QUANTUM EFFICIENCY OF THE LUMINESCENCE OF YTTERBIUM(III) β-DIKETONATES*

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The processes of the energy deactivation of electronic excitation in Yb(III) β-diketonates and their dependence on the nature of β-diketone and the second ligand as well as the environment and its state (complexes in organic solvents and polymer matrix) were studied. Taking as an example the ytterbium thenoyltrifluoroacetonate, it was shown that the energy losses in the ligand and Yb(III) ion, which is due to the high-frequency vibrations of the central C–H group of the β-diketone, can lead to the decreased quantum yield of the luminescence. The increase in the medium rigidity causes the decrease in losses in the ligand, but does not affect the deactivation of the Yb(III) ion excited level. In the mix-ligand complexes the second ligand (1,10-phenanthroline) improves the screening of the central ion providing almost full transfer of the energy, absorbed by ligand, to ytterbium ion.

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1. Introduction

The lanthanide β-diketonates are used not only for the separation of the elements of this series as converters of the light energy, luminescent markers of the biological molecules, etc., [1, 2], but also for the high sensitive detection of Sm(III) and Eu(III) [2], and recently, of Nd(III) and Yb(III) [2–4]. We have studied phy-

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sicochemical and optical properties of these lanthanide compounds with the different derivatives of acetylacetone and found a correlation of some parameters of Ln(III) β-diketonates with the properties of ligands [4, 5]. The energies of the excited triplet T_1 levels of β-diketones lie between 19600 and 23000 cm^{-1}, corresponding to the gap between the T_1 level of the ligand and the excited level of Sm(III) and Eu(III) approximately 4000 cm^{-1}, and for Nd(III), about 7500 cm^{-1}. In contrast to the above lanthanide ions, ytterbium is characterized by one excited $^2F_{5/2}$ and one ground $^2F_{7/2}$ levels. The gap between the T_1 levels of ligands and the $^2F_{5/2}$ level of Yb(III) considerably exceeds that for Sm(III) and Eu(III) and amounts to 10000–13000 cm^{-1}. For this reason, on the one hand, the Yb(III) ion, to a greater degree than Sm(III), Eu(III), and Nd(III) ions, is subjected to quenching by the environment, mainly by water molecules, and on the other hand, it quenches itself the luminescence of lanthanide ions the excited levels of which are located higher.

    Ytterbium β-diketonates are a good model system for the study of the processes of intra- and intermolecular energy deactivation. The availability of only one excited level of Yb(III) ion, the energy of which is (about 10000 cm^{-1}) much lower than the energy of the lower triplet level of the anyone using β-diketones, allows to except from the examination the processes, with the participation of the lanthanide ion high-excited levels, was able to take part in the activation and deactivation processes of the luminescence. In addition, Yb(III) ion is characterized by a high probability of the radiative transition significantly more than that for Eu(III) ion which has the intensive luminescence in the complex with the fluoro-containing β-diketones.

    For this reason, in this paper we studied the deactivation processes of the electronic energy excitation in the ytterbium β-diketonates and their dependence upon the nature of the main (β-diketone, L) and additional (1,10-phenanthroline, Phen) ligands, environment and its aggregate state.

2. Experimental procedures

    Acetylacetone derivatives containing three or more carbon atoms in the fluorinated radical (R_F) were synthesized using the procedure described elsewhere [5]. β-Diketones containing six or eight carbon atoms in R_F ($-C_6F_{13}$ or $-C_8F_{17}$) and also oxygen-containing β-diketones were synthesized for the first time. They were identified by the techniques of IR and NMR spectroscopy, gas-liquid chromatography, and elementary analysis. The purity of β-diketones was 98–99.5%. The organic solvents were additionally purified by distillation according to [6].

    The solid Yb(III) complexes were prepared as described elsewhere [2].

    Deuteration of thenoyltrifluroacetone (TTA) in the central C–H group was realized by replacing hydrogen in deuterated ethanol (C_2D_5OD) for 48 h. Completeness of the deuteration was checked by ^{13}C NMR spectra.

    The chelate solutions in non-polar solvents (toluene, four-chloride carbon) and polymer, poly(methyl methacrylate) (PMMA), were investigated. The polymeric samples were prepared as the films with thickness of 10 μm.

