

Fluorescence and Judd-Ofelt analysis of phenyl-containing europium chelate complexes in polystyrene

A.F.Adadurov, P.N.Zhmurin, V.N.Lebedev, V.N.Kovalenko

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Received March 16, 2011

The fluorescent properties of benzene-containing Eu chelate complexes in polystyrene (PS) have been investigated by fluorescence emission spectra. The influence of polymer medium on spectrometric properties of these complexes was demonstrated. In the Eu complex without phenyl rings the spatial layout of ligands was not fixed and under polystyrene matrix influence can undergo some changes. It was established that the presence of phenyl ring stabilizes its spatial arrangement around coordinate ion. According to measurements results the Judd-Ofelt parameters of Eu chelates-doped PS have been calculated.

Исследованы флуоресцентные свойства бензол-содержащих хелатных комплексов Eu в полистироле. Показано влияние полимерной среды на спектрометрические свойства этих комплексов. В Eu комплексе без фенильных колец пространственное расположение лигандов оказалось нефиксированным и подверженным влиянию полистирольной матрицы. Установлено, что наличие фенильного кольца стабилизирует расположение лиганда вблизи координатного иона. В соответствии с результатами измерений вычислены параметры Джадда-Офелта для Eu хелатов в полистирольной матрице.

1. Introduction

In recent years the fluorescent properties of chelate complexes of rare earth (RE) ions have been paid more and more attention because of their unique combination of rare earth fluorescence and organic ligands absorption. Moreover, these complexes provide an effective collection of triplet states excitation energy [1, 2]. Using rare earth complexes in organic light emitting devices increases their efficiency in almost three times [3]. Being used as activators the complexes allow increase the sensitivity of plastic scintillator to α -particles almost by an order [4, 5].

Usually RE complexes application is related to their introduction to some polymer medium (matrix). The most widely used me-

dioms are polymethylmethacrylate (PMMA) and polystyrene (PS) for their low absorption, relatively simple synthesis and low cost. The influence of MMA-matrix on optical properties of benzene containing europium complexes is investigated rather well [6], whereas for polystyrene it still not done. As far as polystyrene is an active scintillating matrix [7] then searching for new RE complexes which collect effectively the excitation energy of such a matrix opens the way to progress in increasing of an efficiency of plastic scintillators.

This paper analyzes the optical properties of benzene-containing chelate complexes of Eu^{3+} , dissolved in polystyrene. In the analysis the methods suggested by Judd and Ofelt [8, 9] were used.

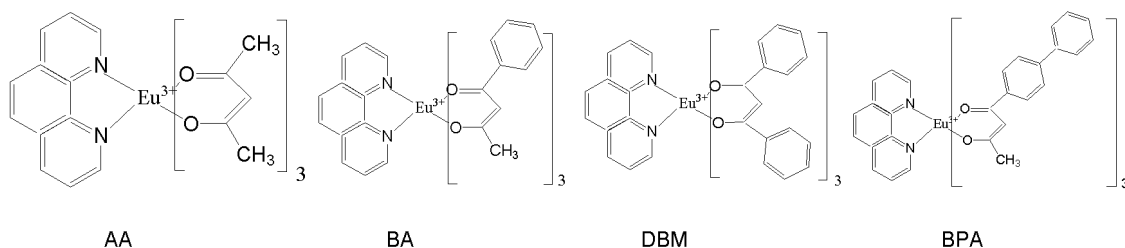


Fig. 1. Chemical structure of Eu chelates with increasing benzene ring substituents ligands.

2. Experimental

In the framework of our investigation four Eu complexes were synthesized with β -diketones containing different substituent radicals (Fig. 1). In all complexes, 1,10-phenanthroline was used as a neutral ligand. Its role was to substitute water molecules in Eu^{3+} inner coordinative sphere that reduce the radiationless processes and increase Eu ions fluorescence.

The synthesis was run as follows. Mixture of ligands containing β -diketone (6 mmol), 1,10-phenanthroline (2 mmol) and sodium hydroxide (6 mmol) was dissolved in 20 ml of 95 % ethanol under heating and intensive mixing. Europium chloride hexahydrate (2 mmol) was dissolved in 2 ml of distilled water and drop by drop was added to the ligands solution. Then the mixture was cooled and obtained yellow precipitate of Eu complex was filtered, washed by ethanol and water and re-crystallized from ethanol.

Europium dibenzoilmethanate phenanthroline ($\text{Eu}(\text{DBM})_3\text{Phen}$) was additionally purified by precipitation by hexane (30 ml) from benzene solution (30 ml).

