

# Determination of Judd-Ofelt Intensity Parameters of Pure Samarium(III) Complexes

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**Abstract** This work reports an alternative approach to obtain the Judd-Ofelt intensity parameters of Sm(III) complexes with the general formula:  $[\text{Sm}(\text{tta})_3(\text{L})_n]$ , with  $\text{L}=\text{H}_2\text{O}$ , triphenylphosphine oxide (tppo), 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen);  $n=2$  for  $\text{H}_2\text{O}$  and tppo and  $n=1$  for phen and bipy, using the absorption spectra of rare earth complexes where the powders are dispersed in KBr pellets. This approach can be applied to other complexes of rare earth ions that have spin allowed transitions and it is validated by comparing the emission spectra of the complexes with those dispersed in KBr pellets.

**Keywords** Luminescence · Samarium · Intensity parameters

## Introduction

Lanthanide ions exhibit interesting luminescent properties due 4f-4f intraconfigurational transitions. The degeneration of 4f<sup>n</sup> orbitals is broken by the high interelectronic repulsion, according to the Russel-Saunders model, promoting an energy difference of approximately  $10,000\text{ cm}^{-1}$ , the spin-orbital coupling promotes an energy difference of approximately  $1,000\text{ cm}^{-1}$  and, on a lower magnitude scale, the ligand field effect promotes an energy difference of about  $100\text{ cm}^{-1}$  between the electronic levels. The free-ion spectroscopic terms generated by all these repulsions have the general formula  $^{2S+1}L_J$ , where  $2S+1$  is the multiplicity term and  $J=L+S$  is the spin-orbital coupling.

The electronic 4f-4f transitions normally have low intensities due to restrictions by Laporte's rule ( $\Delta L=\pm 1$ ) and Spin's rule ( $\Delta S=0$ ). The restrictions of the Laporte's and Spin's rules lead to a low efficiency in photon absorption, consequently a low efficiency in photon emission. Weissman [1] observed that when certain types of organic molecules are bonded to a lanthanide ion, the complex formed exhibits a high emission intensity when excited in the UV region. In a lanthanide complex the excitation can occur by transitions between fundamental and excited singlet (that are allowed by Spin's rule), followed by a conversion of excited singlet to triplet states. Then the energy is transferred from the triplet state to the electronic levels of the lanthanide and finally there is radiative decay from the electronic levels of the lanthanide ions that is characteristic of each rare-earth ion. In the rare earth complexes field, the most common ligands used are, oxygenated ligands [2, 3], nitrogenated ligands [4] and nitrogen and oxygen simultaneously [5] such as:  $\beta$ -diketones [2], 1,10-phenanthroline [4], and 3-(4-nitrophenyl)-1-phenyltriazene *N*-oxide [5], respectively.

The ligand may have special influence on the intraconfigurational transition of the rare earth ions in terms of magnitude, number of lines and ratio of transition intensities. Therefore, the understanding and the control of the ligand influences on the rare earth emission may allow the design of new materials that can be applied in different fields. In order to know the ligands' influence on the emission of rare earth ions, the Judd-Ofelt intensity parameters [6, 7] ( $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ ) can provide a lot of information about several important parameters such as: the covalence degree of the chemical bonds between the metal and the ligand ( $\Omega_2$ ), (ii) the local symmetry around lanthanide ion ( $\Omega_2$ ,  $\Omega_4$ ), (iii) long range effects ( $\Omega_4$ ) and the rigidity of system ( $\Omega_6$ ).

