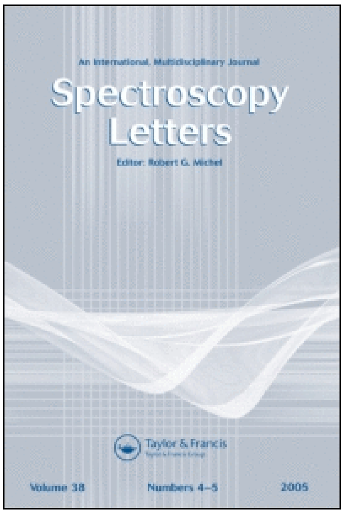

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G. Seeta Rama Raju[a]; S. Buddhudu[a]; A. Varada Rajulu[b]; L. Ganga Devi[b]
[a] Department of Physics, S.V. University, Tirupati, India [b] Department of Polymer Science, S.K. University, Anantapur, India

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Emission Spectra of Tb^{3+}:PVA Polymer Films

G. Seeta Rama Raju and S. Buddhudu
Department of Physics, S.V. University, Tirupati, India

A. Varada Rajulu and L. Ganga Devi
Department of Polymer Science, S.K. University, Anantapur, India

Abstract: This paper reports on the development and optical analysis of Tb^{3+}-doped polyvinyl alcohol (PVA) films. A reference PVA film has also been prepared for which X-ray diffraction (XRD) spectral profile has been carried out; it was found that this polymer possesses a semi crystalline nature. Spectral analysis of the Tb^{3+}:PVA polymer film has been made based on the measurement of the excitation, emission, and decay curves of the emission transitions ($^5D_4 \rightarrow {}^7F_{6,5,4\&3}$). Under a UV source (254 nm), a bright green emission was noticed from the surface of Tb^{3+}:PVA film. The current study reveals that this terbium polymer film could be suggested as a novel green luminescent material.

Keywords: Doped films, emission, excitation, fluorescent systems, polyvinyl alcohol, terbium

INTRODUCTION

It is well-known that optical properties of different rare-earth ion–doped materials are be found to be dependent on the host matrices used.[1–5] In recent times, more emphasis has been made toward the development of polymer-based luminescent optical materials.[6–9] From the literature it has been reported that a prominent green luminescence could be obtained from the terbium (Tb^{3+})-doped glasses and phosphors.[10–15] Polyvinyl alcohol

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Address correspondence to S. Buddhudu, Department of Physics, S.V. University, Tirupati 517502, India. E-mail: drsb99@hotmail.com

(PVA) is widely known as a promising material for its potential uses in industry, pharmaceuticals, film coatings, magnetic media, and so forth.[16–23] Because there has not been any work done in literature on the Tb^{3+} ion–doped polyvinyl alcohol (PVA)-based polymer film, we have undertaken this work for its spectroscopic analysis from the measurement of absorption spectrum, excitation and emission spectra along with the lifetimes of the emission transitions ($^5D_4 \rightarrow {}^7F_{6,5,4,3}$) in the visible wavelength range with an excitation at 374 nm. Even under UV source, these Tb^{3+}-doped PVA polymer films have displayed bright green emission from their surfaces. In order to undertake the analysis of Tb^{3+}:PVA films, we have followed Tb^{3+}-doped sol-gel derived films and polysiloxanes.[24–30]

MATERIALS AND METHODS

In the current work, undoped and terbium-doped (0.1 mol%) PVA (with a molecular weight (MW) of 14,000, Loba Chemie pvt. Ltd) polymer films were developed from aqueous solutions by means of a film-casting method. Polymer films with a uniform thickness of 1 mm were cast by using a thin-layer chromatography (TLC) spreader. Regarding the preparation of Tb^{3+} ions–doped PVA films, $TbCl_3$ (MW = 373.38 g, Aldrich) salt was dissolved separately in a beaker containing double-distilled water at room temperature, then this rare-earth salt–mixed solution was mixed with the PVA solution, and this resultant rare-earth–doped PVA solution was stirred with a magnetic stirrer continuously to ensure homogeneity in the solution mixture, and this solution was used on a TLC spreader in order to produce a 1-mm-thick Tb^{3+}:PVA polymer film 15 cm long and 10 cm wide. These films were cut into different sizes and in the present work; we have used films of 50 mm × 20 mm × 1 mm dimensions for its optical characterization. The XRD spectrum of PVA film was recorded on a X' pert PRO X-ray diffractometer with CuK_α (1.54056 Å) radiation that was operated at 40 kV with about 50 mA anode current. The refractive indices of the reference PVA film have been measured by using Abbe refractometer at three different wavelengths (479.99 nm of Cd-lamp, 589.3 nm of Na-lamp, 643.85 nm of Cd-lamp) and are given in the Table 1. Absorption spectra of reference PVA film and