All Eu complexes have the similar structural scheme which is presented in Fig. 1. They have the following full and short names:

1. (tris(Acetylacetonate)(1,10 — phenanthroline) europium III) [$\text{Eu}(\text{AA})_3\text{Phen}$];
2. (tris(Dibenzoylmethane)(1,10 — phenanthroline) europium III) [$\text{Eu}(\text{DBzM})_3\text{Phen}$];
3. (tris(Bezoylacetonate)(1,10 — phenanthroline) europium III) [$\text{Eu}(\text{BzA})_3\text{Phen}$];
4. (tris(Biphenylacetonate)(1,10 — phenanthroline) europium III) [$\text{Eu}(\text{BPA})_3\text{Phen}$];

So, Eu complex (1) is formed by ligands with methyl radicals only and does not contain any phenyl group. Other three Eu-complexes Eu (2–4) do contain phenyl groups.

Measurements of excitation and fluorescence spectra of the solutions and films were made on spectrofluorometer Fluoromax-4 (HORIBA, Joben Ivon Inc.).

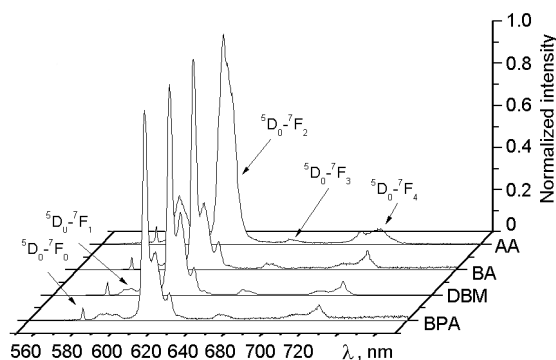


Fig. 2. Fluorescence emission spectra of Eu chelates-doped PS.

3. Results and discussion

3.1. Fluorescence emission spectra of PS doped with Eu^{3+} chelates

The fluorescence emission spectra of Eu^{3+} chelates-doped polystyrene with different benzene groups in coordination ligands under excitation at 265 nm, are shown in Fig. 2.

In fluorescence spectra of all complexes one can easily distinguish peaks corresponding to transitions from 5D_0 level to sublevels of $^7F_{0,1,2,4,6}$ terms. It is clearly seen the fine structure of $^5D_0 \rightarrow ^7F_2$ lines, caused by 7F_2 multiplet splitting by crystal field of ligands environment when there is a benzene ring in the chelate complex. Thus, if $^5D_0 \rightarrow ^7F_2$ line for $\text{Eu}(\text{AA})_3\text{Phen}$ complex is a wide structureless contour (Fig. 2), then in the lines of the same transition in $\text{Eu}(\text{DBM})_3\text{Phen}$, $\text{Eu}(\text{BA})_3\text{Phen}$ and $\text{Eu}(\text{BPA})_3\text{Phen}$ complexes one can clearly distinguish five components corresponding transitions on sublevels split by the to crystal field. Such character of line's behavior can indicate that spatial layout of ligands in $\text{Eu}(\text{AA})_3\text{Phen}$ complex is not fixed and under polystyrene matrix influence can undergo some changes. These changes lead to

crystal field fluctuations which are responsible for nonuniform lines widening. When the benzene ring is added to chelate ligand, the spatial coordination of the complex is stabilized as a result of the polymer environment influence. This can reduce the nonuniform widening of an optical transition line, which ultimately leads to observed fine splitting of ${}^5D_0 \rightarrow {}^7F_2$ transition line (Fig. 2).

In observed fluorescence spectra of all Eu complexes the line of ${}^5D_0 \rightarrow {}^7F_2$ transition is clearly seen while in fluorescence spectrum of Eu(AA)₃Phen complex in polymethylmetacrylate polymer media it totally absent [6]. It is well known that this transition of Eu³⁺ ion is electric- and magnetic-dipole forbidden even when central symmetric crystal field exists. The appearance of this line can be caused by influence of a crystal field which mixes 5D_0 and 7F_2 states with those states for which $J \neq 0$ [10]. Ultimately the intensity level of crystal field in which RE ion is placed can cause the forbidden transition allowing. Comparing to polystyrene the polymer media of polymethylmethacrylate have higher polarity. Such polarity can shield the crystal field of ligands environment acting on the coordinate ion. This shielding acts on those complexes which ligands have flexible layout like Eu(AA)₃Phen complex.

3.2. Judd-Ofelt analysis of PS doped with Eu³⁺ complexes

Fluorescence of rare-earth ions is determined by inter-configuration $4f-4f$ transitions which initially are electrically-dipole forbidden. This causes the low intensity of their absorption and emission lines. But population of rare earth ion excited state can be substantively increased by its coordination by organic ligands. In this case the organic ligands play a role of intramolecular energy transformers which provide an efficient transfer of their absorbed energy to RE ion and therefore increase the intensity of their fluorescence.

