Photoluminescence Analysis of Sm^{3+} and Dy^{3+} Doped PVA Films

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Received 24 March 2007; accepted 1 September 2007
DOI 10.1002/app.27257
Published online 9 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A couple of Poly vinyl alcohol (PVA) films with Sm^{3+} and Dy^{3+} ions have been prepared by a conventional solution cast technique. For these Sm^{3+} and Dy^{3+} doped PVA films, Fourier transform infrared and also absorption spectral measurements have been carried out. Excitation and emission spectra and decay curves have been recorded to understand emission performance of the polymers namely Sm^{3+}: PVA film with λ_{exci} = 400 nm and Dy^{3+}: PVA film with λ_{exci} = 349 nm. Emission performances of these films have been explained in terms of relevant energy level schemes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2480–2485, 2008

Key words: PVA films; Sm^{3+}; Dy^{3+}; emission performance

INTRODUCTION

Rare-earth (RE) ions doped materials have several applications in plasma display panels, field emission display, light emitting diodes, cathode ray tubes, optical amplifier systems, X-ray detectors, electroluminescent, optoelectronic and biosensing device, etc.[1–7] Luminescence from the RE^{3+} originates from transitions between 4f orbitals, these transitions are forbidden on symmetry grounds, that are ($4f^n$) well shielded by $5s^2$ and $5p^6$ orbitals. Therefore, emission transitions yield sharp lines in the optical spectra.[5,8,9] The growing importance of polymer films in integrated optic technology makes them interesting to study their optical properties. These polymer films could be processed from solutions and are found to be mechanically flexible.[10–16]

It has been known for a long time that Sm^{3+} and Dy^{3+} ions show strong fluorescence in variety of lattices. Sm^{3+} shows a strong emission in orange–red region[17–20] and Dy^{3+} exhibits both blue and yellow emissions, which are necessary for the development of full color displaying systems.[18,21–23] Thus, it is interesting to study the luminescence properties of Sm^{3+} and Dy^{3+}: Poly vinyl alcohol (PVA) films. In our earlier articles, bright red and green colors emitting Eu^{3+} and Tb^{3+} ions doped PVA films were reported.[24,25] In the present article, emission analysis of Sm^{3+} and Dy^{3+} doped PVA films has been reported.

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Journal of Applied Polymer Science, Vol. 107, 2480–2485 (2008)

EXPERIMENTAL

Preparation of polymer films

In the present work, RE^{3+} (RE^{3+} = Sm^{3+} and Dy^{3+}) doped (0.1 mol %) PVA (M_w = 14,000, Loba Chemie Pvt) films were made from aqueous solutions by a film casting technique. Films with uniform thickness of 1 mm were obtained by using a thin layer chromatography (TLC) spreader. Regarding the RE^{3+}: PVA films, at first, $SmCl_3$ (M_w = 256.71, Aldrich) and $DyCl_3$ (M_w = 268.85, Aldrich) were dissolved separately in a double distilled water to have their aqueous solutions. These solutions were used to mix with the PVA solution separately and the resultant solutions were thoroughly mixed for achieving homogeneity by using a magnetic stirrer. This resultant RE^{3+}: PVA solutions were cast separately on to a glass plates by using a TLC spreader and thus obtained 1 mm thick RE^{3+}: PVA films from the glass plates upon drying (in a slow evaporation method) them for about 24 h time. Optical analysis of these films (in the dimensions of 60 mm × 30mm × 1mm) has been carried out.