    The absorption spectra of β-diketones and their Yb(III) complexes were recorded with a Specord M-40 spectrophotometer. The luminescence spectra were

obtained on an SDL-2 spectrophotometer (Leningrad Opto-mechanical Association, St. Petersburg, Russia). Xenon lamp was used as an excitation source. The corrected spectra were obtained with a standard lamp. The luminescence lifetime was measured upon the laser excitation ($\lambda = 355$ nm, $t_{imp} = 10$ ms), its intensity was registered at the band maximum (975 nm). The resolution time of the registration system is 100 ns.

Since the reference substance that absorbs in a field of 340 nm and emits in a field of 975 nm is absent, the luminescence quantum yield of Yb(III) β-diketonates was measured by the absolute method on the homemade plant [7].

3. Results and discussion

As an example the luminescence spectra of double and mix-ligand, including 1,10-phenanthroline, Yb(III) complexes with acetylacetone thienyl derivatives are presented in Fig. 1. The obtained molar extinction coefficients (ε), quantum yield and lifetime of luminescence for the Yb(III) complexes with the mentioned β-diketones are given in Tables I and II.
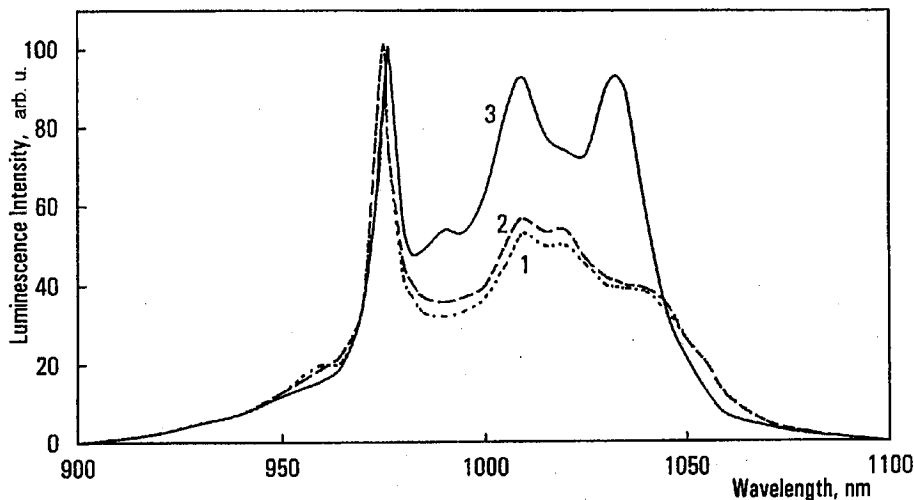

Fig. 1. The luminescence spectra of double (1,2) and mix-ligand (including 1,10-phenanthroline) (3) Yb(III) complexes with acetylacetone thienyl derivatives containing $R_F = CF_3$ (1,3) and $R_F = C_6F_{13}$ (2). Solutions in toluene.

The analysis of the obtained data allows to estimate the role of the main and additional ligands in the processes of deactivation of electronic excitation energy, the role of the medium and the influence of its rigidity.

A comparison of calculated values of molar extinction coefficients shows that in the case of double complexes (YbL$_3$) the lengthening of R_F leads to the increase in their absorbance. However, neither the length of R_F nor medium rigidity affect significantly the absorbance of the mix-ligand complexes (YbL$_3$Phen).

As one can see from the luminescence spectra of the double complexes (YbL$_3$), the lengthening of R_F chain CF$_3$ to C$_6$F$_{13}$ leads to insignificant relative increase in the long wave wing and does not affect the position of the main

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TABLE I

Spectral-luminescence characteristics of double and mix-ligand, including 1,10-phenanthroline, Yb(III) complexes with thienyl derivatives of acetylacetone* in solutions and polymeric matrix.

| Ligands		$\varepsilon \times 10^{-4}$			$\varphi \times 10^{3}$		τ [μs]			$\varphi/\tau \times 10^{-3}$ [s^{-1}]	
β-diketone (R_F)	second (additional)	toluene	CCl$_4$	PMMA	toluene	PMMA	toluene	CCl$_4$	PMMA	toluene	PMMA
CF$_3$	–	4.2	3.8	4.3	3.5	5.5	5.7	4.3	9.7	0.61	0.57
CF$_3$	Phen	4.8	4.4	4.3	11.0	11.1	10.4	11.9	10.7	1.06	1.03
C$_3$F$_7$	–	4.4	4.3	4.1	2.6	3.7	8.6	5.4	11.0	0.30	0.34
C$_3$F$_7$	Phen	6.1	5.5	4.6	12.0	12.0	11.7	11.9	11.1	1.02	1.12
C$_6$F$_{13}$	–	4.3	4.3	4.0	2.4	4.2	9.2	5.6	11.4	0.26	0.37
C$_6$F$_{13}$	Phen	4.7	4.3	4.4	8.8	10.0	11.8	11.3	11.0	0.75	0.91

$*R_F\text{--CO--CH}_2\text{--CO--}$

TABLE II

Spectral-luminescence characteristics of double and mix-ligand Yb(III) complexes with phenyl derivatives of acetylacetone*; solutions in toluene.