Table 1. Physical quantities of the PVA polymer film

Molecular weight (MW) g	14,000
Density (d)	1.35 g/cc
Tb^{3+} ion concentration, N_{Tb}^{3+}	5.808×10^{18}(ions/cm^3)
n_d at 589.30 nm	1.340
n_F at 479.99 nm	1.344
n_C at 643.85 nm	1.337

Tb^{3+}:PVA films were recorded on a Jasco Absorption Spectrophotometer in the wavelength range of 200–500 nm. Both excitation and emission spectra of Tb^{3+}:PVA polymer films were recorded in the wavelength range 200–650 nm on a SPEX Fluorolog-2 Fluorimeter (model II) attached to a Xe-Arc Lamp (150 W). This fluorescence system employs the Datamax Software in acquiring spectral data of the samples used. For the measured emission bands, lifetimes were obtained on the same fluorimeter with an Xe-flash lamp and a phosphorimeter attachment to the main system with a control system while measuring the decay curves of these emission bands. All the above spectra are recorded at room temperature. The physical characteristic parameters of the reference PVA film are given in Table 1.

RESULTS AND DISCUSSION

Tb^{3+}:PVA film has shown a prominent green emission from its surface under UV source as shown in Fig. 1. The measured X-ray diffraction (XRD) spectral profile of the Tb^{3+}:PVA polymer film is given in Fig. 2, which confirms the semicrystalline nature of the polymer, as was reported previously in literature.[21,22] The measured refractive indices are used in evaluating the Cauchy's constants (A&B), and the Cauchy's formula of refractive index (n), as a function of wavelength (λ), is given by $n(\lambda) = A + B/\lambda^2$, which depends on the wavelength employed,[24] and the computed values of the Cauchy's constants are $A = 1.32955$ and $B = 3630.4\ nm^2$. The theoretical plot of refractive indices obtained through a Cauchy's formula as function of wavelength is shown in Fig. 3. With these Cauchy's constants, the correlation between the measured and computed refractive indices at three wavelengths have been found to be good enough. The optical dispersion ν_d^{-1}) of this polymer film has been evaluated based on the refractive indices according to the formula $\nu_d^{-1} = (n_F - n_C)/(n_d - 1)$[25] and the calculated

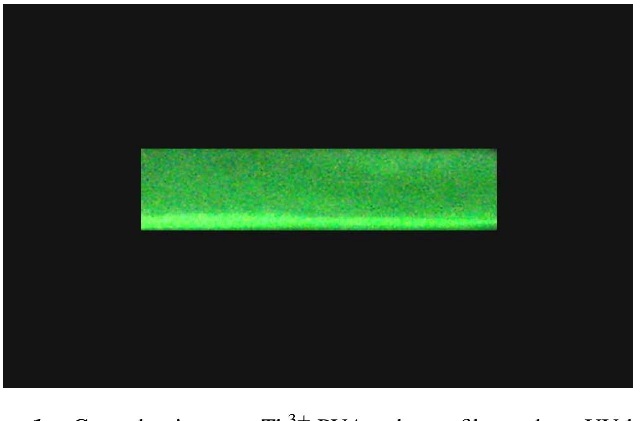

Figure 1. Green luminescent Tb^{3+}:PVA polymer film under a UV lamp.

