Red Emission from Eu^{3+} : PVA Polymer Film

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ABSTRACT: Bright red luminescent Eu^{3+} doped polyvinyl alcohol (PVA) films were made by solution casting technique. The emission performance of these films was studied from the measurement of excitation, emission, and lifetimes. On irradiation with an UV source, the doped films emitted bright red light. Such luminescent polymer films are expected to find potential applications as new optical materials. Emission process in the system was explained by an energy level scheme. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3273–3276, 2006

Key words: Eu^{3+} : PVA polymer film; emission analysis; lifetime

INTRODUCTION

Earlier, from our laboratory, different optical glasses were developed with various transition metal and rare earth ions to understand their spectroscopic properties more systematically.[1–8] In recent times, a special attention is focused to explore the possibility of using polymer films and modified polymer films as potential optical materials.[9–20] Based on the survey made in the literature, it has been found that earlier a little work has been reported on polymers with Eu^{3+} and with other lanthanide ions such as Nd^{3+}, Er^{3+}, etc.[9,12,15–20] From these papers, we understand that polymer films with rare earth (RE) ions have rich applications in different optical fields such as optical sensors, electro luminescent displays, optical amplifiers, and optical wave guides. In our preliminary effort, a basic polymer namely polyvinyl alcohol (PVA) film was developed and its properties, including absorption spectrum, were understood. To develop luminescent material, terbium (Tb^{3+}) was doped in PVA, which was found to emit green light on excitation with UV radiation.[21] Upon going through the literature, it has become quite clear to realize the fact that in PVA film with Eu^{3+} ion no emission analysis has been studied so far, that is why we have chosen it to study its emission behavior. When it was examined under an UV-source, a bright red emission was displayed by this simple PVA film due to the presence of Eu^{3+} ions in its matrix.

EXPERIMENTAL

Polymer films preparation

In the present work, undoped and europium doped (0.1 mol %) PVA (MW 14,000; Loba Chemie pvt. Ltd) films were made from aqueous solutions by film casting method. The films with uniform thickness of 1 mm were cast using a thin layer chromatography (TLC) spreader. Regarding the Eu^{3+} : PVA films, at first, the rare earth chemical $EuCl_3$ (MW 258.32; Aldrich) was dissolved in double distilled water and the Eu^{3+} ions doped aqueous solution was obtained. And this solution was used to mix with the cooled PVA solution and the resultant solution was thoroughly mixed for achieving homogeneity by using a magnetic stirrer. This resultant Eu^{3+} : PVA solution was cast on to a glass plate by using a TLC Spreader and thus 1 mm thick Eu^{3+} : PVA polymer films were obtained from the glass plate upon drying them for 24 h time. For carrying out optical analysis on these films, we did obtain thin films in the dimensions of $60 \times 30 \times 1$ mm^3.

Characterization

The XRD spectrum of pure PVA was measured on a X' pert PRO X-ray diffractometer with Cu Kα (1.5405 Å), and it was operated at 40 KV voltage and 50 mA anode current. The absorption spectra of both PVA and Eu^{3+} : PVA films were measured on a Jasco absorption spectrophotometer in the wavelength range of 200–500 nm. The photoluminescence (excitation and emission) spectra of Eu^{3+} : PVA films were recorded on a Spex Fluorolog-2 Fluorimeter (model-II), with a Xenon arc lamp of 150 W power as an excitation source for a steady state emission

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TABLE I
Physical Properties of PVA Polymer

Properties	Data
Molecular weight, m (g)	14,000
Density, d (g/cc)	1.35
Refractive index, n	1.32
Eu^{3+} ion concentration, $N_{Eu^{3+}}$	5.808×10^{18}

spectrum measurement on this system. While measuring the lifetimes of the observed emission transitions, the decay curves were plotted to evaluate the lifetime 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. The necessary physical characteristic parameters of the reference PVA film are given in Table I.

