

Journal of Alloys and Compounds 451 (2008) 94-98

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The orange emission of single crystals and sol gels based on Sm³⁺ chelates

J. Cybińska^a, J. Legendziewicz^{a,*}, V. Trush^b, R. Reisfeld^c, T. Saraidarov^c

^a Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

^b Department of Chemistry, Kiev State University, Vladimirskaja 64, 2520033 Kiev, Ukraine

^c Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Givat-Ram, 91904 Jerusalem, Israel

Available online 13 April 2007

Abstract

The new type of Sm^{3+} chelates $LnPh\beta_3L$ with orange emission obtained as single crystals as well as incorporated into zirconia-glymo films can find application in electro-luminescent diodes. Absorption, emission and emission excitation spectra at 293, 77 and 4 K, as well as luminescence decay time measurements with different energy of the excitation lines were used to characterize the systems based on the Sm^{3+} L-phosphoro-azo derivative of β -diketone: (CCl₃C(O)NP(O)(OCH₃)₂) and dipyridine SmPh β_3 Ldip in the solid state, gel and solution. The dramatic increase of the luminescence intensities was a result of the efficient exchange energy transfer and increase of rigidity of the system under investigation. © 2007 Elsevier B.V. All rights reserved.

Keywords: β-Diketones; Samarium

1. Introduction

The interest in the photophysical properties of lanthanide ion complexes has grown considerably because such complexes can be used as light conversion devices based on efficient energy transfer thus overcoming the very small absorption coefficient of the lanthanide ions [1,2]. The design of efficient lanthanide complexes has become an important research goal, being published by several research groups [1-5]. The rare earth ions with β-diketones and their derivatives can also find potential application as NMR shifts reagents [5,6] as well as in bioscience [7]. Some important features of these organic fluorophores are their large Stokes' shift, narrow bands emission and long decay times [7]. Among all trivalent lanthanide ions complexes the studies were mainly focused on the europium and terbium β -diketones. The Sm³⁺ systems have been less investigated because in general present low emission intensity. To enhance luminescence intensity, lanthanides β-diketones could be incorporated into silica or zirconia glasses using the sol gel technique, which is the low temperature method for obtaining glass bulks or thin film [5,8–10].

0925-8388/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2007.04.088

This paper is focused on the comparison of the optical properties of Sm^{3+} chelates $\text{LnPh}\beta_3\text{Ldip}$ type as a single crystals as well as incorporated into zirconia glasses. Basing on the model described by Malta et al. for the energy transfer selection rules and considering the possible channels of the energy transfer, we analysed the mechanism responsible for enhancement of luminescence efficiency.

2. Experimental

The absorption spectra of single crystals were recorded in the 220-1600 nm at 4 and 293 K using a Cary Varian 50 spectrometer range equipped with an Oxford CF 1204 helium flow cryostat. The radiative transition probabilities were calculated from absorption spectra.

The high-resolution luminescence spectra with a resolution of 0.01 nm were recorded between 470 and 750 nm by using an Action Research Corporation Spectra Pro 750 monochromator equipped with a Hamamatsu R 928 photomultiplier as the detector. The emission excitation spectra at 77 and 293 K were measured on a SLM AMINCO SPF-500 spectrofluorimeter equipped with a 300 W Xe-lamp and a liquid-N₂ cooled cryostat.

The luminescence decay times at 293 and 77 K were measured using the third harmonic of a Nd-YAG laser as the excitation source and oscilloscope Tektronix TDS 3052 B.

The Raman spectra were recorded on a Nicolet Raman accessory attached to a Nicolet Magna 860 spectrometer and were applied to assign the vibronic lines in the electronic spectra.

Intensities of the f-f transitions were calculated by integration of the Gauss-Lorenz curve and transformed to the oscillator strength values according

^{*} Corresponding author. Tel.: +48 71 3757300; fax: +48 71 3282348. *E-mail address:* jl@wchuwr.pl (J. Legendziewicz).