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The Judd-Ofelt intensity parameters have been widely calculated for Eu(III) complexes [3, 4, 8–10] and for Nd(III), Pr(III) and Sm(III) doped glasses [11–15]. Recently Luo and collaborators [16] have proposed a methodology to calculate the Judd-Ofelt intensity parameters for rare earth-doped nanophosphors ( $\text{NaGd}(\text{WO}_4)_2:\text{Er}^{3+}$  and  $\text{YLiF}_4:\text{Nd}^{3+}$  crystals) using the excitation spectra. The methodology proposed by these authors presents an important approach to calculate the Judd-Ofelt intensity parameters when the excitation spectra match the absorption spectra very well, meaning that the emission quantum efficiency must be high. As already mentioned the Judd-Ofelt intensity parameters have been widely determined for europium complexes from the emission spectra, because there are transitions that only depend of the square matrix  $|\langle {}^7F_2 \| U^{(2)} \| {}^5D_0 \rangle|^2 ({}^5D_0 \rightarrow {}^7F_2)$  and  $|\langle {}^7F_4 \| U^{(4)} \| {}^5D_0 \rangle|^2 ({}^5D_0 \rightarrow {}^7F_4)$  values and the magnetic dipole allowed transition, is taken as a reference.

The Judd-Ofelt intensity parameters have been calculated for several rare earth ions such as Er(III), Nd(III), Ho(III) and Sm(III) always embedded in sol-gel or hybrid matrixes [17–20] or in solutions, such as methyl methacrylate [21]. Consequently, the calculation of JO parameters were carried out in systems that the rare earth complexes were dispersed in different matrixes, that probably chemically interact with the ligands and may influence the optical properties of such complexes.

However, to our knowledge, the determination of the Judd-Ofelt intensity parameters has not been done for pure powder complexes, other than europium(III), or in a matrix that does not or slightly interacts with ligands. Such approach would allow the calculation of JO intensity parameters values that reflects only the influence of the ligands over the optical parameter of the rare earth ions, such as: emission life time, symmetry, ligands long range effects, efficiency and the width of their emission bands. Also, the experimental determination of the JO parameters of the rare earth complexes without the influence of matrixes will allow the studies of the matrixes influences on their optical properties.

This work reports an useful methodology to obtain the Judd-Ofelt intensity parameters of Sm(III) complexes having the general formula:  $[\text{Sm}(\text{tta})_3(\text{L})_n]$ , with  $\text{L}=\text{H}_2\text{O}$ , triphenylphosphine oxide (tppo), 2,2'-bipyridine (bipy) and 1,10-phenantroline (phen);  $n=2$  for  $\text{H}_2\text{O}$  and tppo and  $n=1$  for phen and bipy, using the absorption spectra of rare earth complexes where the powders are dispersed in KBr pellets. The KBr is a useful compound because does not or has small chemical interaction with the complexes. This approach can be applied to other complexes of rare earth ions that have spin-allowed transitions and it can be validated by comparing the emission spectra of the complexes with those dispersed in KBr pellets. That

comparison guarantees that the applied pressure used to prepare the pellets does not significantly change the environment around the rare earth ion.

## Experimental Section

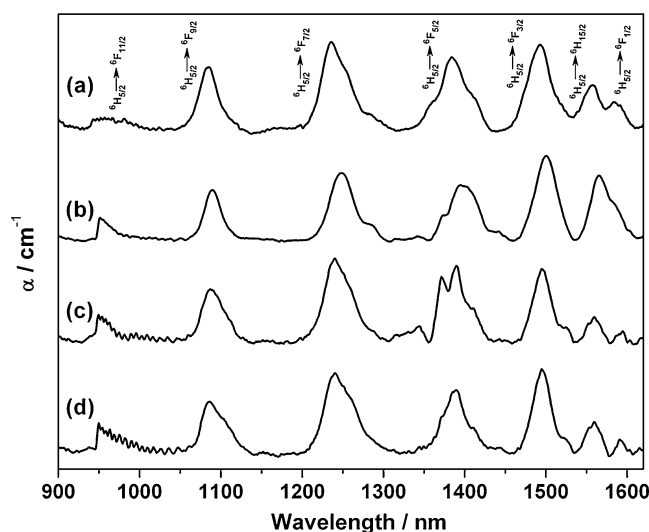
### Synthesis of Samarium(III) Complexes

Samarium oxide, 99.99%, thenoyltrifluoroacetone (Htta), 97%, 1,10-phenantroline (phen), 99%, 2,2'-bipyridine (bipy), 99% and triphenylphosphineoxide (tppo), 99%, were purchased from Aldrich. Hydrochloric acid (37%), ammonium hydroxide and sodium hydroxide were purchased from Synth. All chemicals were used as received.