Ligands		$\varepsilon \times 10^{-4}$	$\varphi \times 10^3$	τ	$\varphi/\tau \times 10^{-3}$
β-diketone (R_F)	second (additional)			$[\mu s]$	$[s^{-1}]$
CF_3	–	3.4	1.1	1.8	0.61
CF_3	Phen	3.8	6.5	10.4	0.63
C_3F_7	–	4.0	1.5	2.5	0.60
C_3F_7	Phen	4.2	8.8	10.7	0.82
C_6F_{13}	–	4.4	1.7	2.6	0.65
C_6F_{13}	Phen	4.6	9.8	11.0	0.89
C_8F_{17}	–	4.8	1.9	2.5	0.76
C_8F_{17}	Phen	4.1	9.2	10.5	0.88

$*R_F–CO–CH_2–CO–\langle\bigcirc\rangle$
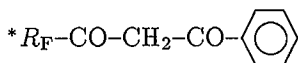
luminescence band (Fig. 1, spectra 1 and 2). This confirms the weak influence of R_F length on the electronic shell of Yb(III) ion and, in accordance with the data of the absorption spectra, is due to the inhomogeneous widening at the lengthening of R_F.

The addition of the second ligand (Phen), causing the long wave shift of the main maximum (980 nm) and the significant increase in the intensity of the long wave wing with the appearance of the pronounced maxima at 1008 and 1033 nm (Fig. 1, spectrum 3), affects much more the luminescence spectrum of Yb(III) ion. In the luminescence spectra of YbL$_3$Phen, as well as in the absorption spectra, no significant influence of the chain length and medium rigidity is observed. All this points out that the addition of the second ligand (Phen) not only screens the Yb(III) ion from the influence of the outer medium, but can transform its outer structure in a larger degree than the lengthening of R_F chain of β-diketone.

The data on the quantum yield of luminescence (φ) confirm the mentioned above hypothesis. Thus, the addition of the second ligand (Phen) leads to the considerable increase in φ, the values of which become close to each other and weakly depend on the nature of β-diketone (Table I, II). At the same time for the double complexes the significant dependence of φ on the ligand nature is observed and it is impossible to explain this only by different screening the lanthanide ion by the ligand from influence of environment, since the values of luminescence lifetime (τ) for all the complexes are close (Table I, II) and, consequently, the probabilities of deactivation of the excited state of Yb(III) are also close. Reducing the ratio of quantum yield to the luminescence lifetime (φ/τ) in double Yb(III) complexes indicates the energy losses of electronic excitation in the ligand as a result, it does not completely reach the central ion. In the mix-ligand complexes including also Phen,

apparently, the total energy of the electronic excitation, absorbed by the ligand, is transferred to the Yb(III) ion. Such a conclusion can be made from a comparison of the φ/τ values with the probability of corresponding emissive transition of the Yb(III) ion which according to [8] is 1500 s^{-1}. The ratio of luminescence quantum yield to luminescence lifetime of Yb(III) ion gives the product of probability of emissive transition by quantum yield of the energy transfer from the ligand to Yb(III) ion. Assuming that probability of emissive transition for Yb(III) ion, as for other Ln(III) ions, the open $4f$-shell of which is screened by the outer $5d$-electrons, does not depend very much on the type of compound containing this ion, then it can be expected that in β-diketone complexes the probability of Yb(III) emissive transition will be about 10^{-3} s.

As can be seen from Table I and II, the φ/τ values for mix-ligand complexes (YbL$_3$Phen) are close to each other and are about 10^{-3} s, i.e. actually all the energy, absorbed by the ligand, is transferred to the central ion. At the same time for the double complexes (YbL$_3$) the φ/τ ratio is by 2–3 times less than in the mix-ligand ones, that may be also connected with the reducing of the probability of emissive $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. However, since τ values for the double and mix-ligand in PMMA are actually the same, the lower φ/τ values, apparently, are connected with increasing the probability of non-radiative deactivation of the energy in the ligand and its competition with intramolecular energy transfer from the ligand to Yb(III) ion.