RESULTS AND DISCUSSION

To examine the fluorescence nature, both the undoped and Eu^{3+} doped PVA films were exposed to UV radiation. No changes were observed when undoped PVA film was irradiated with UV source. However, the Eu^{3+} : PVA film showed red emission from its surface. This is clearly revealed by the photograph of the UV irradiated Eu^{3+} : PVA film presented in Figure 1. This observation preliminarily indicates the fluorescent nature of the Eu^{3+} : PVA system. The measured XRD spectral profile of the reference PVA polymer film is shown in Figure 2 and it confirms the semi crystalline nature of this film, as was reported previously in the literature.[13,14] Figure 3(a, b) shows the absorption spectra of the reference PVA polymer film and Eu^{3+} : PVA polymer film, respectively. From the PVA absorption spectrum [Fig. 3(a)], it was noticed that there is a weak absorption band located at 275 nm, which is in agreement with the value reported in the literature.[10] From Figure 3(b), it was found that

Figure 2 XRD spectrum of pure PVA film.

there is a strong absorption band located at 394 nm for the Eu^{3+} : PVA polymer film and there are four more weaker absorption bands in the spectrum and

(a)

(b)

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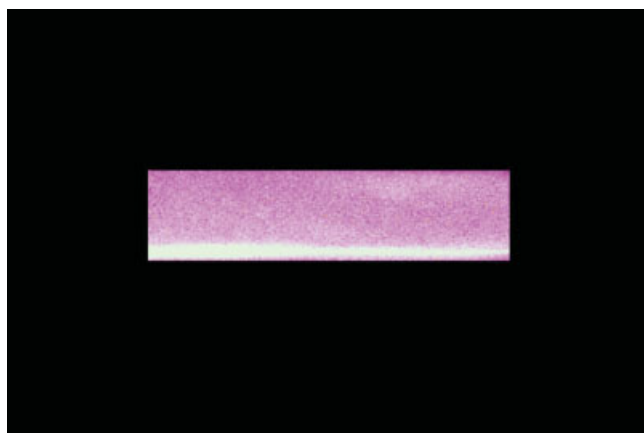