The precursor complex,  $[\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2]$ , was obtained according to the procedure related by Melby et al [22]. The complexes  $[\text{Sm}(\text{tta})_3(\text{L})_n]$  were synthesized according to the procedure related by Brito and collaborators [23]. The methanolic solutions of the ligands were added to a methanolic solution of precursor complex in a molar ratio of 1:1 (for bipy and phen [24, 25] ligands) and 1:2 (for tppo [23] ligands). The solids formed were filtered and washed three times using hot methanol.

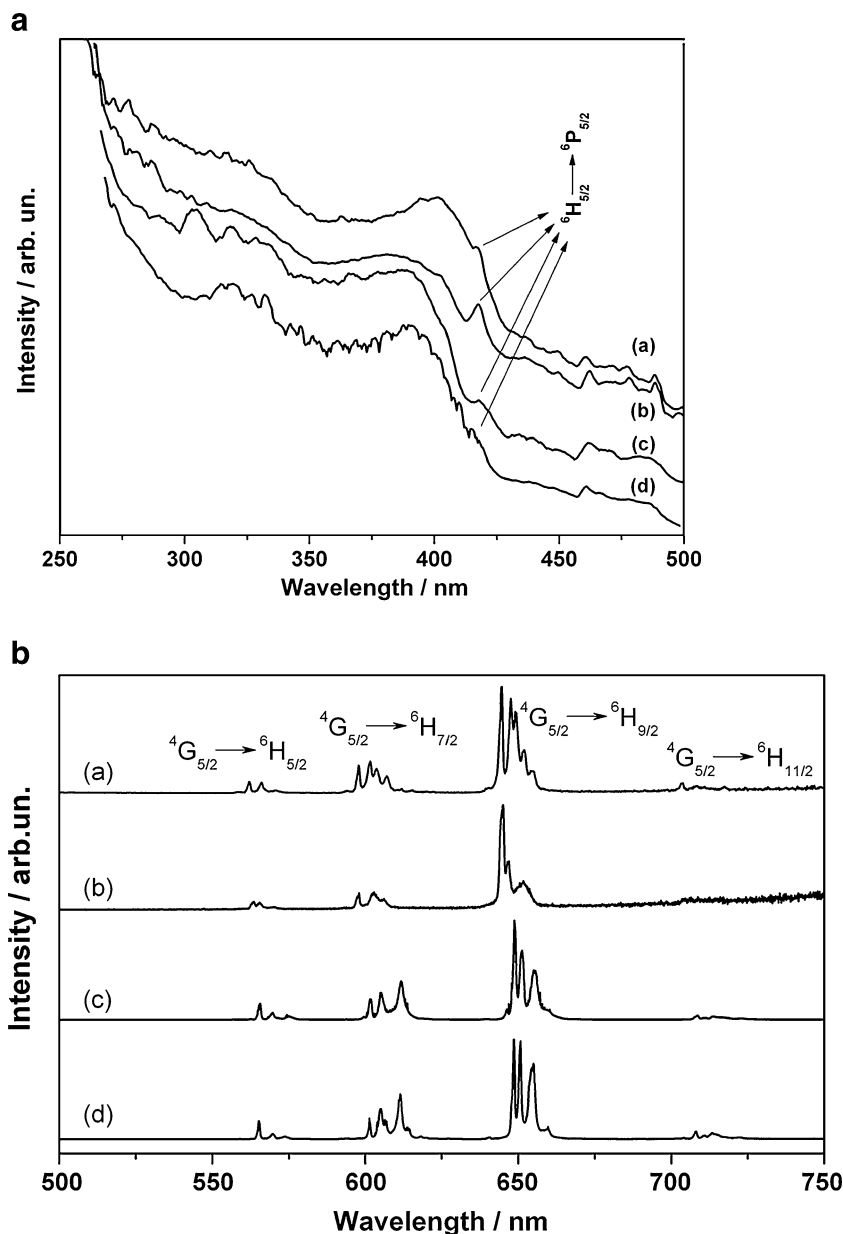
### Measurements

The chemical formulas of the complexes were suggested by samarium(III) complexometric titration using a standard  $0.01 \text{ mol L}^{-1}$  ethylenediaminetetraacetic acid (edta) solution. The near infrared (NIR) absorption spectra were recorded using KBr pellets with proportion 100:6 (wt/wt) KBr: complex on a Cary 5G equipped with an integration sphere.

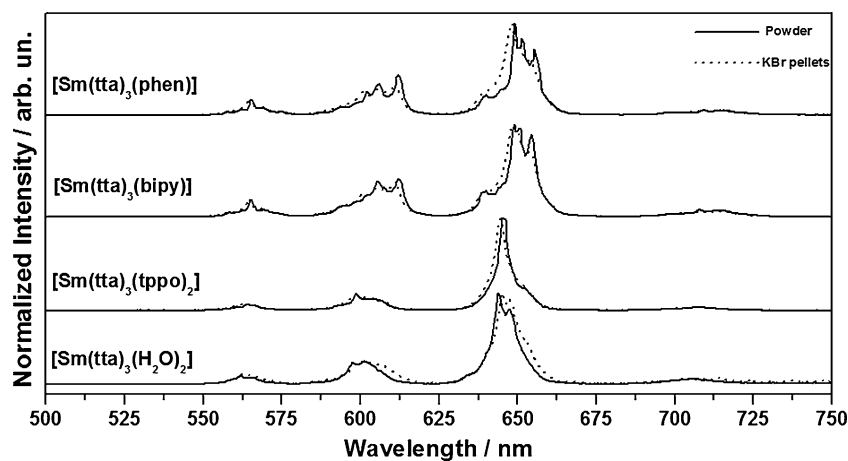


**Fig. 1** NIR absorption spectra of the complexes. **a**  $[\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2]$ , **b**  $[\text{Sm}(\text{tta})_3(\text{tppo})_2]$ , **c**  $[\text{Sm}(\text{tta})_3(\text{phen})]$  and **d**  $[\text{Sm}(\text{tta})_3(\text{bipy})]$

**Fig. 2** **a** Excitation ( $\lambda_{em}=644$  nm) and **b** emission spectra ( $\lambda_{exc}=393$  nm) of the complexes recorded at  $\sim 77$  K. (a)  $[\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2]$ , (b)  $[\text{Sm}(\text{tta})_3(\text{tppo})_2]$ , (c)  $[\text{Sm}(\text{tta})_3(\text{phen})]$  and (d)  $[\text{Sm}(\text{tta})_3(\text{bipy})]$



**Fig. 3** Emission spectra of the complexes obtained at room temperature using powder samples (straight line) or KBr pellets (dotted line)



**Table 1** Values of intensity ratios of the  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  and  ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$  transitions of powder and KBr samples

| Complex   | $\frac{I({}^4G_{5/2} \rightarrow {}^6H_{9/2})}{I({}^4G_{5/2} \rightarrow {}^6H_{5/2})}$ |
|---|---|
| [Sm(tta) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ] powder      | 10.6  |
| [Sm(tta) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ] KBr pellets | 8.8   |
| [Sm(tta) <sub>3</sub> (tppo) <sub>2</sub> ] powder                  | 11.9  |
| [Sm(tta) <sub>3</sub> (tppo) <sub>2</sub> ] KBr pellets             | 11.0  |
| [Sm(tta) <sub>3</sub> (bipy)] powder                                | 8.3   |
| [Sm(tta) <sub>3</sub> (bipy)] KBr pellets                           | 8.2   |
| [Sm(tta) <sub>3</sub> (phen)] powder                                | 8.0   |
| [Sm(tta) <sub>3</sub> (phen)] KBr pellets                           | 7.9   |

