emission transitions. At room temperature we study the lifetime of $^5\text{G}_5$ level of Ho^{3+} ion with an excitation of 370 nm by monitoring the emission at 440 nm. The luminescence decay lifetime analysis was carried by monitoring the emission and excitation wavelengths of 370 nm ($^5\text{I}_8 \rightarrow (^5\text{G}_5, ^3\text{H}_5)$) and 440 nm ($^3\text{G}_5 \rightarrow ^5\text{I}_8$) respectively, for all the Ho^{3+} : PVA/PVP blend polymers and are depicted in a logarithmic plot, are in **Fig.5 (d)**. The evaluated lifetime values for the emission transition of ($^5\text{G}_5 \rightarrow ^5\text{I}_8$) under an excitation of 370 nm ($^5\text{I}_8 \rightarrow (^5\text{G}_5, ^3\text{H}_5)$) are summarized in **Table 3**. Nevertheless, it has been found that all the obtained decay curves of the Ho^{3+}

doped PVA/PVP blend polymer composites are following the second order exponential decay. They are well fitted in second order exponential decay function which is followed the equation as given below

$$I = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2) \quad (6)$$

Where I stand for emission intensity and the rest of the things A_1 and A_2 are the constants. The two exponential components are τ_1 and τ_2 [40]. The average lifetime of the emission transition of the Ho^{3+} doped PVA/PVP blend polymer composites is evaluated by the following equation [41]

$$\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \quad (7)$$

The predominant lifetime has been found to be 0.0049 ms for 0.1 wt% Ho^{3+} doped PVA/PVP blend polymer composite. However, it can be noticed that the lifetime decay values seem to be less and not followed a numerical order. This could be due to the multiple interactions among Ho^{3+} and Ho^{3+} ions at higher concentration. As it can be noticed from Fig.5(d), the lifetime decreases and followed numerical disorder which could be caused either by higher multi-phonon relaxation rates due to freezing of phonons or by lower transition probabilities for the higher lying $^5\text{G}_5$ multiplet which is depopulated at room temperature [42]. Therefore, it can be realized that the decrement in the lifetime of the Ho^{3+} emission is caused by the stronger multiphonon relaxation rate, which means that a higher amount of excited ions decay non-radioactive in the polymer matrix

We calculated the CIE chromaticity coordinates for various concentrations of Ho^{3+} : PVA/PVP polymer films from the emission spectra are shown in Fig.5 (e) and, we present the color coordinates of the polymer films in Table 3. From the Fig 5(e), it is observed that the emission color of the prepared polymer film locates in the blue region equivalent to $^5\text{G}_5 \rightarrow ^5\text{I}_8$ electronic transition at 440 nm wavelength. It shows Ho^{3+} : PVA/PVP blend polymer is suitable to get blue emission applications. Among all the contents 0.4% of Ho^{3+} : PVA/PVP emitted strong blue light.

