

Optical properties and Judd-Ofelt intensity parameters of Eu^{3+} in PMMA:PAAc copolymer samples

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Eu^{3+} -activated PMMA:PAAc copolymers samples with different concentrations of Eu^{3+} ions were prepared and the spectroscopic properties investigated. The mass density, refractive index, UV-Visible absorption and emission spectra and fluorescence decay times were experimentally obtained. These data were used with the Judd-Ofelt theory to calculate the oscillator strengths, the spontaneous emission probabilities and the branching ratios as a function of the europium content; the Eu concentration was varied in the range from 0.1 to 3 mol %. The europium ions affect the polymerization mechanism since their presence produced a steric effect, which reduces the reactivity of the acrylic acid. We analyzed the optical interaction mechanism between the RE^{3+} and the polymeric matrix, which is of radiative type.

Keywords: Energy transfer; Judd-Ofelt theory; optical absorption; copolymers.

Se prepararon muestras de copolímero de PMMA:PAAc activado con Eu^{3+} para estudiar sus propiedades ópticas. Experimentalmente se determinaron las densidades de masa, los índices de refracción, los espectros de absorción y de emisión, así como los tiempos de decaimiento de la fluorescencia. Esta información, junto con la teoría de Judd-Ofelt, se utilizó para calcular las intensidades de oscilador, las probabilidades de emisión espontánea y las razones de intensidad relativa, como función del contenido de europio. El intervalo de concentración en las muestras fue de 0.1 a 3% mol. Los iones de europio afectan las condiciones de polimerización, ya que en la reacción de esterificación entre el ácido acrílico y los iones europio se producen dímeros y trímeros, los cuales, por un lado tienen coeficientes de difusión menores debido a su mayor tamaño, y a que la presencia del europio en el ester produce un efecto estérico, el cual reduce su reactividad. Se pudo determinar el tipo de mecanismo de interacción óptica entre el lantánido trivalente y la matriz polimérica, siendo ésta del tipo radiativo.

Descriptores: Transferencia de energía; teoría Judd-Ofelt; absorción óptica; copolímeros.

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1. Introduction

It is known that the incorporation of rare earth (RE) ions in different host materials modifies, significantly, the optical properties of the original material [1-10]. This allows to produce optical material with other additional properties. In the last decade, an increasing number of papers has been addressed to study the use polymeric materials as a host for RE ions, due to the important technological applications. The use RE-doped polymers allows to obtain, besides the required optical response, several other interesting properties as: high transparency, high impact resistance, the possibility of thermo-casting (to produce optical fibers, waveguides, etc), films, coatings, interfase agents, etc. [1-5]. In this work the synthesis and optical characterization of the PMMA-PAAc copolymer doped with Eu^{3+} ions at different concentrations is reported. Optically the Judd-Ofelt theory allowed to determine the possible mechanisms of relaxation of the trivalent lanthanide ions affected by the emission of the host.

2. Judd-Ofelt theory

The Judd-Ofelt (J-O) theory [11,12] has been widely used to calculate the oscillator strength for transitions from ground

level to the excited states for RE ions implanted in different host; particularly this theory has been applied to Eu^{3+} ions using PMMA:PAAc copolymer as a host, in this work. J-O theory is the most useful and popular method in the analysis of spectroscopic properties of rare earth ions in different hosts. The J-O model has been applied to different types of hosts and is reported elsewhere [6-10]. For a matter of clarity, a brief summary of the J-O theory will be provided, reporting only the important equations required to determine the oscillator strengths, the Judd-Ofelt parameters, the spontaneous emission probabilities and the branching ratios.

It is recognized [11-14] that the observed transitions in the absorption spectra of trivalent lanthanide ions are intra-configurational f-f transitions; the majority of these are induced electric dipole transitions, although a few magnetic dipole transitions are also present. The intensities of these transitions can be characterized by the oscillator strength, f , of each $[(S, L) J] \rightarrow [(S', L') J']$ transition. The oscillator strength is determined from the absorption spectra through the equation

$$f [[S, L] J], [[S', L'] J']] = \frac{mc}{\pi e^2 N} \int \alpha(\nu) d\nu, \quad (1)$$

where m is the electron mass, N the concentration of rare earth ions in the sample, $\alpha(\nu)$ the absorption coefficient as a

function of the frequency ν , and the integral must be taken over the frequency range of the transition [11,12].

