

Terbium-Doped PVA/PVP Blend Films: A Structural and Optical Investigation Toward Photonic Functionality

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Abstract. Terbium doped (Tb^{3+}) and undoped PVA/PVP blended polymer films were successfully prepared using solution casting method. X-ray diffraction (XRD) analysis revealed that the prepared films exhibit semi-crystalline nature. Fourier Transform Infrared (FTIR) spectroscopy was used to study the formation of polymer complexes and interactions between Tb^{3+} ions and polymer functional groups. Photoluminescence (PL) measurements, emission and decay profiles, were carried out to study the luminescent behavior of the films. The PL spectra showed a strong green emission peak centered at 543 nm, which corresponds to the ${}^5D_4 \rightarrow {}^7F_5$ transition of the Tb^{3+} ion, under 370 nm. The luminescence decay curves were non-exponential decay curve suggested the presence of energy transfer processes and interactions between the Tb^{3+} ions in the host matrix. In addition, the chromaticity coordinates of the Commission Internationale de l'Eclairage (CIE) confirmed that the green light emission dominance of in the Tb^{3+} doped PVA/PVP films. Among the different concentrations of doped films, the film doped with Tb^{3+} with 0.5 wt% showed the best luminescent performance. This implies the potential viability of the material as a promising candidate for green-emitting for photonic devices and optoelectronic devices such as, light-emitting diodes, lasers and display technologies.

KEY WORDS: Tb^{3+} , PVA/PVP blend polymer films, XRD, FTIR, Photoluminescence.

1 Introduction

The Creation of advanced functional materials to be used in optoelectronic and photonic applications has made the matter of research an immense focus in the past few decades. Rare earth (RE) doped polymer-based materials have been among the potential candidates due to their excellent luminescent properties,

flexibility, light weight and fabrication ease. Specifically, terbium (Tb^{3+}) ions with their typical green luminescence owing to the effective $^5D_4 \rightarrow ^7F_j$ transitions have been widely studied to be utilized in light-emitting devices and sensors, security inks, bioimaging, and solid-state lasers. The applications of these materials are diverse in nature and they include light emitting devices, sensors, security inks, bioimaging and solid-state lasers. Tb^{3+} ions complex with polymer matrices offer a special platform to create new functional materials that can be customized to particular optoelectronic and photonic applications, which takes advantage of the benefits of both the rare earth element and the polymer host [1, 2].

Rare-earth ions have been found to be an ideal host medium in polymer matrices because of their processability, optical clarity and capability to form thin films. Nevertheless, direct functionalization of rare-earth ions into pure polymers is associated with many difficulties, including phase separation, aggregation, and luminescence quenching, mainly because of inefficient dispersion or coordination. The possible solution to these problems is to combine two or more incompatible polymers. Two of these are polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP), which have received a lot of research due to their water solubility, non-toxicity, biocompatibility, and excellent film-forming properties [3, 4].

PVA is a semicrystalline polymer that has a large number of hydroxyl (-OH) groups and hence allows hydrogen bonding, which provides good mechanical strength and adhesion. It has gained a lot of application in the making of photonic films and wave guides [5]. Conversely, PVP is an amorphous and highly transparent polymer with carbonyl ($> C=O$) groups and is able to bind metal ions as a coordination site thereby enhancing their dispersion through the matrix [6]. A combination of PVA and PVP produces a synergistic compound that incorporates the crystallinity and mechanical strength of PVA and the chemical compatibility and optical transparency of PVP, and is an appropriate host of rare earth ions like terbium.

The inclusion of terbium ions into a PVA/PVP polymer blended system creates a distinct hybrid material which is a combination of the good photoluminescence property of Tb^{3+} with the mechanical and processing benefits of the polymer host. Tb^{3+} is the greenest emitter due to the sharp and intense green emissions and therefore, it can be successfully used in green-emitting devices [7]. In addition, the long lifetime and high color purity of Tb^{3+} emissions make such systems desirable in optoelectronic and anti-counterfeiting applications.

The microstructure and coordination environment of the RE ions play crucial roles in determining the photoluminescence efficiency of polymer films doped with the rare earth elements. In this regard, it is important to know how Tb^{3+} ions will react with the functional groups of PVA and PVP because these reactions may greatly affect the luminescence properties. The hydroxyl groups in PVA and the carbonyl groups in PVP can coordinate with the Tb^{3+} ions and this

may result in stable complexes that inhibit ion clustering and enhance the intensity of emission [8]. It is also essential to optimize the blending ratio and doping concentration to avoid the quenching of concentrations and even distribution of ions.

