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Influence of gamma irradiation on photoluminescence properties of polycarbonate films doped with Eu^{3+} - β -diketonate complex

Pedro L. Forster^a, Duclerc F. Parra^{a,*}, Jiang Kai^b, Hermi F. Brito^b, Ademar B. Lugao^a

^a Instituto de Pesquisas Energéticas e Nucleares, IPEN—CNEN/SP, Av. Professor Lineu Prestes, 2242, 05508-000 São Paulo, SP, Brazil

^b Instituto de Química da Universidade de São Paulo, IQ-USP, Av. Professor Lineu Prestes, 900, 05508-000, São Paulo, SP, Brazil

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ABSTRACT

Luminescent films composed by doping diaquatris(thenoyltrifluoroacetate)europium(III) complex $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ (1% w/w) into a polycarbonate (PC) matrix were prepared and irradiated at gamma radiation with 10, 50 and 100 kGy. The effect of irradiation on the PC matrix can be evaluated by changes in the luminescence properties of the doped system. Changes in photophysical properties due to gamma radiation were observed by emission and excitation spectral data, emission quantum efficiency (η), lifetime (τ) of emitter $^5\text{D}_0$ level of Eu^{3+} ion and Fourier transformed infrared spectra (FTIR). Based on the emission spectra of PC: $\text{Eu}(\text{tta})_3$ 1% films were observed the characteristic bands arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions of Eu^{3+} ion ($J=0-4$), indicating the ability to obtain the luminescent films. The most intense transition of Eu^{3+} is the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, corresponding to a red emission band at 614 nm, indicated that the lanthanide ion is not located in a site with inversion center symmetry. The high luminescence is owing to the efficient energy transfer via triplet state (T) from the tta ligand and polymer to the emitter $^5\text{D}_0$ level of the Eu^{3+} ion. The results suggest that the doped system after gamma irradiation present similar photoluminescence behavior.

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1. Introduction

Nowadays, luminescent lanthanide complexes have attracted much interest for their application as optical materials. Owing to the intrinsic spectroscopic properties of the lanthanide ions (Ln^{3+}), the lanthanide β -diketonate complexes are widely used in the development of new luminescent materials for exhibiting monochromatic emission in several applications such as optical markers, optoelectronic devices, biological labels and sensor devices (Sá et al., 2000). The combination of spectroscopic properties of these metal ions associated to the unique physical and chemical properties of polymers became more attractive in the last decade (Raj et al., 2009a,b).

The “antenna effect” of the Ln^{3+} complexes, usually consists of: (a) efficient ultraviolet light absorption by the organic ligand via its singlet state (S); (b) intersystem crossing from singlet to triplet state; (c) efficient energy transfer from the ligand triplet state (T) to the 4f excited levels and (d) high emission intensity from 4f–4f transitions of the Ln^{3+} ion. In this way, the emitting 4f level is in general populated much more efficiently than by direct excitation of the Ln^{3+} excited levels (Arnaud and Georges, 2003; Bunzli and Piguet, 2002; Evans et al., 2006; Lehn, 1990; Uekawa et al., 1998).

Among the coordination compounds containing Ln^{3+} ions, the trivalent europium and terbium ions with β -diketone ligands have been extensively studied. One of the most investigated β -diketonates complexes is the tenoyltrifluoroacetate of trivalent europium (Eu^{3+}) (Liu et al., 2005a,b; Parra et al., 2004). In the Eu^{3+} complexes, the energy is transferred from the ligand triplet to the $^5\text{D}_{1,0}$ excited levels from which, luminescent transitions to the ground state manifold $^7\text{F}_j$ ($J=0-6$) are observed. The most intense transition of Eu^{3+} is the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, corresponding to a red emission band at around 615 nm. Besides, the tta[−] anion is a bidentate chelating ligand that protects the lanthanide ion from binding with other water molecules by chelating effect.

However, the low thermodynamical performance of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ hydrated complex has been a challenge in the design and development of thermal-stable photonic applications. One of the new interesting ways to achieve enhancement of the Ln^{3+} complex thermal stability may be through of the design luminescent systems combining lanthanide complexes with polymeric structures (Parra et al., 2004; Soares-Santos et al., 2003; Kai et al., 2008; Biju et al., 2009; Liu et al., 2004a,b). Polycarbonate (PC) polymer has excellent properties, for example, optical properties as high clarity, transparency and ratio of refractive indices, low water absorption, exceptional impact resistance, toughness and high glass transition temperature (T_g) (Forster et al., 2009, 2010). Therefore, the PC polymer could act as one promising candidate of host matrix for the optical applications based on Ln^{3+} complexes.