Figure 1 Photograph of red luminescent Eu^{3+} : PVA film under an UV source. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
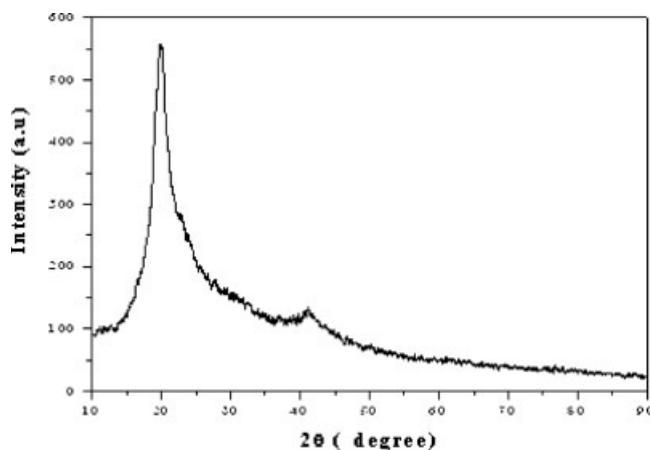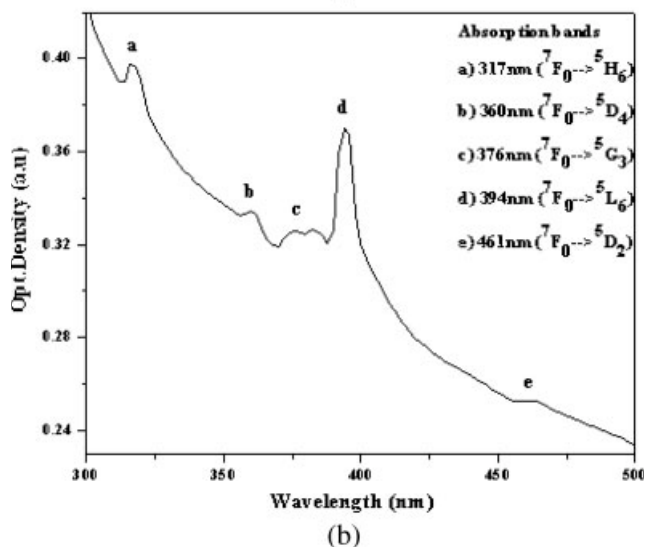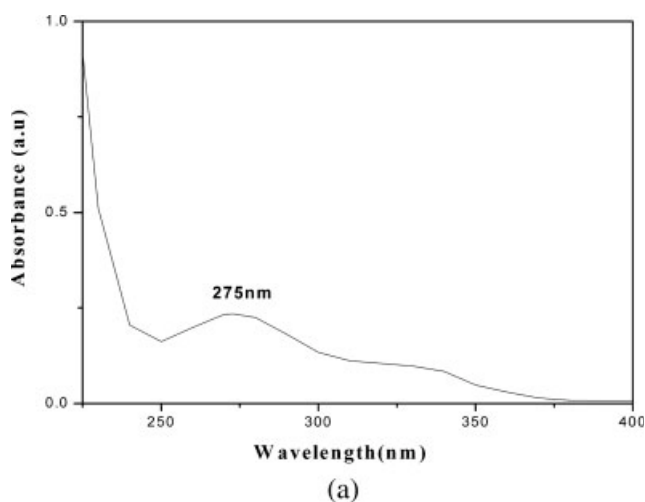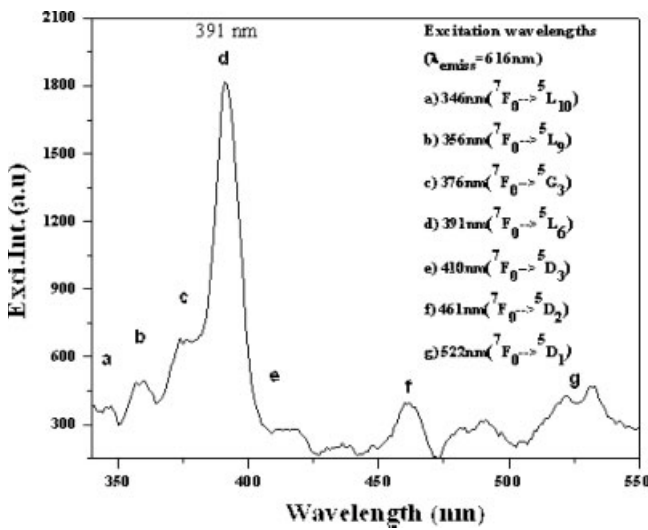
Figure 4 Excitation spectrum of Eu^{3+} : PVA film.

TABLE II
Selection Rules used in Identifying the Electric Dipole and Magnetic Dipole Transitions of Eu^{3+} : PVA Film

Electric dipole transitions	$\Delta s = 0$, $\Delta l = \pm 1$; Δl, $\Delta J \leq 6$ unless J or $J^1 = 0$ when $\Delta J = 2, 4, 6$
Magnetic dipole transitions	$\Delta s = \Delta L = 0$; $\Delta J \leq 1$ except 0–0; $\Delta l = 0$
Electric quadruple transitions	$\Delta s = 0$, ΔL, $\Delta J \leq 2$ (except 0–0, 0–1), $\Delta l = 0$
Vibranic transitions	$\Delta J = 0$, ± 2
Phonon process transitions	ΔL, $\Delta J \leq 6$ unless J or $J^1 = 0$ when $\Delta J = 2, 4, 6$