Characterization

The Fourier transform infrared (FTIR) spectra of the pure PVA and RE^{3+}: PVA films were recorded on a Thermo Nicolet-5700 Spectrophotometer with KBr pellet technique in the wavenumber range of 4000–400 cm^{-1}. The absorption spectra of RE^{3+}: PVA films were measured on a Jasco absorption Spectrophotometer in the wavelength range of 200–2000 nm. The photoluminescence (excitation and emission) spectra of RE^{3+}: PVA films were recorded on YVON

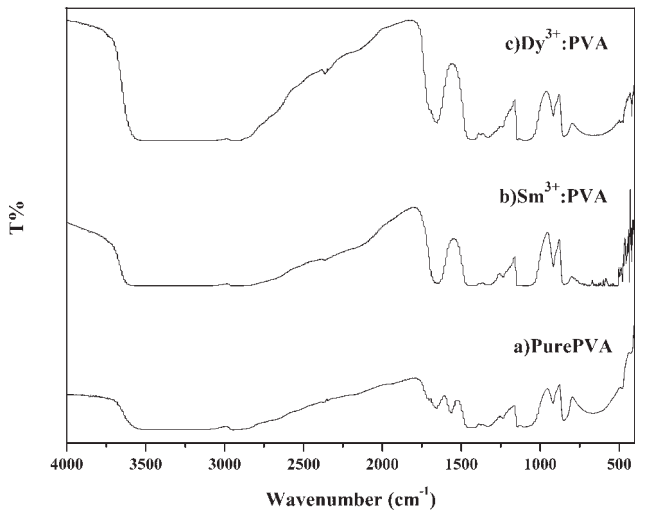

Figure 1 FTIR spectra of (a) Pure PVA (b) Sm^{3+}: PVA (c) Dy^{3+}: PVA films.

Fluorolog-3 Fluorimeter with a Xenon arc lamp of 450W power as an excitation source for a steady state emission spectrum measurement on this system and 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. All the above spectra were recorded at room temperature.

RESULTS AND DISCUSSION

X-ray diffraction spectrum and absorption spectrum of pure PVA film were reported in our earlier articles.[24,25] Figure 1 reports FTIR spectra of both RE^{3+} doped and undoped PVA films. Table I brings out the data and assignments made us the measured FTIR bands.

TABLE I
FTIR Spectra of Pure PVA Film; RE^{3+}: PVA Films

Pure PVA (cm^{-1})	Sm^{3+}: PVA (cm^{-1})	Dy^{3+}: PVA (cm^{-1})	Assignment
3115–3548	3071–3603	3035–3548	O—H stretching
2939	2819	2936	C—H stretching
1623	1649	1649	C=C stretching
1445	1450	1440	C—H bending
1350	1342	1342	C—H wagging
1235	1243	1243	C—C stretching
1100	1090	1105	C—O stretching
919	919	919	C—H rocking
856	847	847	C—C stretching
667	667	667	O—H wagging

Sm^{3+}: PVA film

Figure 2 shows the absorption spectrum of Sm^{3+}: PVA film between 200 and 2000 nm. The absorption bands are due to transitions from the ground state $^6H_{5/2}$ to the various excited states. The ground state absorption transitions within the Sm^{3+} ions are electric dipole (ED) in nature with the selection rule $\Delta J \leq 6$, except for the $^6H_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2}$ transitions, which contain contributions from the magnetic dipole (MD) interactions with the selection rule $\Delta J = 0, \pm 1$.[19] Sm^{3+}: PVA film has reveled absorption bands in UV–vis and NIR regions at 341, 360, 373, 400, 417, 440, 463, 476, 1083, 1242, 1398, 1497, 1693, and 1954 nm are assigned to the transitions $^6H_{5/2}$ to $(^4K,^4L)_{17/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^6P_{3/2}$, $(^6P,^4P)_{5/2}$, $^4G_{9/2}$, $^4I_{13/2}$, $^4I_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6F_{1/2}$, and $^6H_{13/2}$, respectively. Below 320 nm, there is a wide band due to the activator-host lattice interaction. Figure 3(a) shows the excitation spectrum of Sm^{3+}: PVA film. Excitation bands at 343, 361, 373, 400, 415, 440, 440, 462, 478, and 498 nm, assigned to the transitions from Sm^{3+} ground state ($^6H_{5/2}$) to the higher energy states of $(^4K,^4L)_{17/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^6P_{3/2}$, $(^6P,^4P)_{5/2}$, $^4G_{9/2}$, $^4I_{13/2}$, $^4I_{11/2}$, and $^4G_{7/2}$, respectively. The transitions of this excitation spectrum are well correlated with the transitions of absorption spectrum in UV-Vis region and the results are presented in Table II for a comparison. Among them, $^6H_{5/2} \rightarrow {}^6P_{3/2}$ is the strong excitation band, which is located at 400 nm. Figure 3(b) shows an emission spectrum of Sm^{3+}: PVA film, with an excitation at 400 nm ($^6H_{5/2} \rightarrow {}^6P_{3/2}$). The emission transitions of Sm^{3+} are due to the well known intra 4f transitions of Sm^{3+} namely from an excited level ($^4G_{5/2}$) to lower levels ($^6H_{J\,=\,5/2,7/2,9/2}$). Three sharp emission bands are located at 558 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 595 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), and 642 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$). Among them, the most