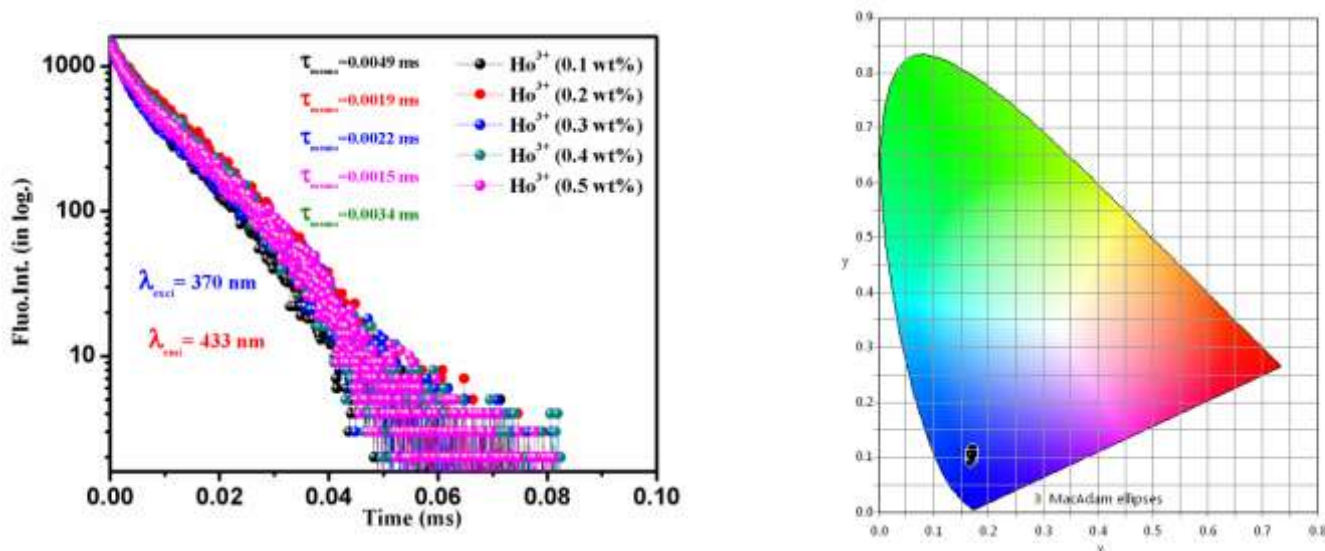


Fig.5 (d) Lifetime decay dynamics of the Ho^{3+} : PVA/PVP blend polymer composites at different concentrations of Ho^{3+} ions

Fig.5 (e) CIE chromaticity diagram for various concentrations of Ho^{3+} : PVA/PVP polymer films

Table 3

Calculate lifetimes, CIE chromaticity coordinates and color purity for an emission transition of $^5\text{G}_6 \rightarrow ^5\text{I}_8$ at 440 nm under the excitation of 370 nm ($^5\text{I}_8 \rightarrow (^5\text{G}_6, ^3\text{H}_5)$).

Polymer blend (concentration in wt %)	Emission Wavelength (nm)	Lifetime (ms)	CIE coordinates (x, y)	Color purity (%)
PVA/PVP : 0.1 Ho^{3+}	440	0.0049	(0.1720, 0.1140)	78.2
PVA/PVP: 0.2 Ho^{3+}	440	0.0019	(0.1711, 0.1028)	80.3
PVA/PVP: 0.3 Ho^{3+}	440	0.0021	(0.1685 0.0908)	81.9

PVA/PVP: 0.4 Ho^{3+}	440	0.0015	(0.1684, 0.0974)	83
PVA/PVP: 0.5 Ho^{3+}	440	0.0034	(0.1699, 0.1)	81.1

IV. Conclusion

In summary, it is concluded that pure PVA/PVP and various concentrations of Ho^{3+} : PVA/PVP blend polymer films were synthesized by solution casting process and to study their structural and optical properties. XRD shows that reduces in the degree of crystallization and causes an increase in the amorphous region. From FT-IR analysis the definite interaction in PVA/PVP polymer and hence the complexation and provides an insight into the possible interactions between Ho^{3+} and PVA/PVP polymer blend. The formation of intermolecular interactions and complexation between the PVA/PVP and Ho^{3+} was confirmed by XRD, FT-IR, UV-Vis, Optical absorption edge and optical band gap. Ho^{3+} : PVA/PVP polymer films exhibited blue emission under UV source. In photoluminescence study an interested blue emission peak observed at 440 nm ($^5\text{G}_6 \rightarrow ^5\text{I}_8$) under an excitation of 370 nm ($^5\text{I}_8 \rightarrow (^5\text{G}, ^3\text{H})_5$). The color chromaticity coordinates are found to locate in the blue region in the CIE 1931 diagram thus in turn recommends that prepared polymer films might be used for various photonic applications. Based on these results, PVA/PVP: 0.4 wt% of Ho^{3+} is suggested as a potential candidate for the development of blue emitting optical devices and intense laser applications at 440 nm.