* Corresponding author.

E-mail address: dfparra@ipen.br (D.F. Parra).

Moreover, the efficiency of Eu^{3+} emission is relatively sensitive to vibronic coupling between the emissive levels of the metal and the O–H bonds of coordinated water molecules in the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ (Sá et al., 2000). In order to prepare europium compound with high emission intensity, the Eu^{3+} ion needs a chemical environment consisting of ligands with adequate chromophoric groups to harvest light and subsequently populate the Eu^{3+} excited energy levels through energy transfer ligand–metal, while simultaneously providing a rigid and protective coordination environment to minimize non-radiative contributions.

The radiation technology is preferred over the other processes due to many advantages when compared with other conventional methods. For initiation processes, radiation differs from chemical initiation. In radiation processing, no catalyst or additives are required to initiate the reaction (Bhattacharya, 2000).

The molecular changes induced by gamma radiation in a polymer may be classified as main chain bond scission, resulting in a decrease in molecular weight and, thus, adversely affecting its mechanical properties; and chain crosslinking, resulting in an increase in molecular weight and formation of network structure. Both chain scission and crosslinking occur primarily in the amorphous region, while some may take place in the boundary between the crystalline and amorphous regions. Chain scission, in general, occurs to polymeric chains at a low radiation dose. At high dose, free radicals could be generated on polymeric chains occurring crosslinking between polymer chains. Radiation modification is the phenomena by which the properties of polymers can be improved (Bhattacharya, 2000). By the fact that the europium precursor complex is a highly efficient probe of the chemical vicinity, effect of irradiation on the PC matrix can be evaluated by changes in the luminescence properties of a Eu^{3+} -doped system.

In this work, we report the preparation and characterization of europium complex doped in polycarbonate matrix. The films were irradiated at doses of 10, 50 and 100 kGy by ionizing radiation of gamma source. The luminescence behavior of doping effect of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex into the PC film was also reported.

2. Materials and method

2.1. Synthesis

The polycarbonate (PC) used was obtained from Bayer Corporation, (Makrolon®), in the form of cylindrical cut granules (\emptyset 2–3 mm, length 2–3 mm). The $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex was prepared by addition of europium chloride aqueous solution to β -diketone ethanol solution of 1:3 molar ratio; followed by addition of concentrated ammonium hydroxide until pH \sim 7. The luminescent system containing the polymer doped with the europium complex in concentration 1% (w/w) was prepared by dissolving the polymer in tetrahydrofuran, THF, then mixing it with the required amount of the luminescent Eu^{3+} complex dissolved in acetone. The homogeneous solutions were heated at around 60 °C until total evaporation of solvent. The mixture was cast into a pyrex® recipient and left to dry in air. The doped films were then cut in slices that were irradiated and analyzed.

2.2. Measurements

The infrared absorption spectra of the solid samples in film form, were measured in the range 4000–400 cm^{-1} by using a Thermo Nicolet model 6700 FTIR spectrophotometer.

The excitation and emission spectra of luminescent films were recorded at room temperatures in a SPEX Fluorolog-2 spectrofluorimeter, model FL212, double grating 0.22 m SPEX monochromators, and a 450 W Xenon lamp as the excitation source. Irradiation took

place in a 6917.4 Ci ^{60}Co Gamma Cell 220 from Atomic Energy of Canada Ltda (AECL), dose rate of 5.72 kGy h^{-1} . The radiation doses applied in the PC: $\text{Eu}(\text{tta})_3$ 1% (PCE 1%) samples were 10, 50 and 100 kGy.

3. Results and discussion

3.1. Fourier transformed infrared spectroscopy (FTIR)

The IR spectra of the irradiated and non-irradiated PCE 1% films and the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ precursor are present in Fig. 1. It is noted that the irradiated PCE systems showed similar spectral profiles in comparison to the non-irradiated film, suggesting no structural changes by exposure to gamma radiation. The peaks related to the H_2O vibrational modes in the precursor complex were attributed at 3500–3200 cm^{-1} (ν_s and ν_{as} OH), at 1630–1600 cm^{-1} (HOH bending). In the irradiated and non-irradiated PCE 1% systems, characteristic peaks of PC polymer of ester group appear approximately at 1725 and 1774 cm^{-1} that are assigned to the $\nu_{\text{C-O}}$ and $\nu_{\text{C=O}}$ stretching modes, respectively. It was also observed the characteristic absorption bands of C–CH₃ stretching bonds in the range 2860–3000 cm^{-1} and the absorption band of the stretching in C–H of the aromatic ring between 3000 and 3100 cm^{-1} .