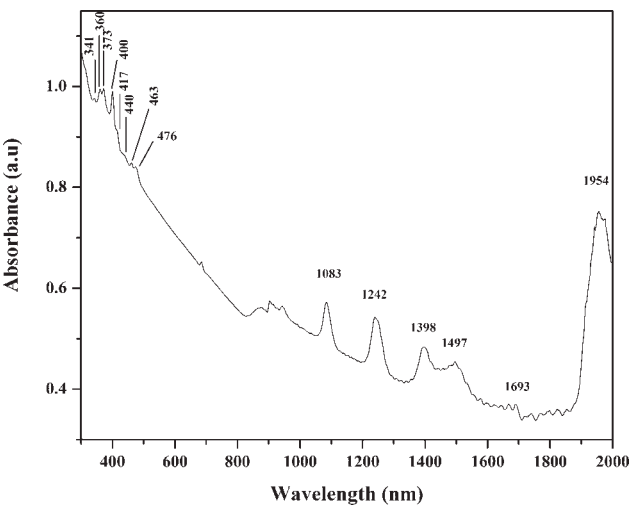

Figure 2 Absorption spectrum of Sm^{3+}: PVA film.

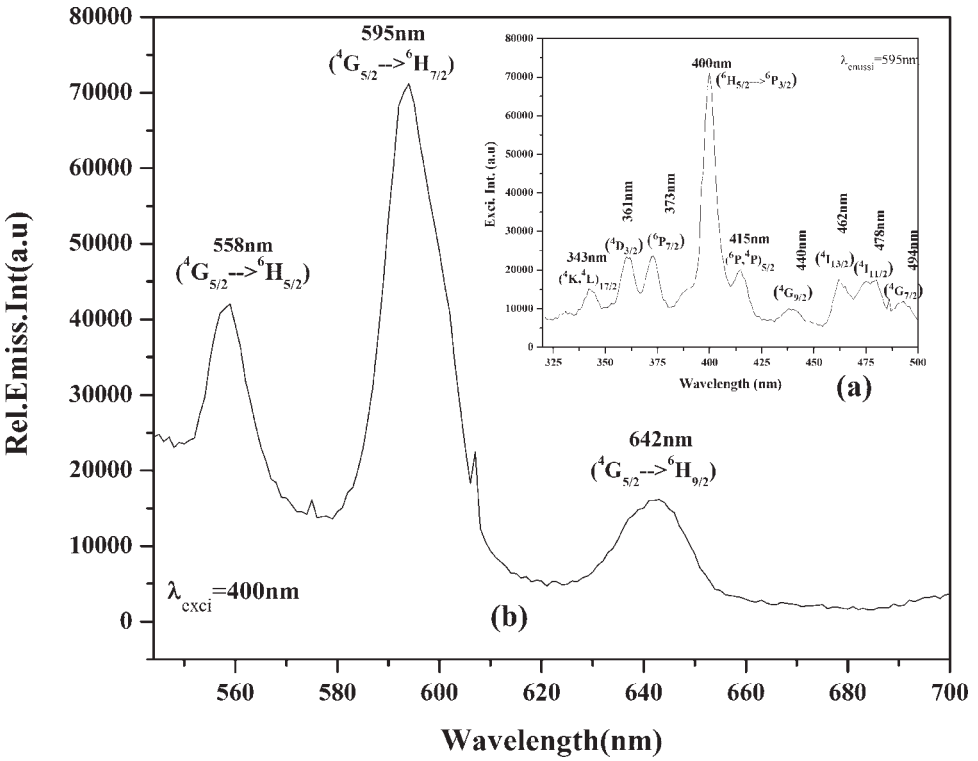

Figure 3 (a) Excitation spectrum of Sm^{3+}: PVA film (b) Emission Spectrum of Sm^{3+}: PVA film.

significant reddish orange emission is due to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ at 595 nm. According to the selection rules,[20] MD transitions obeying $\Delta J = 0$ and ± 1 (J, the angular momentum) and ED transitions that obey $\Delta J \leq 6$ unless J or $J' = 0$ when $\Delta J = 2, 4, 6$. Thus the transitions $^4G_{5/2} \rightarrow {}^6H_{5/2}$ ($\Delta J = 0$) at 558 nm, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ ($\Delta J = 1$) at 595 nm are MD transitions, while the transition $^4G_{5/2} \rightarrow {}^6H_{9/2}$ ($\Delta J = 2$) at 648 nm is a ED transition. Figure 4(a) presents the decay curve of the emission transition $^4G_{5/2} \rightarrow {}^6H_{7/2}$ at 595 nm with an excitation wavelength 400 nm having a lifetime $\tau = 1.10$ ms. Figure 4(b) describes the emission process mechanism in Sm^{3+}: PVA film.[26–28]

TABLE II
Wavelengths and Corresponding Electronic Transitions of Absorption and Excitation Spectra of Sm^{3+}: PVA Film

Absorption wavelengths (nm)	Electronic transitions $^6H_{5/2} \rightarrow$	Excitation wavelengths (nm)
341	$(^4K,^4L)_{17/2}$	343
360	$^4D_{3/2}$	361
373	$^6P_{7/2}$	373
400	$^6P_{3/2}$	400
417	$(^6P,^4P)_{5/2}$	415
440	$^4G_{9/2}$	440
463	$^4I_{13/2}$	462