Fig. 1. Part of the molecular structure of SmPh_{β3}dip in crystal structure.

to the relation:

$$P = \frac{2.303mc^2}{N\pi e^2} \int_{\sigma 1}^{\sigma^2} \varepsilon(\sigma) \,\mathrm{d}\sigma = 4.33 \times 10^{-9} \int_{\sigma 1}^{\sigma^2} \varepsilon(\sigma) \,\mathrm{d}\sigma$$

3. The sample preparation

The phosphoro-azo derivatives of the β -diketones (HL) and its sodium salts (NaL) were prepared according to the procedure described earlier [11]. The relevant conditions for the preparations of the single crystals complex of LnPh β_3 L are disclosed in the patent procedure.

The zirconium thin films were obtained by hydrolysis of zirconium *n*-tetrapropoxide. The procedure for thin films incorporating samarium complex was similar to that reported in the literature [5,9,10].

4. Discussion

The SmPh β_3 dip crystallizes in the space group *C2/c*. The crystal structure of Sm(III) complex is identical with the previously reported europium compound and is created by the monomeric units [5] (Fig. 1). The coordination number of samarium ion is eight. The central ion is bound by six oxygen atoms of phosporo-azo derivatives of β -diketone and by two nitrogen atoms of 2,2'-dypiridine.

The absorption spectra of the SmPh β_3 dip single crystal recorded at RT and 4 K are displayed on Fig. 2a and b. The spectra consist of narrow bands assigned to transitions from ${}^{6}H_{5/2}$ ground state to the higher energy multiplets. The Sm(III) ion has



Fig. 2. The absorption spectra of SmPh β_3 dip single crystal at RT and 4 K.

Table 1

Oscillator strength values ($P \times 10^8$) of the f–f transitions for the SmPh β_3 dip single crystal at RT and 4 K

$\overline{^{6}}H_{5/2} \rightarrow$	$P \times 10^8 \ 293 \ \mathrm{K}$	$P \times 10^8 \; 4 {\rm K}$	Range (nm)
⁶ F _{1/2} , ⁶ H _{15/2}	83.9862	37.9104	1700-1575
⁶ F _{3/2}	77.5851	150.0577	1575-1450
⁶ F _{5/2}	225.4082	166.2738	1450-1317
⁶ F _{7/2}	296.5446	127.7130	1317-1180
⁶ F _{9/2}	207.9782	120.3562	1150-1050
⁶ F _{11/2}	27.3347	72.5448	975-925
⁴ G _{5/2}	2.5138	3.2419	569-550
⁴ F _{3/2}	4.8751	6.1584	535-518
⁴ G _{7/2}	1.4687	14.6235	505-493
⁴ I _{11/2} , ⁴ M _{15/2} , ⁴ I _{9/2}	58.9909	153.8770	494–469
⁴ I _{13/2}	22.2767	53.6622	469-457
⁴ F _{5/2}	3.0222	1.8027	457-450
⁴ I _{15/2} , ⁴ G _{9/2} , ⁴ M _{17/2}	20.8652	29.1478	450-425
⁴ M _{21/2} , ⁴ K _{11/2} , ⁶ P _{3/2} ,	513.6420	216.0506	414-369
⁴ F _{7/2}			
⁴ L _{13/2}	83.5690	77.1177	396-385
⁴ F _{9/2} , ⁴ K _{13/2} , ⁴ L _{17/2} ,	147.3613	82.1248	385-369
⁶ P _{7/2} , ⁴ D _{1/2}			
(⁴ D, ⁶ P) _{5/2} , ⁴ D _{3/2}	147.9616	58.0559	369-358
⁴ H _{7/2}	88.5572	25.9636	358-354
${}^{4}H_{11/2}\ldots {}^{4}K_{15/2}$	34.9580	43.5105	349–344

an odd-electron configuration $(4f^5)$, thus the maximum number of the Stark components for any symmetry lower than cubic is J + 1/2 dublet Kramers. The calculation of radiative transition probabilities were done for all the transitions assigned in the spectra and are collected in Table 1.