these are appropriately identified with the corresponding electronic transitions such as ($^7F_0 \rightarrow {}^5H_6$) at 317 nm ($^7F_0 \rightarrow {}^5D_4$) at 360 nm, ($^7F_0 \rightarrow {}^5G_3$) at 376 nm, ($^7F_0 \rightarrow {}^5L_6$) at 394 nm, ($^7F_0 \rightarrow {}^5D_2$) at 461 nm, respectively and these bands have also been observed from the measured excitation spectrum of the europium doped polymer film. Figures 4 and 5 present the excitation and emission spectra of Eu^{3+} : PVA polymer film. The excitation spectrum reveals seven excitation bands such as ($^7F_0 \rightarrow {}^5L_{10}$) at 346 nm, ($^7F_0 \rightarrow {}^5L_9$) at 356 nm ($^7F_0 \rightarrow {}^5G_3$) at 376 nm, ($^7F_0 \rightarrow {}^5L_6$) at 391 nm, ($^7F_0 \rightarrow {}^5D_3$) at 410 nm, ($^7F_0 \rightarrow {}^5D_2$) at 461 nm, and ($^7F_0 \rightarrow {}^5D_1$) at 522 nm. Among them, one transition ($^7F_0 \rightarrow {}^5L_6$) at 391 nm has the maximum excitation intensity and hence with this excitation band the emission spectrum has been obtained. It is well known that because of the shielding effect experienced by $4f^6$ electrons from the 5s and 5p electrons, Eu^{3+} : PVA exhibits nar-
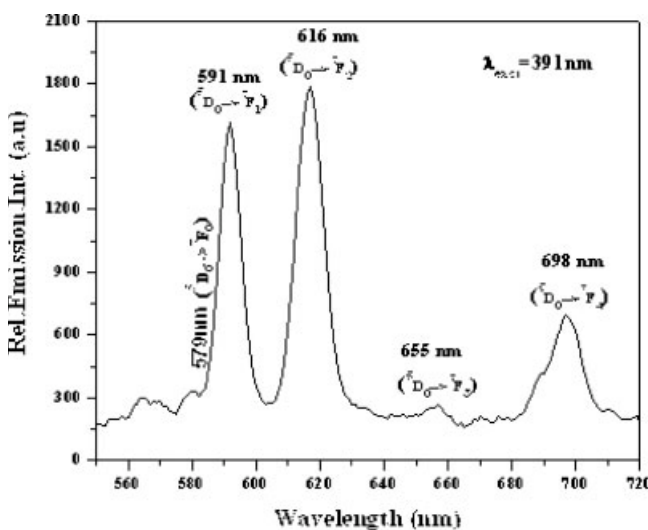
row emission bands because of high non-radiative relaxations from the excited states of energy higher than $^5D_0$ state. The intense emission bands in the range of 590–700 nm are assigned to the electronic transitions of ($^5D_0 \rightarrow {}^7F_{J=1,2,3,4}$), and the transitions such as $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions are electric dipole (ED) transitions. In particular, the red emission ($^5D_0 \rightarrow {}^7F_2$) is considered to be hypersensitive transition that follows the selection rule of $\Delta J = 2$ and hence demonstrates a very bright emission from Eu^{3+} : PVA polymer film. Another transition ($^5D_0 \rightarrow {}^7F_1$) with $\Delta J = 1$ has been identified as a magnetic dipole transition (MD), which is a bright orange emission band. It is well known that the host matrix environment around the Eu^{3+} ions could significantly influence the emission intensity of the hypersensitive transition ($^5D_0 \rightarrow {}^7F_2$). The intensities of the electric dipole transitions could be changing based on centre of symmetry variations due to change in the host environment around the luminescent rare earth ion. Conversely, the ($^5D_0 \rightarrow {}^7F_1$) emission around 591 nm is allowed by MD consideration; therefore, it is relatively weak in intensity compared to that of the hypersensitive transition. When Eu^{3+} ions are situated
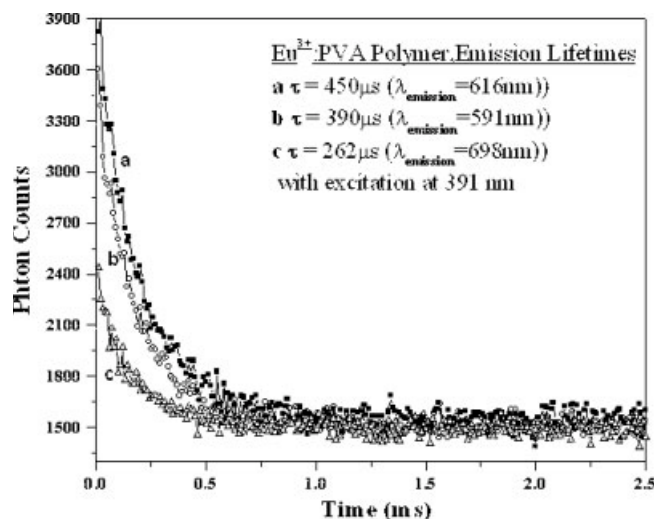

Figure 5 Emission spectrum of Eu^{3+} : PVA film.