476	$^4I_{11/2}$	478
–	$^4G_{7/2}$	498
1083	$^4F_{9/2}$	–
1242	$^6F_{7/2}$	–
1398	$^6F_{5/2}$	–
1497	$^6F_{3/2}$	–
1693	$^6F_{1/2}$	–
1954	$^6H_{13/2}$	–

Dy^{3+}: PVA film

Figure 5 shows the absorption spectrum of Dy^{3+}: PVA film. All the absorption transitions of Dy^{3+}: PVA films are ED natured, except the $^6H_{15/2} \rightarrow {}^6H_{13/2}$, $^4I_{15/2}$ transitions, which contain a substantial MD moment. The absorption spectrum of Dy^{3+}: PVA film consist of 10 bands with $^6H_{15/2}$ as the ground state and are identified with the necessary electronic transitions such as $^6P_{3/2}$ at 324 nm, $(^4M,^4I)_{15/2}$ at 349 nm, $^4I_{11/2}$ at 364 nm, $^4I_{17/2}$ at 448 nm, $^6F_{3/2}$ at 755 nm, $^6F_{5/2}$ at 805 nm, $^6F_{7/2}$ at 907 nm, $^6H_{7/2}$ at 1097 nm, and $^6F_{11/2}$ at 1293 nm, respectively. The absorption bands in the UV region are also observed in the excitation spectrum of Dy^{3+}: PVA film and these results are presented in Table III. The excitation spectrum of Dy^{3+}: PVA film is shows in Figure 6(a). The excitation bands at 294, 324, 349, 364, and 386 nm, are assigned to the electronic transitions from ground state $^6H_{15/2}$ to the higher excitation states $^4H_{11/2}$, $^6P_{3/2}$, $(^4M,^4I)_{15/2}$, $^6P_{5/2}$, and $^4I_{13/2}$, respectively. Among them $^6H_{15/2} \rightarrow (^4M,^4I)_{15/2}$ at 349 nm is the intense one and by using this, emission spectrum has been recorded as shown in Figure 6(b). Two emission bands at 476 nm