The intensity of absorption can be determined by transition oscillator strength which is proportional to the area under the absorption curve. The oscillator strength can be expressed in terms of molecular extinction ϵ , transition energy (in wave numbers) σ and a medium refraction index n by the following equation [11]:

$$f = \frac{2303mc^2}{N\pi e^2} \frac{9n}{(n^2 + 2)^2} \int \epsilon(\sigma) d\sigma = 4.31 \cdot 10^{-9} \frac{9n}{(n^2 + 2)^2} \int \epsilon(\sigma) d\sigma.$$

The coefficient of molar extinction is not greater than 10, therefore the oscillators strength is about 10^{-6} .

Judd [8] has showed that oscillator strength of electric-dipole transition, induced by external crystal field, can be defined in the following way:

$$f = \frac{8\pi^2 mc\omega}{3\hbar(2J+1)} \frac{(n^2 + 2)^2}{9n} \sum_{\substack{\Omega_\lambda \\ \text{even}\lambda}} \Omega_\lambda (f^n \Psi_J \| U^{(\lambda)} \| f^n \Psi_{J'})^2.$$

After digitalization of the RE ion full energy matrix the eigenvectors Ψ_J for each ion are:

$$|f^n \Psi_J\rangle = \sum_{\alpha LS} C(\alpha LS) |f^n \alpha LS J\rangle.$$

Basic wave functions $|f^n \alpha LS J\rangle$ are used directly to calculate the values of unit irreducible tensor operator:

$$(f^n \alpha LS J \| U^{(\lambda)} \| f^n \alpha' L' S J') = (-1)^{S+L+J+\lambda} \cdot \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & J' & \lambda \\ L' & L & S \end{Bmatrix} (f^n \alpha LS \| U^{(\lambda)} \| f^n \alpha' L' S).$$

In this equation the value $|f^n \alpha LS \| U^{(\lambda)} \| f^n \alpha' L' S\rangle$ is now directly calculable according to the formulas presented elsewhere [12]. Knowledge of the intensity of RE ion absorption allows to determine three parameters $\Omega_{2,4,6}$ and to reconstruct all optical characteristics of its spectrum.

Applying this approach to Eu³⁺ ion is faced with some difficulties. The point is that the values of irreducible tensor operators $\|U^{(\lambda)}\|^2$, that determines the intensities of excited electric-dipole transitions, for Eu³⁺ are different from zero only for a few transitions. Therefore there is no sufficient number of equations to determine the Judd parameters. Moreover, among three presented matrix elements for absorption bands from ground and first excited states, element $\|U^{(4)}\|^2$ equals to zero (Table 1), which makes it impossible the Ω_λ full determination.

In fluorescence spectra the ${}^5D_0 \rightarrow {}^7F_1$ is the magnetic dipole permitted transition of Eu³⁺ ion with known calculable value of the transition intensity which is electrically-dipole forbidden (Table 2). At the same time intensities of fluorescent lines ${}^5D_0 \rightarrow {}^7F_{2,4,6}$ are totally determined by Ω_λ coefficients;

Table 1. Matrix elements for the different absorption transitions

Transition	Reduced matrix element		
	$\ U^{(2)}\ ^2$	$\ U^{(4)}\ ^2$	$\ U^{(6)}\ ^2$
${}^7F_0 \rightarrow {}^5F_2$	0.0008	0.0000	0.0000
${}^7F_0 \rightarrow {}^5D_4$	0.0000	0.0011	0.0000
${}^7F_0 \rightarrow {}^5G_4$	0.0000	0.0007	0.0000
${}^7F_0 \rightarrow {}^5G_2$	0.0006	0.0000	0.0000
${}^7F_0 \rightarrow {}^5L_6$	0.0000	0.0000	0.0155

therefore they can simply be determined from ${}^5D_0 \rightarrow {}^7F_1$ lines ratio and fluorescence lines intensities

$$I_J = \hbar\omega A_{radJ} N({}^5D_0),$$

where

$$A_{radJ} = \frac{4e^2\omega^3}{3\hbar c^3} \frac{n(n^2 + 2)^2}{9} \sum_{\lambda} \Omega_{\lambda} |\langle {}^7F_J \| U^{\lambda} \| {}^5D_0 \rangle|^2.$$

For magnetic-dipole transition ${}^5D_0 \rightarrow {}^7F_1$, $A_{rmd} = n^3 A_{md0}$ is known and equal to 14.65 s^{-1} [13].