On the other hand, the oscillator strength is also given in terms of the electric dipole line strength, S_{ed} , for the multiplet to multiplet transitions, by

$$f [|[S, L] J\rangle, |[S', L'] J'\rangle] = \frac{8\pi m \nu}{3h(2J+1)e^2 n^2} \chi_{ed} S_{ed} [|[S, L] J\rangle, |[S', L'] J'\rangle], \quad (2)$$

being n the refractive index, e the electron charge, ν the frequency of the transition and χ_{ed} the field correction for the rare earth in the initial manifold given by

$$\chi_{ed} = \frac{n(n^2 + 2)^2}{9}. \quad (3)$$

The line strength (S_{ed}) which is proportional to the square of the matrix element (U^t) can be expressed by

$$S_{ed} [|[S, L] J\rangle, |[S', L'] J'\rangle] = e^2 \sum_{t=2,4,6} \Omega_t |\langle [S, L] J | U^t | [S', L'] J' \rangle|^2. \quad (4)$$

The Judd-Ofelt parameterization of the matrix elements used in this work is reported by Carnall [16,17] and Weber [18,19]. These matrix elements were used because the doubly reduced tensor operators $\langle [S, L] J || U^t || [S', L'] J' \rangle$ are usually considered to be host invariant. The Judd-Ofelt parameters Ω_t ($t = 2, 4, 6$ for rare earth), for a given rare earth ion-host combination, are determined by fitting the observed oscillator strengths from Eq. (1). Once the Judd-Ofelt parameters are determined, they are used to calculate the oscillator strengths, and other transition properties between ground and the excited states of the RE ion.

For instance, the relaxation rate corresponding to an electric dipole transition from the $[|S', L'] J'$ multiplet to the $[|S, L] J$ multiplet is related to the line-strength by

$$A [|[S', L'] J'\rangle, |[S, L] J\rangle] = \frac{64\pi^4}{3h(2J+1)\lambda^3} \chi_{ed} S_{ed} [|[S', L'] J'\rangle, |[S, L] J\rangle]. \quad (5)$$

The radiative lifetime of multiplet, τ_{rad} , is related to the radiative decay rate through

$$\frac{1}{\tau_{rad}} = \sum_{[S', L'] J'} A [|[S', L'] J'\rangle, |[S, L] J\rangle], \quad (6)$$

where the summation is over lower energy multiplets. Accordingly, the branching ratio, β , for the transition from an initial level, characterized by the quantum numbers $[|S', L'] J'$ to a lower level $[|S, L] J$, is defined by

$$\begin{aligned} \beta [|[S', L'] J'\rangle, |[S, L] J\rangle] &= A [|[S', L'] J'\rangle, |[S, L] J\rangle] \tau_{rad} \\ &= \frac{A [|[S', L'] J'\rangle, |[S, L] J\rangle]}{\sum_{S, L, H} A [|[S', L'] J'\rangle, |[S, L] J\rangle]}. \quad (7) \end{aligned}$$

In Eq. (7) the branching ratio, β , is a measure of the ratio of the relative intensity of a transition to the total emission intensity of all transitions originating on a given multiplet.

2.1. Experimental

The copolymer synthesis was carried out by mixing fresh distilled monomers of methyl meta acrylate (MMA) (Aldrich Chem. Co.) and acrylic acid (AAc) (Aldrich Chem. Co.) in a relative concentration of 1:1 mol % with 1-butanol (Baker Chem. Co.) which was used as medium. The initiator of the polymerization reaction was 2, 2'-azo bis iso butire nitrile (AIBN) in a molar relation 1:1000 respect to monomers, to produce polymeric chains with an average molecular weight of 45,000. EuCl_3 was used as europium source and added to the monomer mixture under agitation until it dissolves completely; the concentration of Eu^{3+} ions was varied from 0.1% to 3.0 mol %, being the last salt concentration practically the saturation concentration. The polymerization reaction was carried out at 80 °C under strong agitation during 180 minutes. The reaction time was increased significantly due to the presence of the Eu^{3+} ions. These ions react with the acrylic acid monomers producing europium acrylate and hydrochloric acid which evaporates; this is a esterification reaction. Due to the trivalent character of the cations, each of these can react with more than one acrylic acid monomer producing dimmers and, possible, trimmers. The presence of these structures increases the reaction time due to two main reasons: a) a reduction in the diffusion coefficient (mobility) of the reactants and b) a reduction in the monomer reactivity due to the steric effects. The structures can also produce, when the RE concentration is large, the crosslinking of polymer molecules.