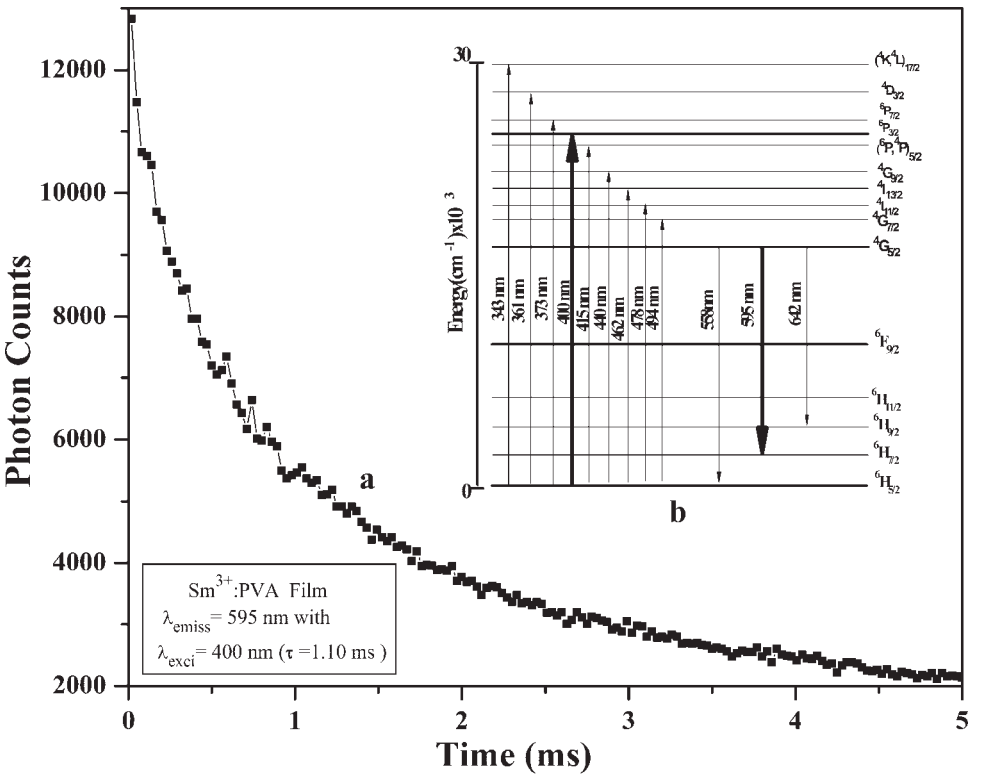

Figure 4 (a) Decay Curve of emission transition (b) Energy level scheme for the emission mechanism in Sm^{3+}: PVA film.

(blue) $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and 576 nm (yellow) $^4F_{9/2} \rightarrow {}^6H_{13/2}$ are observed. Among them $^4F_{9/2} \rightarrow {}^6H_{15/2}$ is mainly magnetically allowed and the transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is a forced ED natured with $\Delta J = 2$, which is strongly influenced by the host environment of Dy^{3+}.[21] The decay behavior for the luminescence of Dy^{3+}: PVA film strongly depends on the excitation situations.[29] Figure 7(a) shows the typical decay curves of Dy^{3+} emission at 476 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) with excitation at 349 nm ($^6H_{15/2} \rightarrow (^4M,^4I)_{15/2}$) and 364 nm ($^6H_{15/2} \rightarrow {}^6P_{5/2}$), respectively. The lifetimes of Dy^{3+} emission at 476 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) are determined to be τ = 0.63 and 0.59 ms, respectively, at two different excitation wavelengths. Figure 7(b) describes the emission mechanism in Dy^{3+}: PVA film.[26–28]