As far as

$$\int J_J(\sigma) d\sigma / \int J_1(\sigma) d\sigma = A_{radJ} / A_{rmd},$$

then to determine Ω_{λ} parameter it is sufficient to obtain the areas ratio from fluorescence spectra (Fig. 2). In this figure we can clearly distinguish the ${}^5D_0 \rightarrow {}^7F_1$ transition (17271 cm^{-1}). Since all different from $\|U^{(2,4)}\|^2$ values of unit irreducible tensor operator equal to zero, the intensity of

${}^5D_0 \rightarrow {}^7F_{2,4}$ transition is determined only by one summand which is proportional to $\Omega_{2,4}$. So, the $\Omega_{2,4}$ is uniquely determined from intensities of corresponding transitions (Table 2).

It is not possible to determine Ω_6 from fluorescence spectra because the line of ${}^5D_0 \rightarrow {}^7F_{2,4}$ transition is weak, and practically can not be registered.

Obtained Ω_2 values differ in 10 % limit from the same coefficients obtained for the same complexes dissolved in polymethylmethacrylate [6]. This can tell us about small decreasing of a covalence of RE bonds with ligands surrounded.

4. Conclusions

The analysis of fluorescence of Eu^{3+} chelate complexes in polystyrene allowed us to define the Judd-Ofelt parameters and to estimate the influence of polymer medium on spectrometric properties of these complexes. It was established that the presence of the phenyl ring in a ligand stabilized its spatial arrangement around coordinate ion.

References

1. R.C.Evans, P.Douglas, C.J.Winscom, *Coordination. Chem. Rev.*, **250**, 2093 (2006).
2. K.Binnemans, *Chem. Rev.*, **109**, 4283 (2009).
3. L.D.Hou, L.Duan, J.Qiao et al., *Appl. Phys. Lett.*, **92**, 263301-1 (2008).
4. A.F.Adadurov, P.N.Zhmurin, V.N.Lebedev, V.N.Kovalenko, *Nucl. Instrum. and Meth. in Phys. Res. A.*, **621**, 354 (2010).
5. I.H.Campbell, B.K.Crone, *Appl. Phys. Lett.*, **90**, 012117-1 (2007).
6. H.Liang, F.Xie, Zh.Jin et al., *Spectrochim Acta Part A*, **71**, 588 (2008).

Table 2. Matrix elements for the different fluorescence transitions

Transition	Energy (cm^{-1})	Reduced matrix element		
		$\ U^{(2)}\ ^2$	$\ U^{(4)}\ ^2$	$\ U^{(6)}\ ^2$
${}^5D_0 \rightarrow {}^7F_0$	17228	0	0	0
${}^5D_0 \rightarrow {}^7F_1$	16920	0	0	0
${}^5D_0 \rightarrow {}^7F_2$	16362	0.0032	0	0
${}^5D_0 \rightarrow {}^7F_3$	15462	0	0	0
${}^5D_0 \rightarrow {}^7F_4$	14224	0	0.0023	0
		$\Omega_2(10^{-20})\text{cm}^2$	$\Omega_4(10^{-20})\text{cm}^2$	
Eu(AA) ₃ Phen		5.44	1.35	
Eu(BA) ₃ Phen		13.4	1.40	
Eu(DBA) ₃ Phen		16.4	1.22	
Eu(BPA) ₃ Phen		12.1	1.35	

7. J.B.Birks, *The Theory and Practice of Scintillation Counting*, Pergamon Press (1964).
8. B.R.Judd, *Phys. Rev.*, **127**, 750 (1962).
9. G.S.Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).
10. T.Kushida, M.Tanaka, *Phys.Rev.B*, **65**, 195118 (2002).
11. W.T.Carnall, P.R.Fields, B.G.Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).
12. B.R.Judd, *Operator Techniques in Atomic Spectroscopy*, McGraw-Hill, New York (1963).
13. M.J.Weber, T.E.Varitimos, B.H.Matsinger, *Phys. Rev. B*, **8**, 47 (1973).

Флуоресценція і Джадд-Офелт аналіз бензол-вмісних хелатних комплексів європію у полістиролі

О.Ф.Ададуров, П.М.Жмурін, В.Н.Лебедев, В.Н.Коваленко

Досліджено флуоресцентні властивості бензол-вмісних хелатних комплексів Eu у полістиролі. Показано вплив полімерного середовища на спектрометричні властивості цих комплексів. У Eu комплексі без фенільних кілець просторове розташування лігандів виявилось нефіксованим і схильним до впливу полістирольної матриці. Встановлено, що наявність фенільного кільця стабілізує розташування ліганда поблизу координаційного іону. У відповідності з результатами вимірювань обчислено параметри Джадда-Офелта для Eu хелатів у полістирольній матриці.