References

- [1]. Y.Y. Zhang, L.F. Shen, E.Y.B. Pun, B.J. Chen, H. Lin, Optics Communications, vol. 311, pp. 111–116, 2013.
- [2]. K. Prabha, H.S. Jayanna, Open Journal of Polymer chemistry, vol. 5, pp. 47-54, 2015
- [3]. S.H. Lim, S.M. Hudson, Journal Macromolecular Science. Pol. R., Vol. 43, pp. 223-269, 2003
- [4]. MH Makled, E.Sheha, TS Shanap, MK .El-Mansy, Journal Advance Research, vol.4, pp.531-538, 2013.
- [5]. B. Ceroni, E. Chiessi, S. Margheritelli, L. Oddo and G. Paradossi, Biomacromolecules, vol.12, pp. 593–601, 2011.
- [6]. Angesh Chandra, R.C. Agrawal, Y.K. Mahipal, Journal of Physics D: Applied Physics, Vol.42, pp. 135107(4pp), 2009.
- [7]. T. Ohnaga, T.Sato, Polymer, Vol. 37, pp. 3729-3735, 1996.
- [8]. X. X.Zu, Xie, R. Mod, Chemical Engineering (china), vol.12, pp. 15, 1995.
- [9]. M.M. Feldstein, G.A. Shandryuk, S.A. Kuptsov, N.A. Plate, Polymer, vol. 41, pp. 5327-5338, 2001.
- [10]. S.N.Cassu, M.I. Felisberti, Polymer, vol. 38, pp. 3907-3911, 1997.
- [11]. C.B.Xiao, L.N. Zhang, Y.S. Lu, Journal of Applied Polymer Science, vol.81, pp.1049-1055, 2001.
- [12]. L.C. Cesteros, E. Meaurio, I. Katime, Polym Int. , vol. 34, pp. 97-103, 1994.
- [13]. M.T.Quraski, H.S. Rlaik, S.J Allen, Journal of Applied Polymer Science , vol. 46, pp. 255, 1992.
- [14]. Y.Shi Y, D. Xiong, Wear, vol.305, pp.280-285, 2013.
- [15]. WH Eisa, YK Abdel-Moneam, AA Shabaka, and A.M HosamandSpectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. vol. 95, pp.341, 2012
- [16]. E.M. Abdelrazek, IS.Elashmawi and S.Labeeb Physica B. vol.405, pp.2021-2027, 2010
- [17]. ShadpourMallakpour and Atefeh Jarahiyan Polymer-Plastics Technology and Engineering vol. 56, pp.1059-1067, 2017.
- [18]. T. Satyanarayana, T. Kalpana, V. Ravi Kumar, N. Veeraiyah, Journal of Luminescence, Vol.130, pp.498-506, 2010.
- [19]. Neeraj Kumar Giri, S.B. Rai, Anita Rai, Spectrochimica Acta Part A vol.74, pp. 1115-1119, 2009
- [20]. H. Lin, D.Q. Chen, Y.L. Yu, A.P. Yang, Y.S. Wang, Optics Letters, Vol.36, pp.876-878, 2011.
- [21]. F.Lahoz, I.R. Martin and J.M. Calvilla-Quintero, Applied Physics Letters, vol.86, pp. 51106-51108, 2005.
- [22]. I. kamma and B. Rama Reddy, Journal of Applied Physics, Vol. 107, pp. 113102-11306, 2010
- [23]. B.Shanthi, S.Muruganand International journal of Scientific Engineering and Applied Science, vol.1, Nov. 2015
- [24]. M. Morita, F.Araki, N. Yoshimoto, M. Ishikawa, H. Tsutsumi, Solid State Ionics vol136 pp.1167- 1173, 2000
- [25]. EM Abdelrazek, IS Elashmawi, Polymer Composites, vol.29, pp.1036-1043, 2008.
- [26]. X.Qi, X.Yao, S.Deng, T.Zhou, Q.Fu, Journal of Materials Chemistry A vol. 2, pp. 2240-2249, 2014
- [27]. M. Abdelaziz, E.M. Abdelrazek, Physica B vol.390, pp.1-9, 2007
- [28]. Ragab HM, Ahmad F, Radwan ShN, Journal of Physica B vol.502, pp.97-102, 2016