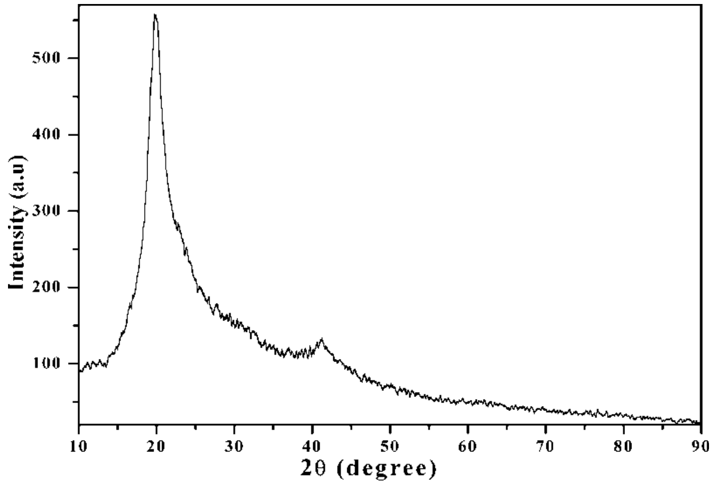

Figure 2. XRD profile of the PVA polymer film.

value is 0.0206. Absorption spectra of the reference PVA film and Tb^{3+}:PVA films are shown in Figs. 4a and 4b, respectively. From the PVA absorption spectrum (Fig. 4a), it is noticed that there is a weak absorption band at 275 nm, which is in agreement with the reported value.[23] From Fig. 4b, it is observed that there exists a strong absorption band at 263 nm for the Tb^{3+}:PVA besides nine more weaker absorption bands at 284 nm, 295 nm,

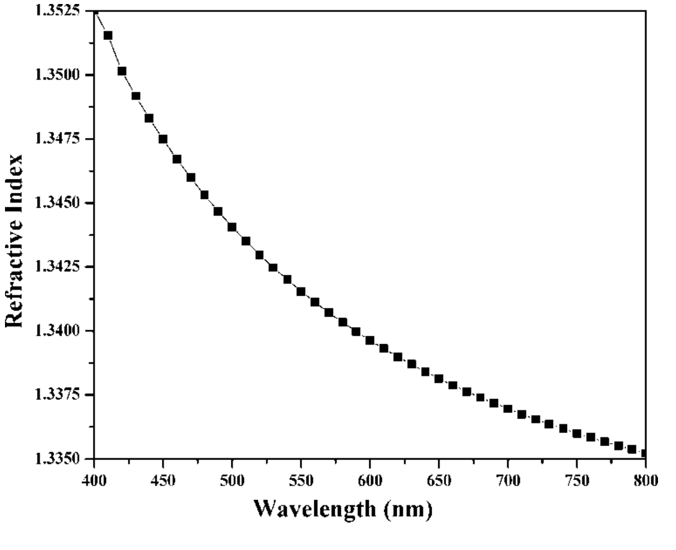

Figure 3. Refractive indices of PVA polymer film from cauchy's method.

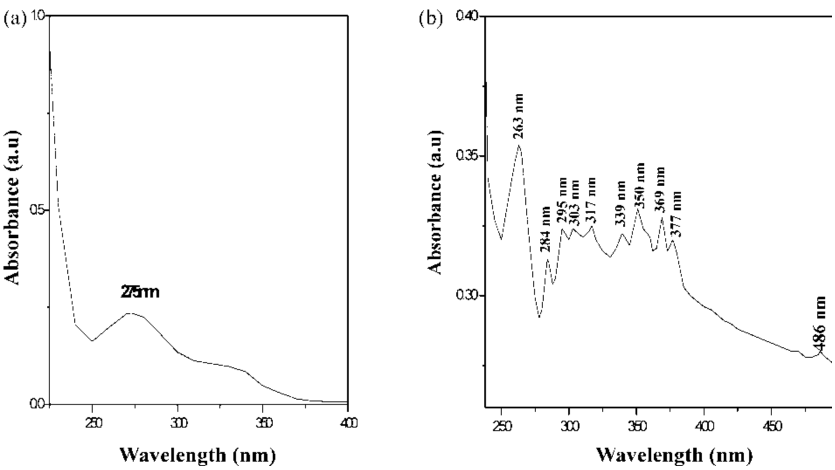

Figure 4. (a) Absorption spectrum of pure PVA film. (b) Absorption spectrum of Tb^{3+}:PVA film.