The luminescent properties of Tb^{3+} -doped polymer films have been demonstrated in several studies. For instance, Balakrishna et al. (2020) reported enhanced luminescence in Tb^{3+} -doped PVA films due to efficient energy transfer and favorable coordination within the polymer network [9]. Correspondingly, Chithra et al. (2018) reported Tb^{3+} doped PVP films and observed a strong green emission that can be used in applications in flexible displays [10]. Nonetheless, very little research has been conducted regarding the synergistic properties of incorporating PVA and PVP with Tb^{3+} doping, which may provide a better platform on which the optical and structural characteristics of the resultant composite films can be modulated.

The present work focuses on the synthesis and characterization of Tb^{3+} -doped PVA/PVP blend polymer films, emphasizing their structural and optical properties. The novelty of this study lies in examining the synergistic effects of PVA/PVP blending to enhance the luminescence efficiency and stability of Tb^{3+} ions within the matrix. The influence of varying Tb^{3+} concentrations on the structural, bonding, and photoluminescent behaviors of the films is systematically analyzed using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, and photoluminescence (PL) measurements. The outcomes of this investigation are expected to contribute to the development of efficient, flexible luminescent materials for photonic and display technologies.

2 Experimental Procedure

2.1 Raw materials and films preparation

Polyvinyl alcohol (PVA) with a molecular weight of 85,000 and polyvinyl pyrrolidone (PVP) with a molecular weight of 40,000 were used as base polymers, while terbium nitrate hexahydrate [$Tb(NO_3)_3 \cdot 6H_2O$], all with 99.9% purity, were procured from Sigma-Aldrich. The polymer blend was prepared using the solution casting method, in which equal proportions of PVA and PVP (50:50) were dissolved in distilled water. The resulting solution was magnetically stirred at room temperature for 7 hours to ensure thorough mixing and complete dissolution. To remove entrapped air bubbles, the homogenous degassed solution was subsequently transferred into clean glass Petri dishes and left to dry at room temperature in one week. Following full drying, the freestanding films were peeled carefully and they were kept in desiccators until their characterization.

For doping, aqueous solutions of terbium nitrate were prepared in various concentrations (0.1 wt%, 0.3 wt%, 0.5 wt%, and 0.7 wt%). Each Tb^{3+} solution

was added dropwise into the PVA/PVP blend under constant magnetic stirring for 7 hours to achieve uniform dispersion of terbium ions throughout the polymer matrix. The resulting doped solutions were processed in the same manner as the undoped blend to obtain the corresponding doped films.

2.2 Characterization techniques

All the samples prepared, which include both the undoped PVA/PVP blend and the Tb^{3+} -doped PVA/PVP polymer films, underwent various characterization methods. Structural analysis was performed using X-ray diffractometer (Shimadzu XRD- 6000) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), with diffraction patterns recorded over a 2θ range of 10° to 60° . Functional group analysis was conducted through Fourier Transform Infrared (FTIR) spectroscopy using a Jasco FT-IR 430 spectrometer, covering the wavenumber range from 400 cm^{-1} to 4000 cm^{-1} . The Photoluminescence properties, including emission spectra and lifetime (decay) measurements were recorded using an Edinburgh FLS-980 UV-Vis-NIR spectrometer under 370 nm excitation.

3 Results and Discussion

3.1 Structural analysis (XRD)

Figure 1 presents the XRD patterns of pure PVA/PVP blend polymer and PVA/PVP: $x \text{ wt\% Tb}^{3+}$ ($x = 0.0, 0.1, 0.3, 0.5,$ and 0.7 wt\%) blend polymer films recorded in the 2θ range of 10° to 60° . The diffraction patterns show that characteristic peaks were detected at about 15° and 22° , which corresponds to the semicrystalline nature of the polymer blend and (200) reflection plane, as reported in the literature (JCPDS card No. 65-2870) [13–15].

The intensity of the diffraction peaks is gradually decreased with an increase in the concentration of Tb^{3+} ion from 0.1 to 0.7 wt%. This reduction in intensity provides strong evidence for the successful incorporation of Tb^{3+} ions into the PVA/PVP polymer matrix, leading to disruption of the ordered assembly of polymer chains. At lower dopant concentrations, the diffraction peaks are still relatively sharp and intense, which means there is a higher degree of structural ordering. However, at higher concentration of Tb^{3+} , the peaks broaden and weaken, indicating a decrease in crystallinity, which can be explained by the interference between intermolecular interactions between PVA and PVP chains.