It is expected that the lowering of the temperature leads to decrease of the intensities, which is caused by depopulation of the Stark components of ${}^{6}\text{H}_{5/2}$ term splitted by crystal field and by the effect of vibronic coupling. In the system under investigation, we observed decrease in the intensity of almost all transitions, however, in some case the intensity increase but the values of oscillator strengths remain in the same order of magnitude. The ${}^{6}\text{H}_{5/2} \rightarrow {}^{6}\text{F}_{1/2}$ is the hypersensitive transition (obeying the selection rules $\Delta J = 2$, $\Delta L = 2$) for Sm(III) ions. In our compound this transition is overlapped by ${}^{6}\text{H}_{5/2} \rightarrow {}^{6}\text{H}_{15/2}$ transition, thus the detailed analysis of the spectra is rather difficult. The second transition, which obeys the selection rules for the hypersensitive transition is ${}^{6}\text{H}_{5/2} \rightarrow {}^{6}\text{F}_{9/2}$ one. The intensity of this transition decrease with lowering temperature, indicating no structural transformations.

The system under investigation shows a very efficient orange luminescence as a single crystal, sol as well as incorporated into zirconia thin film. Fig. 3 presents the emission spectra of SmPh β_3 dip single crystals under the UV excitation. The emission spectra of a SmPh β_3 dip single crystal at 293 and 77 K consist of four main bands ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ (565 nm), ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (610 nm), ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ (650 nm), ${}^4G_{5/2} \rightarrow {}^6H_{1/2}$ (710 nm). The ${}^4G_{5/2} \rightarrow {}^6H_{3/2}$ transitions (in the spectral range ~530 nm) were not detected probably because of concentration quenching. The highest relative intensity exhibits the ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition magnetic dipole forbidden and electric-dipole allowed. According to the X-ray data, the Sm(III) ion occupies the low symmetry site, thus the transitions should



Fig. 3. The emission spectra of SmPh $\beta_3 dip$ single crystal at RT and 77 K.

be splitted into maximum number (J + 1/2) components. In the single crystal emission spectra apart from ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ transition, which consist of three components, all other bands are not splitted into maximum number of Stark components. In the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transitions, the broadening and overlapping of the bands was observed. The decrease the temperature from 77 to 4 K most probably could lead to the separation of all Stark components.

The luminescence decay curve for the SmPh β_3 dip single crystal was analysed and the decay times at RT as well as 77 K were established. The decay functions were monoexponential. The decay times are practically temperature independent and they are equal to 60 and 80 μ s at RT and 77 K, respectively. These values are in good agreement with the data reported by Malta for different kind of Sm(III) β -diketone with phosphine oxides ligand [12].

The emission excitation spectra of the single crystals at 293 and 77 K exhibit some narrow lines of f–f transitions of Sm(III), and in UV range broad ligand transitions (Fig. 4). This indicates



Fig. 4. The emission excitation spectra of $\text{SmPh}\beta_3\text{dip}$ single crystal at RT and 77 K.



Fig. 5. The absorption and emission excitation spectra of SmPh β_3 dip single crystal at RT.