- [29]. E.M.Abdelrazek, Physics B, vol.403, pp.2137-2142, 2008
- [30]. E.M. Abdelrazek, A.M.Abdelghany and A.A. Aldhabi, Material Science, vol.10, pp. 1-11, 2013.
- [31]. W.T. Carnall, P.R. Fields and K. Rajnak Spectral Intensities of the Trivalent Lanthanide and Actinides in solution .II. Pm^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} and Ho^{3+} . Journal of Chemical Physics, vol. 49, pp. 4412-4423, 1968
- [32]. C.K. Jorgensen, B.R. Judd. Hypersensitive pseudoquadrupole transitions in lanthanides. Molecular Physics, vol. 8, pp.281-290, 1964
- [33]. Jia Zhang, Chen Jin, Electronic structure, up conversion luminescence and optical temperature sensing behavior of $\text{Yb}^{3+}\text{-Er}^{3+}/\text{Ho}^{3+}$ doped NaLaMgWO_6 , Journal of Alloys and Compounds, Vol. 783, pp. 84-94, 2019
- [34]. Sk. Mahamuda, K. Swapna, M. Venkateswarlu, A. Srinivasa Rao, Suman Shakya, G. Vijaya Prakash, Journal of Luminescence Vol.154, pp. 410-424, 2014.
- [35]. Jia Zhang, Chen Jin, Electronic structure, up conversion luminescence and optical temperature sensing behavior of $\text{Yb}^{3+}\text{-Er}^{3+}/\text{Ho}^{3+}$ doped NaLaMgWO_6 , Journal of Alloys and Compounds, Vol.783 (2019), pp. 84-94, 2017.
- [36]. O.G. Abdullah, B.K. Aziz, D.M. Salh, Structural and optical properties of PVA: $\text{Na}_2\text{S}_2\text{O}_3$ polymer electrolytes films, Indian Journal of Applied Research. vol. 3, pp.477–480, 2013.
- [37]. F.M. Reicha, M. Ishra, and M.M. Gabr, "On the physical and electrical properties of polypropenal prepared by electro polymerization technique", Journal of Physics and Chemistry of Solids, Vol. 64, pp.1157-1161, 2003.
- [38]. Abdelaziz M. Electron spin resonance and optical studies of poly (methyl methacrylate) doped with CuCl_2 , Journal of Applied Polymer Science, Vol.108,pp.1013-1020, 2008.
- [39]. R. Murri, L. Schiavulli, N. Pinto, T. Ligonzo, Journal of Non-Crystalline Solids, vol.139, pp. 60-66, 1992

- [40]. F. Yakuphanoglu, G. Barim, I. Erol, *Physica B* vol.391, pp. 136-140, 2007.
- [41]. Jia Zhang, Chen Jin, Electronic structure, upconversion luminescence and optical temperature sensing behavior of Yb³⁺-Er³⁺/Ho³⁺ doped NaLaMgWO₆, *Journal of Alloys and Compounds*. Vol. 783, pp. 84-94, 2019
- [42]. Qiang Ren, Baoxing Wang, Xiulan Wu, Tengyue Wei, ZhezheHuo, Luminescence properties and energy transfer in Dy³⁺ and Eu³⁺ codoped Sr₃Y (PO₄)₃ phosphor, *Journal of Alloys and Compounds*, Vol.684, pp. 677-682, 2016
- [43]. F. Reichert, F. Moglia, P. W. Metz, A. Arcangeli, D.-T.Marzahl, S. Veronesi, D. Parisi, M.
- [44]. Fechner, M. Tonelli, G. Huber, Prospects of Holmium-doped fluorides as gain media for visible solid-state lasers, *Optical Materials Express*, Vol.5, pp. 88-101, 2014