The polymer solution was dried at 110 °C under reduced pressure during 4 hours. The dried polymer was then thermoformed at 120°C at moderate pressure (30 Kg/cm²) to produce small transparent discs of 1.2 mm thickness.

Continuous fluorescent spectra were obtained using a Perkin-Elmer model 650-10S spectrofluorometer equipped with a 150 W Xenon lamp. The photoluminescence measurements were also carried out with a Perkin-Elmer fluorescence spectrophotometer to obtain the emission and excitation spectra. The light source was a 10 W pulsed Xenon lamp with a width at half peak intensity of 0.01 ms. Lifetime and laser time resolved spectroscopy data were obtained using an EGG 2100 tuneable Dye laser as the excitation source. The sample fluorescence was monitored by a 0.45 m Czerni-Turner monochromator, detected by a cooled Hamamatsu R-943-03 photomultiplier tube and processed by an EGG/Par 162 Boxcar averager.

3. Results and discussion

In Fig. 1a the absorption spectrum of Eu^{3+} -doped PMMA:PAAc sample with 3 mol % of europium is shown.

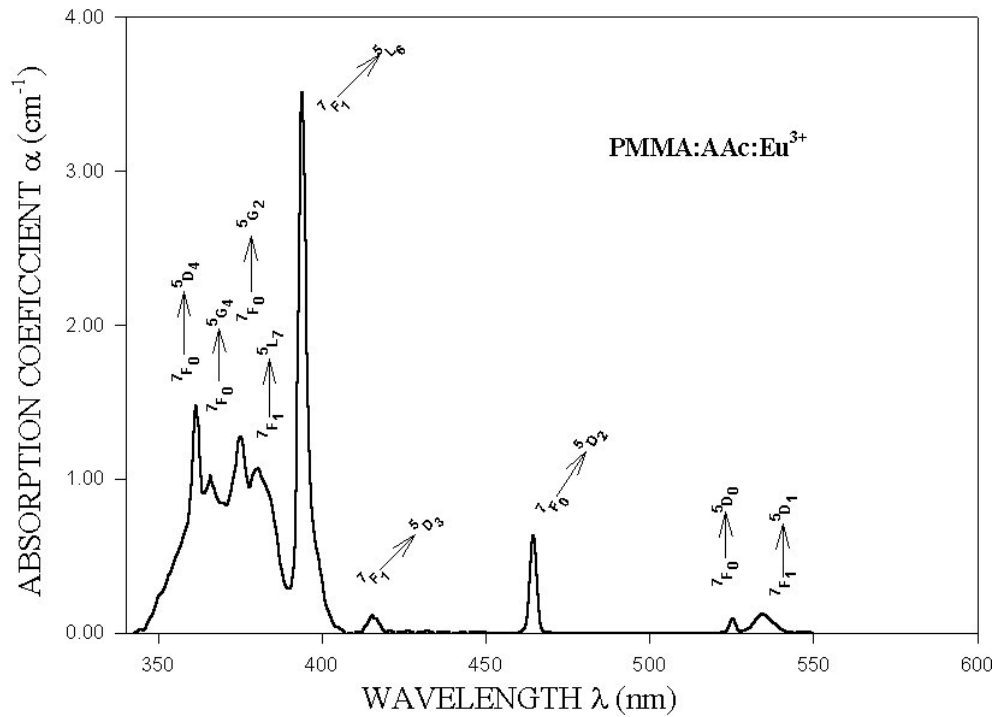


FIGURE 1. (a) Room temperature absorption spectra of Eu^{3+} -doped PMMA-PAAC (3 mol %) copolymer sample. (b) Partial energy-level diagram of Eu^{3+} ions in the copolymer samples.