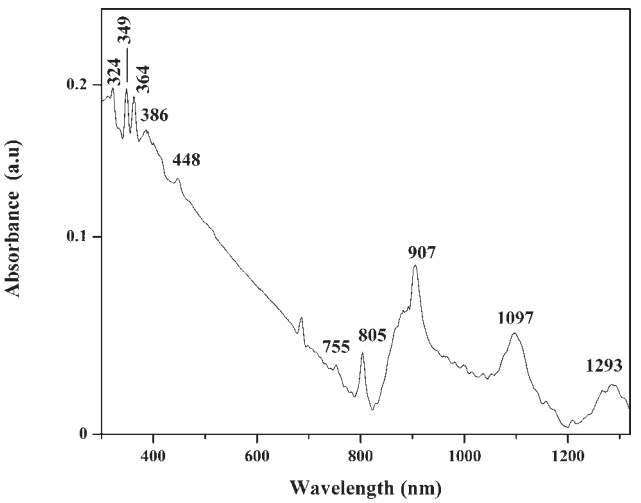

Figure 5 Absoption spectrum of Dy^{3+}: PVA film.

CONCLUSIONS

We have successfully developed Sm^{3+} and Dy^{3+}: PVA films by employing a solution cast technique, and their emission properties are analyzed. On the

TABLE III
Wavelengths and Corresponding Electronic Transitions of Absorption and Excitation Spectra of Dy^{3+}: PVA Film

Absorption wavelengths (nm)	Electronic transitions $^6H_{15/2} \rightarrow$	Excitation wavelengths (nm)
–	$^4H_{11/2}$	294
324	$^6P_{3/2}$	324
349	$(^4M,^4I)_{15/2}$	349
364	$^4I_{11/2}$	364
–	$^4I_{13/2}$	386
448	$^4I_{17/2}$	–
755	$^6F_{3/2}$	–
805	$^6F_{5/2}$	–
907	$^6F_{7/2}$	–
1097	$^6H_{7/2}$	–
1293	$^6F_{11/2}$	–