Figure 6 Decay curves for emission transitions of Eu^{3+} : PVA film.
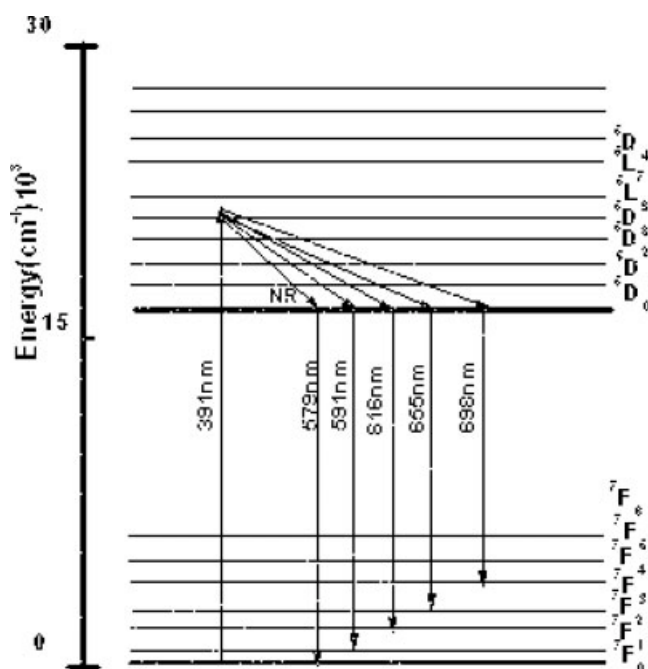
Figure 7 Energy levels scheme for the emission processes in Eu^{3+} : PVA film.

at low symmetry sites, the ED transition has larger probability than the MD transition.[22] Intra-f electrons could occur via ED, MD radiations, electric quadrapole, vibronic transitions, phonon assisted energy transfer (ET), which arise from Eu^{3+}–Eu^{3+} ions coupling, and multiphonon emissions. These transitions could be restricted by certain selection rules as listed in Table II.[23,24] The ratio between the emission intensities of the transitions such as ($^5D_0 \rightarrow {}^7F_2$) ED and ($^5D_0 \rightarrow {}^7F_1$) MD could bring out enough information on the richness of red color emission in comparison with the orange emission in order to develop strongly red luminescent display systems. For Eu^{3+} : PVA polymer film the R/O ratio is found to be 1.1. Figure 6 presents the decay curves of the three emission bands, ($^5D_0 \rightarrow {}^7F_{1,2,4}$) with an excitation wavelength at 391 nm. Because of the weak intensities displayed by the other two emission bands $^5D_0 \rightarrow {}^7F_{0,3}$, decay curves for these two bands could not be measured. However, for the remaining bands the decay curves have been plotted in evaluating the lifetimes. Figure 7 describes the emission process mechanism in Eu^{3+} : PVA polymer film.[23–29]

CONCLUSIONS

Very synthesis of PVA film has been well known over the past several years. Incorporation of Eu^{3+} ions in PVA film has not been done so far, hence we have made an attempt here to examine its fluorescence richness. The Eu^{3+} : PVA films were made by solution film casting technique. On UV irradiation, these films emitted bright red light, indicating their

fluorescent nature. Using the absorption, excitation, emission spectra, and decay curves, the emission properties of these films were studied. The resulting emission process was explained by the energy level diagram. The aforementioned studies indicate that Eu^{3+} : PVA film is a potential fluorescent optical material in red region and this can be used in electro luminescent displays.

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