The crystallinity reduction with the rare earth ions concentration suggests that the Tb^{3+} ions act as a structural modifier by changing the microstructural organization of the polymer matrix. This conclusion can also be substantiated by the FTIR analysis (Figure 2), which demonstrates that the position of the bands is changed, as well as the intensity of the bands is reduced, which proves that the polymer functional groups are coordinated with the Tb^{3+} ions. The XRD

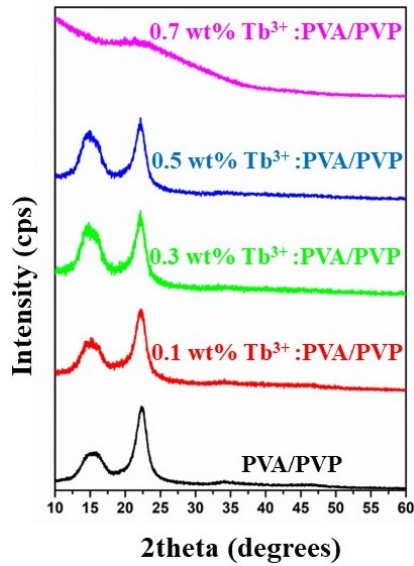


Figure 1. XRD patterns of pure PVA/PVP blend and Tb^{3+} -doped PVA/PVP polymer films with varying Tb^{3+} concentrations.

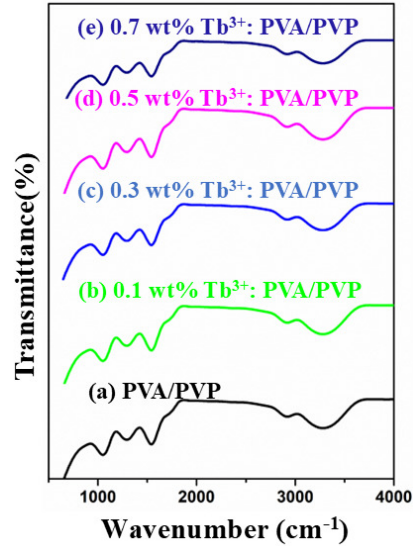


Figure 2. FT-IR spectra of pure PVA/PVP blend and Tb^{3+} doped PVA/PVP polymer films with varying Tb^{3+} ion concentrations.

and FTIR findings taken together prove the existence of polymer-metal interactions and indicate that Tb^{3+} doping has an essential impact on the structure and bonding properties of the PVA/PVP blend films.

3.2 FTIR spectroscopy

The FT-IR spectra of the pure PVA/PVP polymer blend and the Tb^{3+} -doped PVA/PVP films of different concentrations are shown in Figure 2. The typical vibrational bands that represent C–H bending and CH_2 twisting (out-of-plane) are the ones at 1050 cm^{-1} and 1300 cm^{-1} , respectively [16]. The $C = N$ stretch of the pyridine ring of PVP is the absorption band at 1533 cm^{-1} [17]. Also, the bands at around 2917 cm^{-1} and 3294 cm^{-1} represent the CH_2 asymmetric stretching and OH stretching bands of the PVA/PVP blend, respectively [18].

All the significant characteristic peaks were sustained with slight variations in the pure PVA/PVP blend indicating the presence of hydrogen bonding between the hydroxyl groups of PVA and carbonyl groups of PVP. When Tb^{3+} ions were incorporated, some significant shifts were observed and the intensity of some of the absorption bands decreased. These spectral changes are evidence of the coordination of the functional groups of the polymer matrix with Tb^{3+} ions,

resulting in the creation of a polymer-metal complex. These interactions modify the local structure environment around the rare-earth ions, hence, affecting the physicochemical characteristics of the doped polymer films.

3.3 Photoluminescence analysis

The PL emission spectra (Figure 3) of Tb^{3+} -doped PVA/PVP films exhibited four sharp emission bands centered at 543 nm (${}^5D_4 \rightarrow {}^7F_5$), 584 nm (${}^5D_4 \rightarrow {}^7F_4$), and 620 nm (${}^5D_4 \rightarrow {}^7F_3$), characteristic of Tb^{3+} ions [19]. Among these, the green emission at 543 nm was the most intense, dominating the spectrum. Among the observed transitions, the green emission corresponding to the ${}^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} at 543 nm is the most intense. This strong emission arises due to the shielding of the 4f electrons by the outer 5s and 5p orbitals, which effectively isolates them from external ligand fields. As a result, the 4f–4f transitions exhibit very sharp and well-defined spectral lines, in contrast to the broader d–d transitions typically seen in d-block elements. The narrow emission bands are primarily influenced by the weak perturbations from the surrounding ligand field. The ${}^5D_4 \rightarrow {}^7F_5$ transition is a magnetic dipole transition and obeys to Laporte's selection rule, where the change in total angular momentum quantum number $\Delta J = \pm 1$ is allowed. The emission intensity initially increases with increasing Tb^{3+} concentration, reaching a maximum at 0.5 wt%. Beyond this optimal concentration, a gradual decrease in intensity is observed due to concentration quenching effects. This phenomenon occurs when the aver-