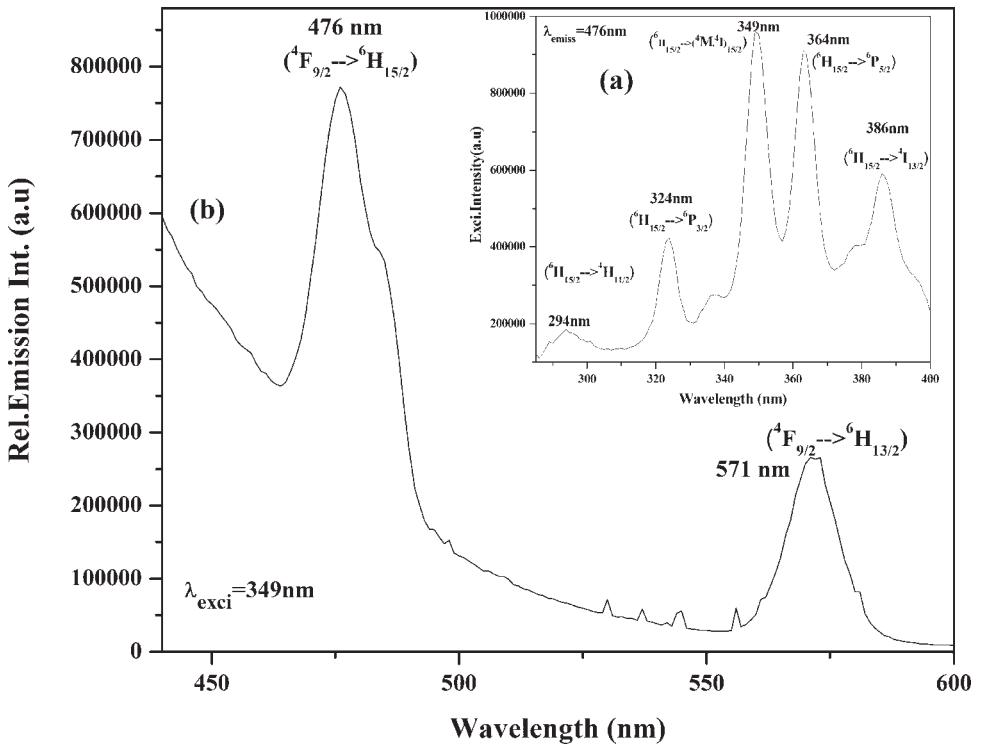

Figure 6 (a) Excitation spectrum of Dy^{3+}: PVA film (b) Emission Spectrum of Dy^{3+}: PVA film.

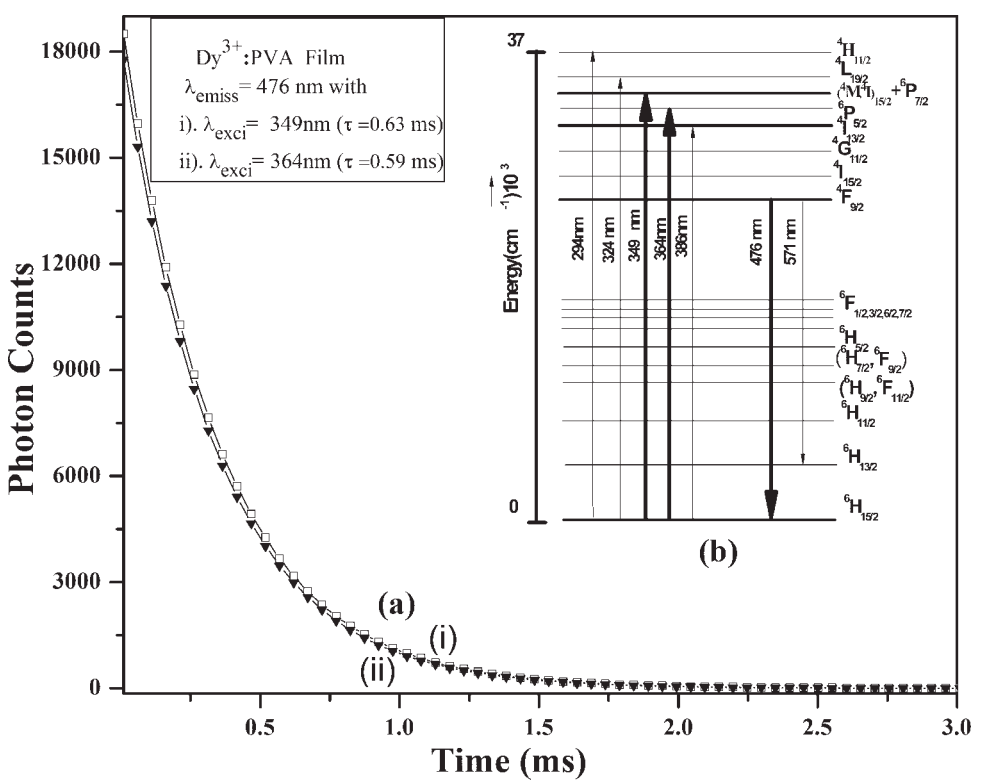

Figure 7 (a) Decay Curve of emission transitions (b) Energy levels scheme for the emission mechanism in Dy^{3+}: PVA film.

basis of the results obtained in the present work, we could suggest these films could consider as novel optical materials for display applications.

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