In lanthanide precursor complex is observed only one absorption band of thiophene at 1508 cm^{-1} . For irradiated and non-irradiated PCE systems, this band is overlapped by a peak present at 1505 cm^{-1} , attributed to vibrations of PC skeleton involving

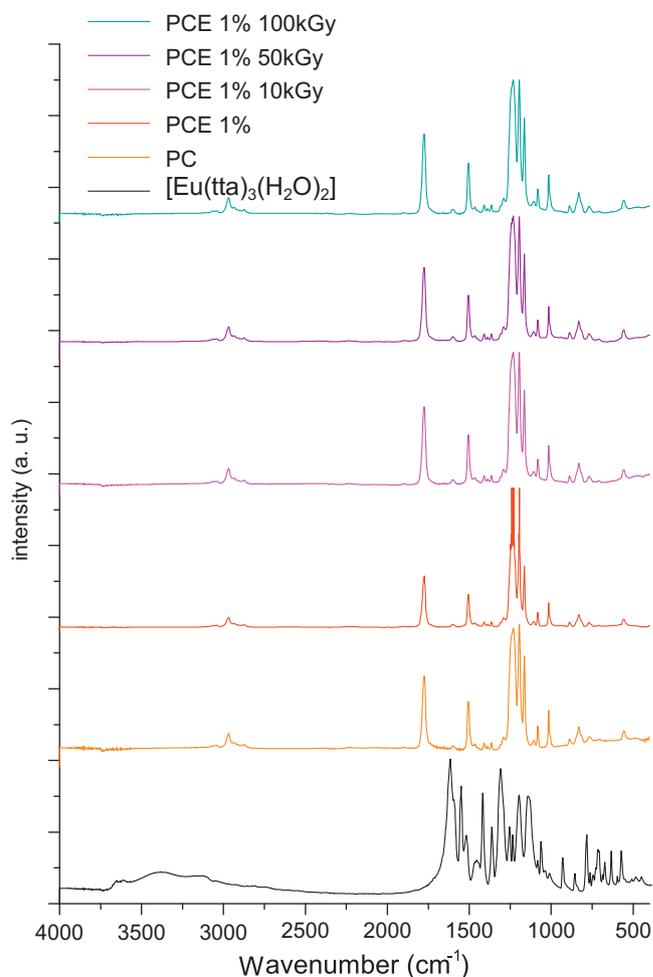


Fig. 1. Infrared absorption spectra of non-irradiated and irradiated PCE 1% films (at 10, 50 and 100 kGy) and the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ precursor complex.

axial deformation C–C bonds in the aromatic ring of PC polymer. The absence of absorption bands around $1725\text{--}1709\text{ cm}^{-1}$ assigned to the symmetric stretching mode ($\nu_s\text{ C=O}$) forms *cis* and *trans* of diketone, shows the absence of the keto form and confirms the presence of enol form in precursor complex. It was also identified in the PCE 1% systems bands in the regions of 933 cm^{-1} assigned to $\nu(\text{C=C+C=O})$ and 1139 cm^{-1} attributed to the asymmetrical stretching $\nu(\text{CF}_3)$, corresponding to the presence of the tta^- ligand in the irradiated and non-irradiated PCE 1% systems.

The broad absorption band assigned to the H_2O vibrational modes in the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex precursor spectrum in the $3500\text{--}3200\text{ cm}^{-1}$ region $\nu_s(\text{OH})$ and $\nu_{as}(\text{OH})$ is absent for the irradiated and non-irradiated PCE systems, indicating that the luminescent polymer systems are anhydrous.

3.2. Photoluminescent properties

The excitation spectra of the PCE 1% film and the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex recorded at 298 K in the spectral range 250–500 nm, by monitoring the emission at 613 nm are illustrated in Fig. 2. As shown in the spectral region from 250 to 400 nm an intense broad band which is assigned to the PC polymer absorption. On the other hand, the excitation spectrum of $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ precursor presents broad band overlap of the photoexcitation process of the Eu^{3+} ion via the $S_0 \rightarrow S_1$ transition of tta ligand. It can also be seen in this figure narrow absorption peaks assigned to the $4f\text{--}4f$ transitions ${}^7F_0 \rightarrow {}^5L_6$ (394 nm), ${}^7F_0 \rightarrow {}^5D_3$ (415 nm) and ${}^7F_0 \rightarrow {}^5D_2$ (464 nm) of Eu^{3+} ion which exhibit less absorption intensities than that broad band corresponding to the ligand state.