Among the investigated Yb(III) β-diketonates the influence of aggregate state of the medium on luminescence quantum yield is pronounced in a greatest degree for Yb(DBM)$_3$Phen, for which the quantum yield is reduced by 7 times when traveling from the polymeric matrix ($\varphi = 0.91 \times 10^{-3}$) to the solution in toluene ($\varphi = 0.13 \times 10^{-3}$). In this case the luminescence lifetime of Yb(III) ion changes very weakly ($\tau = 8$ and 9 μs in PMMA and toluene respectively) indicating the rise of additional losses rather in a ligand than in Ln(III) ion and can be explained by the formation of the conformers in non-rigid media, arising from the excited states of the ligand, for instance, as a result of the rotation of phenyl rings around a single bond. For the thienyl derivatives the influence of medium rigidity on luminescence quantum yield is considerably weaker and in the case of mix-ligand complexes it is actually absent (see Table I).

The absence of the dependence of luminescence lifetime and, consequently, all the processes of the excited state deactivation of Yb(III) ion on aggregate state of the medium in all the investigated mix-ligand complexes (see Table I) should be especially noted. A slight decrease in luminescence lifetime of the double Yb(III) β-diketonates when traveling from the polymeric matrix to the solution can be connected with the presence of water traces in the organic solvent that is included into the first coordination sphere of Yb(III) ion to increase the probability of its non-radiative deactivation.

Analysis of the data obtained demonstrates that rigidity of the medium in fact does not affect the deactivation processes of the excited state of Yb(III) ion but can significantly influence the non-radiative deactivation processes in the ligand competing with intramolecular energy transfer from the ligand to the ytterbium ion. However, when the second ligand (Phen) is incorporated the influence of the

medium rigidity is relaxed and in this case it can be explained by the increased rigidity of the complex.

The presence of losses in ligand reduces the luminescence quantum yield of Yb(III) β-diketonates, however, the main reason for its low value is the quenching of Yb(III) excited level. As it can be seen from Tables I and II, luminescence lifetime of Yb(III) in all the investigated complexes is actually the same and about 10^{-5} s that is significantly less than the lifetime of its emissive transition (10^{-3} s). The general reason for quenching the excited states of Ln(III) ions is the energy transfer to the corresponding overtones of high-frequency vibrations of nearest environment [8]. Here, the high-frequency vibrations of both ligand and solvent can participate in the deactivation of the excited states of Ln(III) ion. As it can be seen from Table I, the traveling from toluene to CCl_4, containing no high-frequency vibrations, does not lead to the increase in luminescence lifetime which confirms the dominating role of the ligand. The close τ values for the double and mix-ligand complexes, including also Phen, point out the slight participation of second ligand in the process of deactivation of Yb(III) excited level. In addition, the τ values do not depend on the β-diketone nature.

The combination of all the obtained data may be explained with the assumption that overtones of high-frequency vibration of the central C–H group, present in all β-diketones, perform the main role in deactivation of Yb(III) excited level, here the role of side substituents (R_1 and R_2) is insignificant.

The dominating role of the central C–H group, apparently, is explained by the fact that it is a single hydrogen-containing one in six-member chelate cycle, formed by Yb(III) ion and β-diketone.
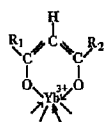
Deactivation of Yb(III) ion excited state by high-frequency vibrations of β-diketone C–H groups was studied taking as an example the thenoyltrifluoroacetonate complexes. Replacing H_2O by D_2O in the double complex leads to the increase by 1.46 times of luminescence quantum yield of Yb(III) ion and the deuteration of β-diketone gives the additional increase in φ by 1.15 times. In the case of mix-ligand complexes the relative increase in φ was 1.46 and 1.05 respectively.

As follows from the above, the share of non-radiative losses, expanding in high-frequency vibrations of OH oscillators, is considerably higher than in the vibrations of ligand C–H groups.

Thus, the performed investigation has demonstrated that the losses of energy both in the ligand itself and in Yb(III) ion, that are determined by high-frequency vibrations of the central C–H groups in β-diketone, can lead to the increase in luminescence quantum yield of Yb(III) ion in the complexes with β-diketones. The increase in medium rigidity causes reducing the losses in ligand but does not affect the deactivation of the excited state of Yb(III) ion. The formation of mix-ligand complex upon introduction of neutral ligand (Phen) into the Yb(III) β-diketonate molecule improves screening of the central ion providing actually complete transfer of energy, absorbed by the ligand, to the ytterbium ion.

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