that most of the excitation energy is absorbed by the ligand and then the energy is transferred to Sm(III) ion levels and the orange emission occurs. It is well known that the efficiency of luminescence in lanthanide β -diketones depends on the energy levels of organic ligand and metal ions. The data reported previous by Legendziewicz et al. for EuPhB3dip and TbPhB3dip single crystals show that the energy transfer in the same kind of compound occurs mainly from singlet and triplet states of dipyridine ligand [5]. Since the efficiency of emission depends on energy of excitation, therefore also in this chelate sensitization of the emission is due to dipyridine states. It is worth to notice that the intensity of the ligand bands in UV region for SmPhB₃dip is lower than in EuPhB3dip UV spectra. According to the calculation of the probability of E-T in europium systems by Malta et al., the C-T state should decrease the efficiency of energy transfer. In consequence, for Sm(III) the E-T should be more efficient because the C-T state not take part in the energy transfer mechanism. Thus, the other mechanism is responsible for the decrease of emission intensity in SmPh_{β3}dip complex, which could be explained by comparison of UV absorption and excitation spectra. Fig. 5 displays absorption and excitation spectra of SmPh₃dip chelate in 200–500 nm range. Basing on the results presented in Fig. 5, we can conclude that the surface quenching in Sm (III) chelate is similar as in Eu(III) chelate spectra, but because the energy of triplet state is almost in resonance with $^4F_{5/2}$ state of Sm(III) and the energy gap between $T{-}^4G_{5/2}$ state is large, the multiphonon relaxation should fad the emitting level, moreover, we should take into account the back energy transfer from ${}^{4}F_{5/2} \rightarrow T$ state. On the other hand, from two possible mechanisms proposed by Malta for energy transfer in the case of Sm(III) the exchange mechanism seems to be operative, whereas the dipole–dipole and dipole– 2^{λ} pole mechanism are less important.

For the dipole–dipole, dipole– 2^{λ} pole ($\lambda = 2, 4$ and 6) and exchange mechanisms one can use the following expressions for the transfer rate W_{ET} proposed by Malta et al. [13]:

$$W_{\rm ET} = \frac{2\pi}{\hbar} \frac{e^2 S_L}{(2J+1)GR_L^6} F \sum_{\lambda=2,4,6} \Omega_{\lambda}^{ed} \langle \alpha' J' || U^{(\lambda)} || \alpha J \rangle^2$$
$$W_{\rm ET} = \frac{2\pi}{\hbar} \frac{e^2 S_L}{(2J+1)G} F \sum_{\lambda=2,4,6} \gamma_{\lambda} \langle \alpha' J' || U^{(\lambda)} || \alpha J \rangle^2$$
$$W_{\rm ET} = \frac{8\pi}{3\hbar} \frac{e^2 (1-\sigma_0)^2}{(2J+1)R_L^4} F \langle \alpha' J' || S || \alpha J \rangle^2 \sum_m$$
$$\left| \left\langle \phi \left| \sum_k \mu_z(k) s_m(k) \right| \phi' \right\rangle \right|^2$$

It is worth noting that for the large $U^{(4)}$, $U^{(6)}$ matrix elements most probably the ${}^{4}I_{13/2}$ level takes part in the E–T process. It is also important that the energy of the ligand S state (31,000 cm⁻¹) is localized in the range of the Sm(III) levels with very low $U^{(\lambda)}$ matrix elements, thus other direct S–Sm(III) states only slightly affect the final quantum yields of the sensibilized Sm(III) emission.

Fig. 6 shows the emission spectra of the crystal under investigation in the form of sol obtained by conventional sol-gel methods. The bands are much broader, but the main features of the spectra remain the same as for the single crystals, which allow us to conclude that the structure of the complex was not destroyed during the process of the sol gel preparation. The situation is different when we compare the emission spectra of SmPh β_3 dip single crystals with the spectra of a compound incorporated into zirconia glasses (Fig. 7). In the single crystal spectra, the electronic dipole transition ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ band is more intensive than the magnetic dipole transition ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$. In the spectra of a compound incorporated in zirconia-glymo films both transitions are overlapped. The maximum of this broad band peaks at 610 nm ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$, which may suggest some structural transformation.



Fig. 6. Emission spectra of single crystal and sol of $Sm\beta_3 dip$ single crystal dissolve into acetone or methanol, respectively.

abs.spectrum of Sm-complex (5.7M%) in Zr-Glymo film



Fig. 7. Emission excitation, emission and absorption spectra of $Sm\beta_3$ dip single crystal incorporating into Zr-glymo film.