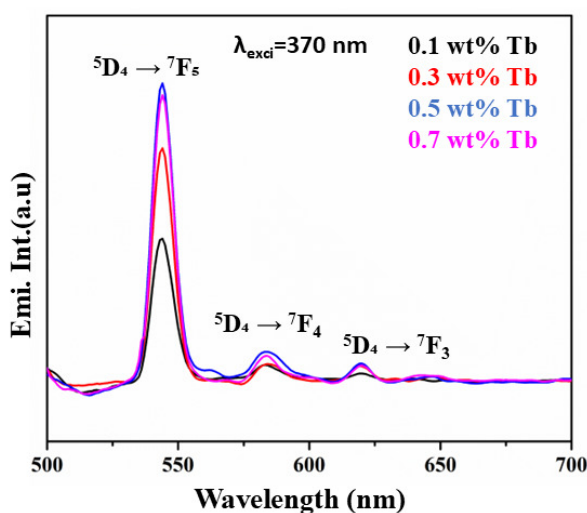


Figure 3. Photo luminescence of the Tb^{3+} doped PVA/PVP blend polymer films with the excitation at 370 nm.

age distance between Tb^{3+} ions become small enough to facilitate non-radiative energy transfer processes. The concentration quenching effect ultimately leads to a reduction in the overall luminescence efficiency of the material at higher dopant levels.

Figure 4 displays a partial energy level diagram for the Tb^{3+} ion when excited at 370 nm, highlighting the related excitation and de-excitation paths among the energy levels. The diagram depicts non-radiative transitions that arise from a cross-relaxation process between two excited states, which have an energy difference of 5864 cm^{-1} .

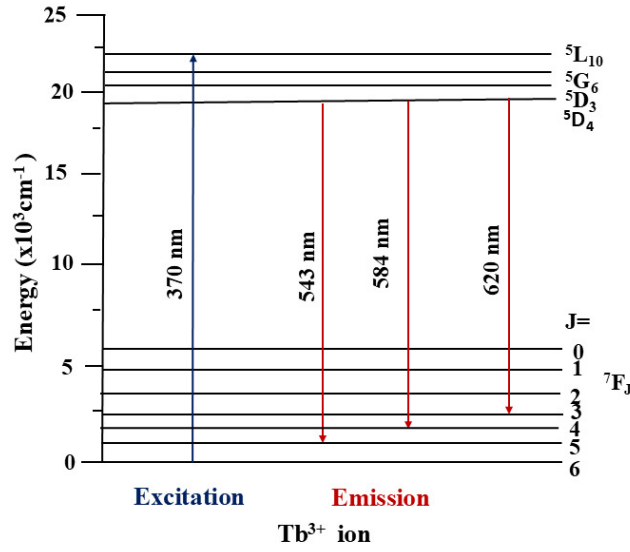


Figure 4. Schematic Energy level representation of Tb^{3+} ions in the PVA/PVP blend polymer film.

The luminescence decay behavior of Tb^{3+} ions doped in the PVA/PVP polymer matrix provides valuable insight into the dynamic processes governing excited state relaxation and energy transfer mechanisms. To evaluate these characteristics, time-resolved photoluminescence measurements were carried out by monitoring the green emission at 543 nm ($5D_4 \rightarrow 7F_5$) following pulsed excitation at 370 nm. The decay curves for the $5D_4$ excited state were recorded for various concentrations of Tb^{3+} ions (0.1 wt%, 0.3 wt%, 0.5 wt%, and 0.7 wt%) and are presented in Figure 5.