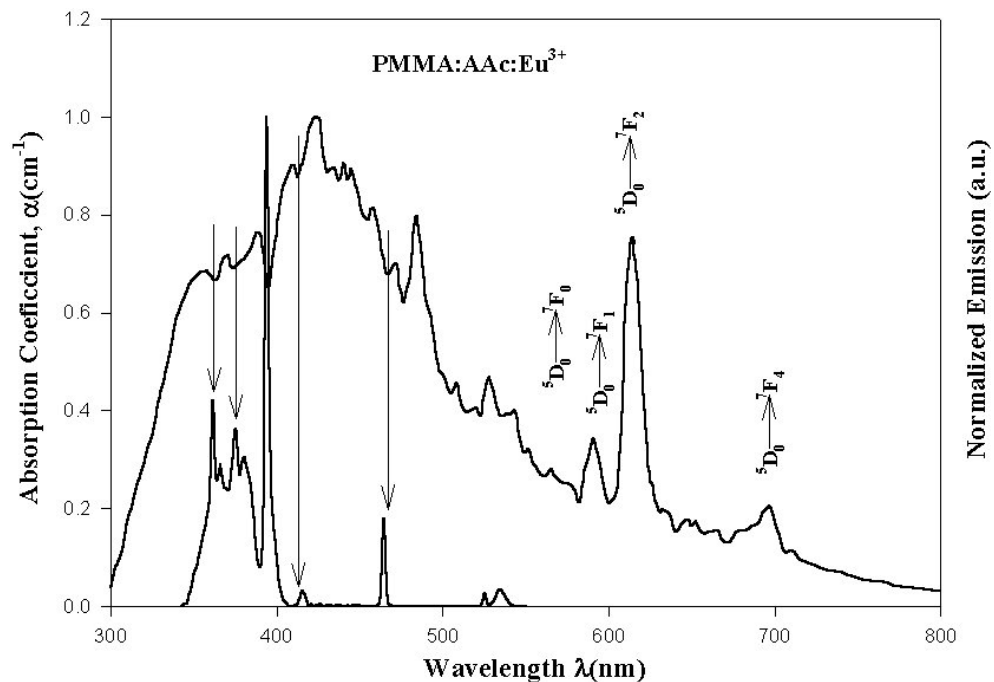


FIGURE 2. Characteristic photoluminescent (PL) spectrum of PMMA:PAAC: Eu^{3+} (3 mol %) copolymer samples excited at 390 nm. This is compared with the absorption spectrum of samples with different content of Eu^{3+} ions.

This has been normalized taking into account the sample thickness. This spectrum consists of several sharp lines associated with transitions from the ground state $7F_0$ to the Stark components of the excited state of the $4f^6$ configuration of the Eu^{3+} ion. Figure 1b, shows the partial energy level diagram for this sample.

Figure 2 portrays the RE emission spectrum for the same sample with 3 mol % of europium excited at 260 nm (thick line). The strongest bands at 500-800 nm corresponds to radiative transitions from the excited state $5D_0$ to the $7F_1$ and $7F_0$ levels of the Eu^{3+} ion, while the broad structured blue emission at 440 nm has been associated with the

PMMA:PAAc copolymer host [20]. This figure also shows the characteristic absorption spectrum of the sample (thin line). The intensities of the spectra were adjusted in size in order to compare their shapes. From this figure a radiative energy transfer mechanism from the host material to the Eu^{3+} ions is clearly demonstrated because the re-absorption band just appeared in the range of the emission spectrum at the wavelengths of the Eu^{3+} absorption bands.

Time-resolved experiments were also performed. In Fig. 3 the concentration dependence of the characteristic delay time constant, τ_0 , is shown; this is associated with the relaxation curves of the Eu luminescence from the $^5\text{D}_0$ excited state to ground level $^7\text{F}_2$. It was found that τ_0 is sensitive to the total Eu^{3+} content in the sample: a reduction of the lifetime of the Eu^{3+} emission was observed at high concentrations of ions. Such behavior could be associated with a resonant cross relaxation mechanism between the Eu ions in the polymeric matrix. These are similar to those found for the europium emission in heavily doped systems [13,14,19] where segregation of the RE impurity is expected to occur.

In order to get a better insight on the influence of the specific environment of the europium ions, the characteristics of the transitions responsible for the bands observed in the absorption and fluorescence spectra were analyzed on the basis of the Judd-Ofelt theory. Calculated values of the J-O parameters are shown in Table I along with the experimental values of mass density and the refractive index of our samples. Starting with the optical absorption spectra, the experimental and theoretical values for the oscillator strengths of the optical transitions were obtained.

From the spectra, ten bands between 350 and 700 nm could be resolved clearly enough for the calculations. The mean wavelengths of these bands as well as the experimental line strengths derived from Eqs. (1) and (2) are shown in the Table II. The calculated line strengths obtained from the intensity parameters are shown also in this table. To evaluate the accuracy of the J-O parameters obtained by least-squares fitting, the goodness of fit was calculated according to the following equation,

$$\delta_{rms} = \left[\frac{\sum (f_c - f_m)^2}{(\text{no. of transitions} - \text{no. of parameters})} \right]^{1/2}, \quad (8)$$

where f_m and f_c are the measured and calculated line strengths, respectively, and summation is taken over all bands used to calculate the Ω parameters. The agreement between these values was quite good as it is shown in Table I and Table II.

