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Structural and Optical analysis of Eu³⁺: PVA polymer films

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Abstract : The present paper reports on the development and optical analysis of PVA and Eu³⁺: PVA polymer films. For reference PVA film, the XRD spectral profile has been carried out and found that this polymer possesses a semi crystalline nature. Spectral analysis for different concentrations of (0.1, 0.15, 0.2 mol %) Eu³⁺: PVA polymer film has been made based on the measurement of the excitation, emission spectra. A Bright red emission was noticed from the Eu³⁺ doped polyvinyl alcohol (PVA) films .Under a UV source (254 nm) ,a bright red emission was noticed from the surface of Eu³⁺:PVA polymer film. Such emission polymer films are expected to find potential applications as new optical materials. **Keywords**: Optical materials; PVA polymer film; emission analysis;

Introduction

In recent times, a special attention is focused to explore the possibility of using polymer films and modified polymer films as potential optical materials. Based on the survey made in the literature, it has been found that earlier a little work has been reported on polymers with Eu³⁺and with other lanthanide ions such as Nd³⁺,Er³⁺,etc^{1,2,3}. 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. Upon going through the literature ^{4,5,6,7,8}, it has become quite clear to realize the fact that in PVA film with Eu³⁺ no emission analysis has been studied so far, that is why we have chosen it to study its emission behavior. When it was explained under an UV source, a bright red emission was displayed by this simple PVA film due to the presence of Eu³⁺ ions in its matrix^{9,10,11}.

Experimental studies

Polymer films preparation

In the present work, pure PVA(Mwt. 1, 25,000; S D Fine Chem. Ltd) and Eu^{3+} doped (0.1, 0.15, 0.2 mol %) PVA films were made from aqueous solutions by film casting method. Regarding Eu^{3+} : PVA films, EuNO₃ chemical was dissolved in PVA solution. These chemicals were dissolved in a small beaker (250 cc) containing double distilled water in different concentrations and then they were mixed by using a magnetic stirrer in a little warm condition for a homogenous mixing, later on these solutions were cast into polymer films

in flat based dishes through a slow evaporation method. Thus clearer and highly transparent PVA films were obtained.

Characterization

The XRD spectrum of pure PVA was measured on an X pert PRO X-ray diffractometer with cu k_{α} (1.5405 A⁰), and it was operated at 40 KV voltage and 50mA anode current. The absorption of both PVA and Eu³⁺: PVA films were measured on a Jusco absorption spectrophotometer in the wavelength range of 200-900 nm. The photoluminescence (excitation and emission) spectra of Eu³⁺: PVA films were recorded on a spex fluorolog -2 fluorimeter (model II), with a Xenon arc lamp of 150w power as an excitation source for a measurement of emission spectrum.

Results and Discussion



Figure 1 shows the measured XRD spectral profile of the reference PVA polymer film. And it confirms the semicrystalline nature of this film, as was reported previously in the literature^{13,14}.



Figure 2 shows the absorption spectrum of the pure PVA polymer film. From the PVA absorption spectrum it was noticed that there is a weak absorption band located at 275nm, which is in agreement with the value reported in the literature¹⁰.





Figure 3 (a, b) shows the excitation and emission spectra of Eu^{3+} : PVA polymer film. The excitation spectrum reveals six excitation bands such as $({}^{7}F_{0} \rightarrow {}^{5}D_{4})$ at 363 nm, $({}^{7}F_{0} \rightarrow {}^{5}G_{2})$ at 379 nm, $({}^{7}F_{0} \rightarrow {}^{5}L_{6})$ at 395 nm, $({}^{7}F_{0} \rightarrow {}^{5}D_{2})$ at 466 nm, $({}^{7}F_{0} \rightarrow {}^{7}F_{3})$ at 534 nm. Among them, one transition $({}^{7}F_{0} \rightarrow {}^{5}L_{6})$ at 395 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 4f⁶ electrons from the 5s and 5p electrons, Eu^{3+} : PVA exhibits narrow emission bands because of high non radiative relaxations from the excited states of energy higher than ${}^{5}D_{0}$ state. The intense emission bands in the range of 590 – 700 nm are assigned to the electronic transitions of $({}^{5}D_{0} \rightarrow {}^{7}F_{j=1, 2, 3, 4})$ and the transitions such as ${}^{5}D_{0} \rightarrow {}^{7}F_{j=2,4,6}$ transitions are electric dipole (ED) transitions. In particular, the red emission $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ is considered to be hypersensitive transition that follows the selection rule of ΔJ =2 and hence demonstrates a very bright emission from Eu^{3+} : PVA polymer film. Another transition $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ with ΔJ =1 has been identified as a magnetic dipole transition (MD) which is a bright orange emission band. Two weaker emission bands also observed in the spectrum and these are appropriately identified with the corresponding electronic transitions such as $({}^{5}D_{0} \rightarrow {}^{7}F_{3})$ at 654 nm, $({}^{5}D_{0} \rightarrow {}^{7}F_{4})$ at 696 nm. The measurement of emission spectrum with different concentrations (0.1, 0.15\&0.2), the 0.2 concentration is the most intense one. Then we calculate the decay lifetime for 0.2 concentration only. It is observed in figure4.



Conclusions

In summary, it could be concluded that transparent and more clear pure PVA and Eu^{3+} : PVA polymer films have successfully been developed by a solution cast method. For these polymer samples XRD studies have been carried out to understand their structural properties. From the measurement of host PVA we can conclude that a small weak absorption band. Photoluminescence spectra have been carried out for Eu^{3+} : PVA of concentration (0.1, 0.15 and 0.2 mol %). From the emission spectral measurement, it is clear that the red emission intensity increases with increase Eu^{3+} concentration.

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