Emission spectra of irradiated and non-irradiated PCE 1% samples and the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ recorded in the range from 550 to 720 nm (Fig. 3), under excitation on tta^- anion bands at 360 nm, at room temperature (298 K), present characteristic emissions of the ${}^5D_0 \rightarrow {}^7F_J$ ($J=0\text{--}4$) transitions of Eu^{3+} ion with the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition ($\sim 613\text{ nm}$) showing the highest emission intensity. The presence of the ${}^5D_0 \rightarrow {}^7F_2$ transition indicates that the Eu^{3+} ion is found in non-centrosymmetric chemical environment due to the mixing of opposite parity electronic configurations, produced by the odd components of a non-centrosymmetric ligand field. Furthermore, the emission spectra of all films do not exhibit the broad band of tta ligands, indicating an efficient intramolecular energy transfer from the tta ligands to the Eu^{3+} ion.

It is observed in Fig. 3 similar emission band profiles of the ${}^5D_0 \rightarrow {}^7F_{0-4}$ transitions in irradiated and non-irradiated PCE systems,

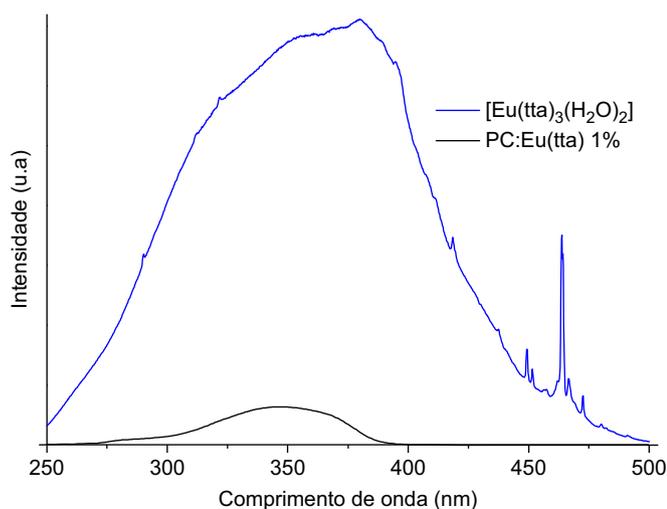


Fig. 2. Excitation spectra of irradiated PCE 1% films and comparison with $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ precursor complex recorded at room temperature ($\sim 298\text{ K}$).

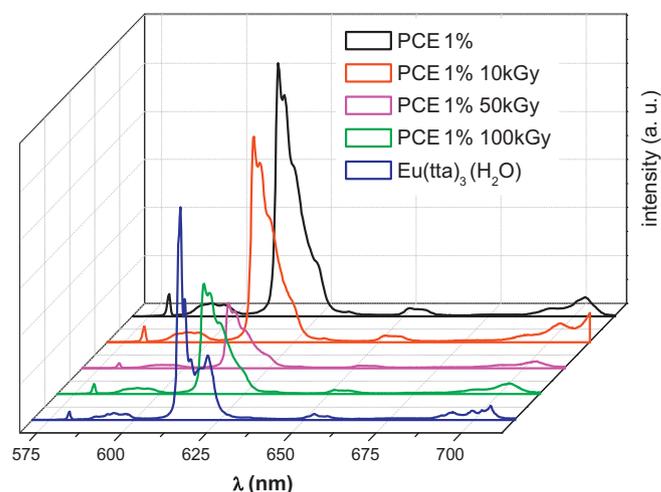


Fig. 3. Emission spectra of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ precursor complex, non-irradiated and irradiated PCE 1% films recorded under irradiation at 10, 50 and 100 kGy.

suggesting that no significant changes around the Eu^{3+} ion chemical environment occur when the films were irradiated by gamma rays. However, the emission bands are broadened for the doped films compared with $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex precursor because of the inhomogeneous line broadening effect, owing to the interaction between polymer and europium ion, indicating changes in chemical environment of the irradiated and non-irradiated PCE 1% systems. The presence of the non-degenerate ${}^5D_0 \rightarrow {}^7F_0$ transition ($\text{FWHM} > 20\text{ cm}^{-1}$) of irradiated, non-irradiated PCE and $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ systems corroborates with the C_n , C_{nv} or C_s site symmetries around of Eu^{3+} ions.