The branching ratios were calculated from the Judd-Ofelt parameters using Eq. (5) and Eq. (7). The probabilities associated with these transitions are reported in Table III along with the computed branching ratios. The branching ratios for the five concentrations are quite similar. The sum of the transition probabilities in the denominator of the Eq (7) represents the total transition probability. All values are quite similar except for the 0.1 mol% sample.

A slight increase in both the mass density and the refractive index was observed in our samples, as a function of the Eu^{3+} concentration. They could be related to the crosslinking effects produced by steric reaction. Experiments are being performed in order to verify this conclusion.

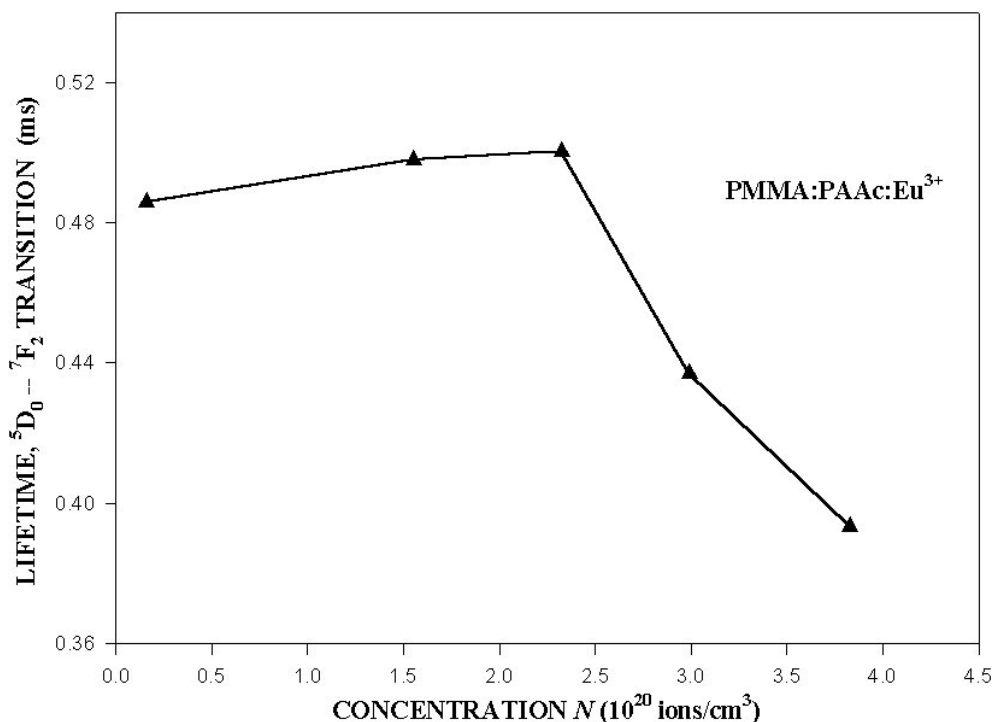


FIGURE 3. Dependence of the lifetime of the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (616 nm), of the europium, as a function of the concentration.

TABLE I. Mass density, refractive index and J-O parameters Ω_t ($t = 2, 4, 6$) for PMMA-PAAc copolymers doped with different concentrations of Eu³⁺ ions.

Sample <i>Eu</i> (%mol)	$N_{Eu} \times 10^{20}$ (Ions/cm ³)	Density (gr/cm ³)	Refraction Index, n $\times 10^{-20}$	Ω_2 (cm ²) $\times 10^{-20}$	Ω_4 (cm ²) $\times 10^{-20}$	Ω_6 (cm ²)
0.1	0.160	1.24	1.4916	1.20 ± 0.26	6.90 ± 1.38	0.73 ± 0.11
1	1.552	1.27	1.4932	1.09 ± 0.15	4.95 ± 0.59	1.45 ± 0.04
1.5	2.324	1.29	1.4960	1.95 ± 0.42	4.58 ± 0.31	1.36 ± 0.19
2	3.000	1.30	1.4961	1.59 ± 0.17	4.98 ± 0.83	1.39 ± 0.17
2.5	3.828	1.32	1.4982	1.69 ± 0.08	4.66 ± 0.22	1.25 ± 0.15
3	5.237	1.34	1.4995	1.73 ± 0.22	5.27 ± 0.80	1.31 ± 0.07

TABLE II. Experimental and calculated values of the oscillator strength, f , for the transitions from the ground state 7F_i ($i = 0, 1$) to [S^1, L^1]J' excited states of Eu³⁺ ions in PMMA:PAAc.