5. Conclusions

The SmPh β_3 dip complex exhibits a very strong orange emission under UV excitation both in single crystal as well as in sol and incorporated into zirconia glasses.

The effective energy transfer from ligand T and S states strongly sensibilizes the orange emission of Sm(III) ion.

The decay times are in the range of tens microseconds and almost temperature independent.

In the single crystal spectra, the electronic dipole transition ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ is more intensive than the magnetic dipole transition ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$. In the spectra of the compound incorporated into zirconia-glymo films both transitions are overlapped. The maximum of this broad band peaks at 610 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$), which may suggest some structural transformation.

Acknowledgement

Financial support from the Polish Committee for Scientific Research (KBN, grant no. 20401331/0289) is gratefully acknowledged.

References

- P. Gawryszewska, J. Sokolnicki, J. Legendziewicz, Coord. Chem. Rev. 249 (21/22) (2005) 2489.
- [2] J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.
- [3] G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, L.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr., Coord. Chem. Rev. 196 (2000) 165; O.L. Malta, J. Lumin. 71 (1997) 229.
- [4] M. Latva, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149.
- [5] M. Borzechowska, V. Trush, I. Turowska-Tyrk, W. Amirkhanov, J. Legendziewicz, J. Alloys Compd. 341 (2002) 98;

R. Reisfeld, J. Legendziewicz, M. Puchalska, T. Saraidarov, Opt. Mater. 26 (2004) 191.

- [6] J. Legendziewicz, J. Alloys Compd. 341 (2002) 34-44.
- [7] H. Hakala, P. Liitti, K. Puukka, J. Peuralahti, K. Loman, J. Karvinen, P. Ollikka, A. Ylikoski, V.-M. Mukkala, J. Hovinen, Inorg. Chem. Commun. 5 (2002) 1059–1062.
- [8] P. Lenaerts, Ch. Görller-Walrand, K. Binnemans, J. Lumin. 117 (2006) 163–169.
- [9] T. Saraidarov, R. Reisfeld, A. Sashchiuk, E. Lifshitz, J. Sol-Gel Sci. Technol. 26 (2003) 533; A Sashchiuk E Lifshitz P. Paisfeld T. Saraidarov M. Zelper, A. Willenz, A. Sashchiuk E. Lifshitz, P. Paisfeld, T. Saraidarov, M. Zelper, A. Willenz, A. Sashchiuk, E. Lifshitz, P. Paisfeld, T. Saraidarov, M. Zelper, A. Willenz, A. Sashchiuk, E. Lifshitz, P. Paisfeld, T. Saraidarov, M. Zelper, A. Willenz, A. Sashchiuk, E. Lifshitz, J. Sol-Gel Sci. Technol. 26 (2003) 533;

A. Sashchiuk, E. Lifshitz, R. Reisfeld, T. Saraidarov, M. Zelner, A. Willenz, J. Sol–Gel Sci. Technol. 24 (2002) 31.

- [10] R. Reisfeld, T. Saraidarov, E. Ziganski, M. Gaft, S. Lis, M. Pietraszkiewicz, J. Lumin. 102/103 (2003) 243.
- [11] A.V. Kiersanov, G.I. Derkatch, Zh. Org. Khim. 26 (1956) 263;
 V.M. Amirkhanov, V.A. Trush, Zh. Org. Khim. 65 (1995) 112.
- [12] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, J.F.S. Menezes, C.F.B. Silva, C.S. Tomiyama, C.A.A. Carvalho, J. Alloys Compd. 344 (2002) 293.
- [13] O.L. Malta, J. Legendziewicz, E. Huskowska, I. Turowska-Tyrk, R.Q. Albuquerque, C. de Mello Donegá, F.R.G. e Silva, J. Alloys Compd. 323/324 (2001) 654.