303 nm, 317 nm, 339 nm, 350 nm, 369 nm, 377 nm, and 486 nm, respectively, and those have appropriately been assigned to the electronic transitions such as ($^7F_6 \rightarrow {}^5I_5$) at 263 nm, ($^7F_6 \rightarrow {}^5I_8$) at 284 nm, ($^7F_6 \rightarrow {}^5H_5$) at 295 nm, ($^7F_6 \rightarrow {}^5H_6$) at 303 nm, ($^7F_6 \rightarrow {}^5H_7$) at 317 nm, ($^7F_6 \rightarrow {}^5L_6$) at 339 nm, ($^7F_6 \rightarrow {}^5L_9$) at 350 nm, ($^7F_6 \rightarrow {}^5L_{10}$) at 369 nm, ($^7F_6 \rightarrow {}^5G_6$) at 377 nm,

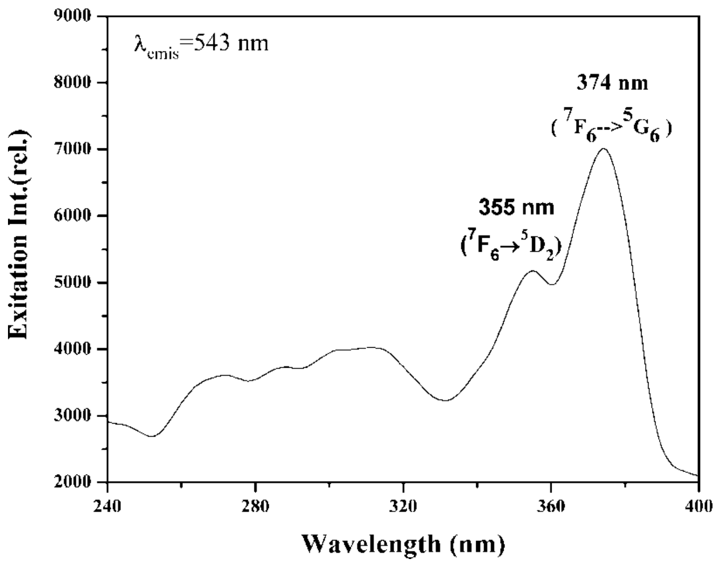

Figure 5. Excitation spectrum of Tb^{3+}:PVA polymer film.

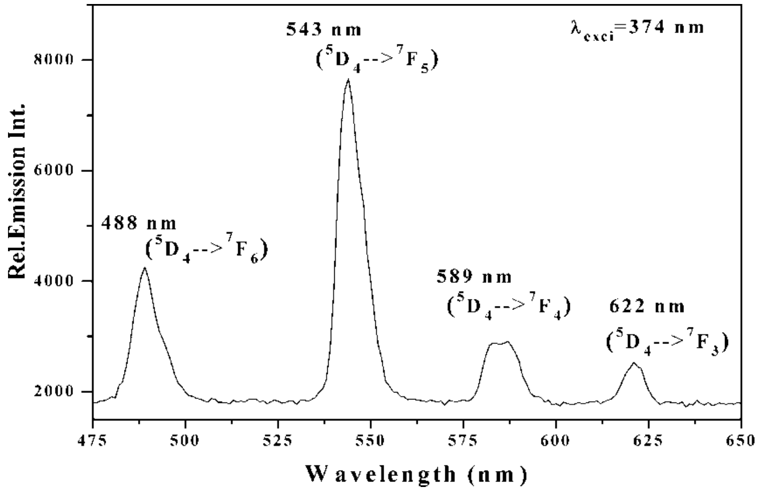

Figure 6. Emission spectrum of Tb^{3+}:PVA polymer film.

and ($^7F_6 \rightarrow {}^5D_4$) at 486 nm, which are also in agreement with the reported values.[15] The excitation spectrum (240–400 nm) of the terbium-doped polymer is shown in Fig. 5. It consists of a number of lines in the region from 240 nm to 320 nm, a weak band at 355 nm to the spin forbidden transition and a strong band at 374 nm to the spin allowed transition of Tb^{3+}, which belong to the electronic transitions ($^7F_6 \rightarrow {}^5D_2$) and ($^7F_6 \rightarrow {}^5G_6$), respectively. The lines correspond with absorption of the forbidden f-f