Transition	Wavelength	Sample (0.1%)	Sample (1%)	Sample (1.5%)	Sample (2%)	Sample (2.5%)
	Frequency					
	λ (nm)	$f_{calc}(10^{-7})$	$f_{exp}(10^{-7})$	$f_{exp}(10^{-7})$	$f_{exp}(10^{-7})$	$f_{exp}(10^{-7})$
	ν (cm ⁻¹)	$f_{exp}(10^{-7})$	$f_{calc}(10^{-7})$	$f_{calc}(10^{-7})$	$f_{calc}(10^{-7})$	$f_{calc}(10^{-7})$
${}^7F_1 \rightarrow {}^5D_1$	535 18692	0.48 1.78	0.46 0.85	0.45 0.69	0.53 1.29	0.49 1.12
${}^7F_0 \rightarrow {}^5D_1$	464 21552	1.81 0.69	1.39 0.33	1.14 0.27	1.41 0.50	1.34 0.43
${}^7F_1 \rightarrow {}^5D_3$	415 24096	4.99 4.72	1.14 1.98	0.70 2.87	1.01 1.98	1.04 1.98
${}^7F_1 \rightarrow {}^5L_6$	396 25253	4.95 4.27	4.24 4.63	3.41 3.90	4.07 4.03	3.35 3.74
${}^7F_0 \rightarrow {}^5L_6$	393 25445	6.98 7.36	8.26 8.03	7.05 6.76	7.37 6.99	6.71 6.48
${}^7F_0 \rightarrow {}^5G_3$	381 26247	5.92 5.80	2.44 2.44	1.20 3.60	2.34 2.41	2.34 0.35
${}^7F_0 \rightarrow {}^5G_2$	379 26385	2.62 0.55	0.77 0.33	0.51 0.50	2.22 1.12	1.42 2.43
${}^7F_0 \rightarrow {}^5G_4$	375 26667	4.67 2.83	2.36 1.18	3.16 1.77	0.27 1.81	2.48 1.14
${}^7F_1 \rightarrow {}^5D_4$	364 27473	1.77 2.90	0.99 1.21	3.82 1.82	1.67 1.15	3.15 1.17
${}^7F_0 \rightarrow {}^5D_4$	361 27701	3.79 4.62	2.04 1.92	5.73 2.89	1.83 1.83	1.91 1.86
<i>rms</i>		1.23×10^{-7}	0.67×10^{-7}	1.84×10^{-7}	1.06×10^{-7}	1.20×10^{-7}

TABLE III. Transition probabilities of emission, A, and branching ratios, β , of the Eu³⁺ ions in PMMA:PAAc for each concentration.

Transition	Concentration					
	0.1%	1%	1.5%	2%	2.5%	3%
${}^5D_0 \rightarrow {}^7F_2$	A = 87.64 (s ⁻¹)	A = 62.70 (s ⁻¹)	A = 68.21 (s ⁻¹)	A = 69.48 (s ⁻¹)	A = 54.12 (s ⁻¹)	A = 73.74 (s ⁻¹)
	$\beta = 0.2938$	$\beta = 0.0581$	$\beta = 0.0586$	$\beta = 0.0564$	$\beta = 0.0563$	$\beta = 0.0578$
	$\beta = 0.7062$	$\beta = 0.0839$	$\beta = 0.0756$	$\beta = 0.1108$	$\beta = 0.1112$	$\beta = 0.0882$
${}^5D_0 \rightarrow {}^7F_4$	A = 210.62 (s ⁻¹)	A = 90.66 (s ⁻¹)	A = 103.78 (s ⁻¹)	A = 107.63 (s ⁻¹)	A = 106.87 (s ⁻¹)	A = 112.51 (s ⁻¹)

Finally, the J-O parameters associated with the optical transitions of the Eu in our samples were found to be constant as a function of the europium concentration, except for the 0.1 mol% concentration sample. This result indicates that the local environment of the ion does not change to high concentrations.

4. Conclusions

Evidence of an active radiative energy transfer mechanism between the copolymer host and the Eu ions has been determined. From the data in Tables I and II it could be concluded

that, while the europium content produces a change in both the mass density and the refractive index of the samples, the J-O parameters remain constant; whenever the Eu concentration is over 0.1 mol %. This means that the local environment of the europium ions is quite similar in all the samples.

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