All the luminescence decay curves of the Tb^{3+} -doped PVA/PVP polymer films exhibit a good fit with a single-exponential decay model, described by the equation

$$I = I_0 \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

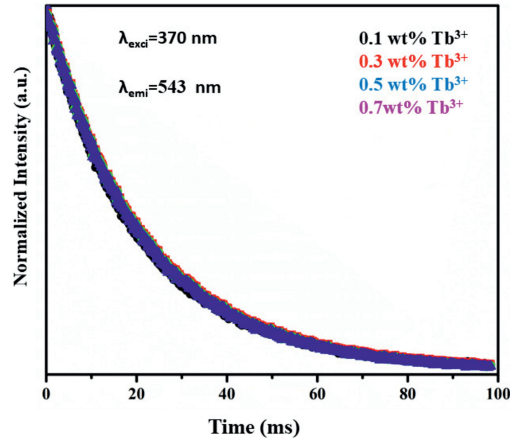


Figure 5. Lifetime decay dynamics of Tb^{3+} doped PVA/PVP blend polymer films at various Tb^{3+} ion concentrations.

where τ is the radiative decay time, and I and I_0 represent the luminescence intensities at time t and at $t = 0$, respectively. The observation of a single-exponential decay suggests a uniform distribution of Tb^{3+} ions within the polymer matrix, implying that all dopant ions occupy similar local environments and exhibit consistent relaxation dynamics.

Furthermore, the photoluminescence lifetimes gradually decrease from 1.58 ms to 1.50 ms as the Tb^{3+} concentration increases from 0.1 wt% to 0.7 wt%. This reduction in lifetime is likely due to enhanced non-radiative pathways, which may arise from increased defect densities and lowered local symmetry around the dopant ions at higher concentrations. These defects can act as quenching centers, promote non-radiative relaxation and thereby shorten the emission lifetime.

The CIE (Commission Internationale de l'Éclairage) chromaticity coordinates of PVA/PVP: $x\text{Tb}^{3+}$ blend polymer films under 370 nm UV excitation, for varying concentrations of Tb^{3+} ions ($x = 0.1$ wt%, 0.3 wt%, 0.5 wt%, and 0.7 wt%), are graphically illustrated in Figure 6. The corresponding CIE coordinates (x, y) were determined to be (0.2391, 0.6706), (0.2892, 0.6545), (0.2876, 0.6634), and (0.2914, 0.6482). These coordinates were also used to calculate the correlated color temperature (CCT), offering insight into the spectral characteristics of the emitted light. The grouping of these coordinates in the green region of the CIE 1931 chromaticity diagram confirms the dominant green photo luminescence of the Tb^{3+} -doped PVA/PVP films, as depicted in Figure 6. This pronounced green emission highlights the potential of these materials for use in display technologies and solid-state lighting. The application of the CIE 1931 chromaticity diagram provides a standardized and quantitative approach for representing color

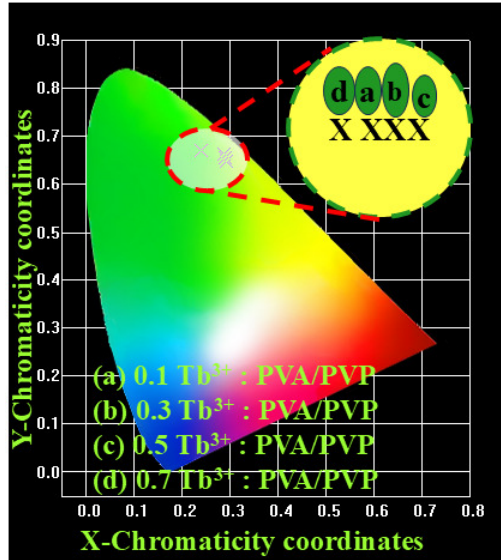


Figure 6. Concentration dependent CIE chromaticity behavior of Tb^{3+} doped PVA/PVP polymer films.

properties, facilitating accurate comparisons with other luminescent materials and industry color standards.

4 Conclusions

The solution casting technique was successfully used to fabricate the rare-earth ion (Tb^{3+}) doped polymer films by utilizing PVA/PVP blended solutions. The X-ray diffraction (XRD) analysis has indicated the semi-crystalline character of the polymer blend, whereas the FTIR spectra have shown strong evidence of intermolecular interactions as well as complex formation between the host polymers and the Tb^{3+} ions. A strong green emission at 543 nm (${}^5D_4 \rightarrow {}^7F_5$) was observed under 370 nm excitation (${}^7F_6 \rightarrow {}^5L_{10}$), which is the typical luminescence of Tb^{3+} ions.

The decay curves of the photoluminescence were non-exponential, which can be explained by the increased non-radiative transition due to the interaction between Tb^{3+} ions and the polymer matrix. Furthermore, the chromaticity coordinates of the films changed systematically with the concentration of Tb^{3+} suggesting tunable emission features. This tunability along with the high green luminescence highlights the possible applications of these films in the green light-emitting diodes (Green-LEDs). Overall, the results indicate that the Tb^{3+} doped PVA/PVP blend films have great potential as novel optical materials for display and photonic device applications.

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