The emission quantum efficiency (η) of the emitter 5D_0 level of the europium ion is determined based on the emission spectra and lifetimes (τ). The emission intensity, (I), taken as the integrated intensity (S) of the ${}^5D_0 \rightarrow {}^7F_J$ ($J=0\text{--}4$) emission curve, is given by

$$I_{0 \rightarrow J} = \hbar \omega_{0 \rightarrow J} A_{0 \rightarrow J} N_0 \equiv S_{0 \rightarrow J} \quad (1)$$

where 0 and J are the initial 5D_0 and final levels 7F_J ($J=0\text{--}4$), respectively, $\omega_{0 \rightarrow J}$ is the transition energy, $A_{0 \rightarrow J}$ is the Einstein coefficient of spontaneous emission, and N_0 is the population of the emitter 5D_0 level. The ${}^5D_0 \rightarrow {}^7F_5$ and ${}^5D_0 \rightarrow {}^7F_6$ transitions must be neglected as they are not experimentally detected.

Since the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ transition is insensitive to the chemical environments around the Eu^{3+} ion, it is considered as a reference for the whole spectrum. Then, the experimental coefficients of spontaneous emission, $A_{0 \rightarrow J}$, were determined by the following equation:

$$A_{0 \rightarrow J} = \frac{\sigma_{0 \rightarrow 1} S_{0 \rightarrow J}}{S_{0 \rightarrow 1} \sigma_{0 \rightarrow J}} \quad (2)$$

Where $\sigma_{0 \rightarrow 1}$ and $\sigma_{0 \rightarrow J}$ are the baricentres of the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_J$ transitions, respectively. Lifetime (τ), radiative (A_{rad}) and nonradiative (A_{nrad}) transition rates are related through the total rate, $A_{\text{tot}} = 1/\tau = A_{\text{rad}} + A_{\text{nrad}}$, where $A_{\text{rad}} = \sum A_{0 \rightarrow J}$. Assuming that only nonradiative and radiative processes are essentially involved in the depopulation of the 5D_0 state, η can be expressed as (Sá et al., 2000)

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (3)$$

Table 1 presents the lifetimes (τ) of the 5D_0 emitter state of the Eu^{3+} ion of hydrated precursor compound and irradiated and non-irradiated PCE 1% films recorded at $\sim 298\text{ K}$. Comparing the emission quantum efficiency (η) of the emitter 5D_0 level of the

Table 1

Based on emission spectra data recorded at ~298 K, emission quantum efficiencies (η), lifetimes (τ), radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) emission coefficient rates $R_{\text{Eu}} = {}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ for samples of irradiated and non-irradiated PCE 1% samples and $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex.

Luminescent System	$A_{\text{rad}} (\text{s}^{-1})$	$A_{\text{nrad}} (\text{s}^{-1})$	$A_{\text{tot}} (\text{s}^{-1})$	τ (ms)	η (%)	R_{Eu}
PC: $\text{Eu}(\text{tta})_3$ 1%	742	2767	3509	0.285	21	11
PC: $\text{Eu}(\text{tta})_3$ 1% 10 kGy	790	2914	3704	0.270	21	13
PC: $\text{Eu}(\text{tta})_3$ 1% 50 kGy	804	2540	3344	0.299	24	12
PC: $\text{Eu}(\text{tta})_3$ 1% 100 kGy	792	2741	3533	0.283	22	12
$[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$	1110	2923	3846	0.260	29	14

Eu^{3+} ion between the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ with PCE 1% films, it is noted small decrease for the PCE systems, indicating that in the polymeric matrix present non-radiative contribution, fact also observed when doped films irradiated at low dose of gamma irradiation showed a decrease in luminescence intensity with increasing of the dose.

From the emission spectrum (Fig. 3) the R_{Eu} intensity parameter, which is the ratio between the intensities of the $R_{\text{Eu}} = {}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions, was determined (Table 1). The values of R_{Eu} parameter of the PCE 1% films are higher than 1, corroborating with the non-centrosymmetric sites. On the other hand, these values are practically constant in comparison with the complex precursor, suggesting that the doped polymers are insensitive to gamma irradiation.

4. Conclusion

Infrared spectral data suggest that the Eu^{3+} -complex is anchored in the PC polymeric network via carbonyl oxygen atoms of the host polymer matrix towards the Eu^{3+} ions. The excitation spectra of the irradiated PCE 1% films demonstrated lower absorption band compared with that of $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ precursor complex indicating less efficient intramolecular energy transfer to the Eu^{3+} ion. The emission spectra of irradiated PCE 1% films at 10, 50 and 100 kGy exhibited characteristic bands from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions ($j=0-4$) of the europium ion. Very high intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition indicating that lanthanide ion is also not located in a site with inversion center symmetry in all luminescent doped systems, corroborating by the values of R_{Eu} parameter of the PCE 1% films which are higher than 1.

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