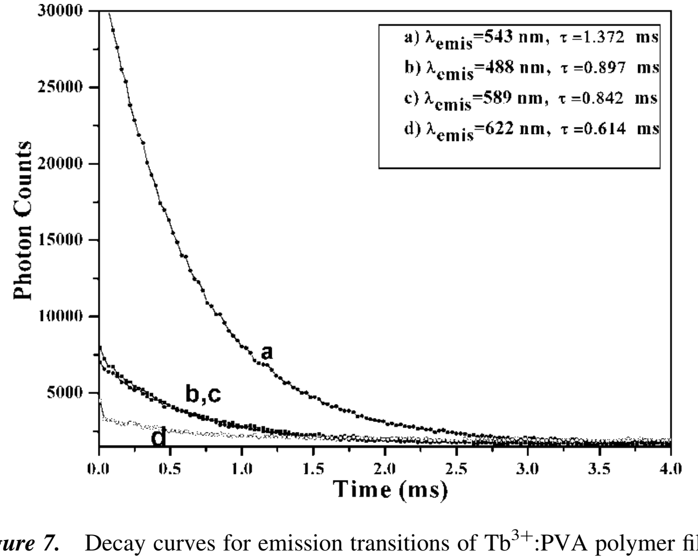

Figure 7. Decay curves for emission transitions of Tb^{3+}:PVA polymer film.

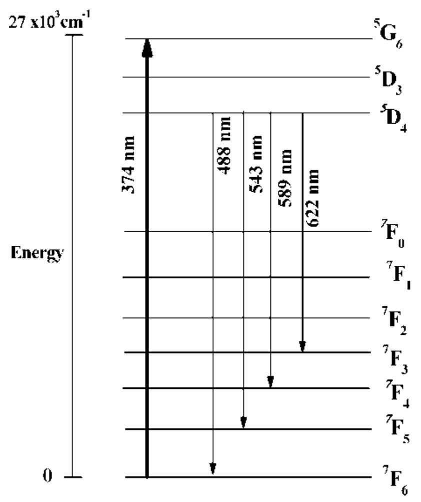

Figure 8. Emission mechanism in Tb^{3+}:PVA polymer film.

transitions of Tb^{3+} ions. Emission spectrum of this polymer film is shown in Fig. 6, which demonstrates an intense *green* emission ($^5D_4 \rightarrow {}^7F_5$) at 543 nm, a medium intense *blue* emission ($^5D_4 \rightarrow {}^7F_6$) at 488 nm, a weak *orange* emission ($^5D_4 \rightarrow {}^7F_4$) at 589 nm, and a weaker *red* emission ($^5D_4 \rightarrow {}^7F_3$) at 622 nm. Among these four emission bands, the green emission band ($^5D_4 \rightarrow {}^7F_5$) is a magnetic dipole transition satisfying the selection rule of $\Delta J = \pm 1$. Figure 7 presents the exponential decay curves of the Tb^{3+}-doped PVA polymer film for four emission transitions with the ($^5D_4 \rightarrow {}^7F_5$) transition having a longer lifetime of 1.372 ms; other three emission transitions have the lifetimes $^5D_4 \rightarrow {}^7F_6$ (0.897 ms), $^5D_4 \rightarrow {}^7F_4$ (0.842 ms), and $^5D_4 \rightarrow {}^7F_3$ (0.614 ms). An energy level scheme is given in Fig. 8 to explain the mechanism involved in the emission process in the Tb^{3+}:PVA polymer film with a pump wavelength at 373 nm, which belongs to the transition of ($^7F_6 \rightarrow {}^5G_6$). The emission intensity of $^5D_3$, $^5D_4 \rightarrow$ $^7F_0$, $^7F_1$, $^7F_2$ were weak enough and were neglected.

CONCLUSIONS

In summary, it could be stated that we have successfully developed Tb^{3+}: PVA polymer films, and their optical properties have been carried out systematically based on their spectral profiles. Apart from this, under a UV source these films have shown bright green luminescence from their surfaces. In view of these, it could be suggested as a novel optical material of significant technical importance as luminescent systems for various display applications.

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