The proportions were changed according to the percent lanthanide in the complexes. A density of lanthanide around 10 [19] ions cm<sup>-3</sup> is necessary to give absorption spectra with good quality. The excitation and emission spectra of the samarium complexes were carried out at ~77 K in a Horiba Jobin Yvon spectrofluorimeter, FL3-222 model, 450 W Xenon lamp as excitation source. The emission lifetimes of the samarium complexes were obtained at room temperature, using the phosphorimeter (Jobin Yvon FL-1040 model) accessory coupled to the spectrofluorimeter.

## Results and Discussion

### Microanalysis Results

The percentage of the Sm(III) ions are consistent with the proposed stoichiometry of the complexes.

% Sm (calc./exp.): [Sm(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (17.7/17.8), [Sm(tta)<sub>3</sub>(phen)] (15.1/14.8), [Sm(tta)<sub>3</sub>(bipy)] (15.5/16.2), [Sm(tta)<sub>3</sub>(tppo)<sub>2</sub>] (11.0/11.7)

### Absorption Spectra

NIR absorption spectra are shown in Fig. 1. The bands are attributed to spin-allowed transitions from the ground state level  ${}^6H_{5/2}$  to the excited levels  ${}^6F_J$  ( $J=1/2; 3/2; 5/2; 7/2; 9/2$  and  $11/2$ ) and also to the excited level  ${}^6H_{11/2}$ .

**Table 2** Squared reduced matrix elements of transitions

| $J'$           | $ \langle {}^6H_{5/2}    U^{(2)}    J' \rangle ^2$ | $ \langle {}^6H_{5/2}    U^{(4)}    J' \rangle ^2$ | $ \langle {}^6H_{5/2}    U^{(6)}    J' \rangle ^2$ |
|----------------|--|--|--|
| ${}^6F_{1/2}$  | 0.1938   | 0  | 0  |
| ${}^6F_{3/2}$  | 0.1444   | 0.1365   | 0  |
| ${}^6F_{5/2}$  | 0.0331   | 0.2844   | 0  |
| ${}^6F_{7/2}$  | 0.0020   | 0.1429   | 0.4301   |
| ${}^6F_{9/2}$  | 0  | 0.0205   | 0.3416   |
| ${}^6F_{11/2}$ | 0  | 0.0006   | 0.0516   |
| ${}^6H_{15/2}$ | 0  | 0  | 0.0043   |

## Photoluminescence Spectroscopy

The excitation spectra, Fig. 2a, of the complexes show similar profiles, with broad bands that correspond to ligand excitation and narrow bands attributed to  ${}^6H_{5/2} \rightarrow {}^6P_{5/2}$  (416 nm),  ${}^6H_{5/2} \rightarrow {}^6I_{13/2}$  (460 nm),  ${}^6H_{5/2} \rightarrow {}^4M_{15/2}$  (480 nm) transitions of the samarium(III) ion. The emission spectra, Fig. 2b, of the complexes show all characteristic transitions of samarium(III) attributed to  ${}^4G_{5/2} \rightarrow {}^6H_J$  ( $J=5/2; 7/2; 9/2$  and  $11/2$ ), with  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  the most intense. The  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  is more intense than  ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  in complexes indicating that the samarium(III) ions lie in a non-centrosymmetric center. The emission spectra of complexes and those of the complexes in KBr pellets (Fig. 3) were carried out in order to verify the influence of the pressure used for pellet preparation on the chemical environment of the samarium(III) ions. The ratio between the electric dipole transition ( ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ ) and the magnetic dipole transition ( ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ ) are shown in Table 1. The results (Fig. 3 and Table 1) show that the chemical environments of the samarium(III) ions are not significantly changed in KBr pellets, indicating that the proposed approach to calculate the intensity parameters using the NIR absorption spectra can be used.

### Judd-Ofelt Intensity Parameters

The strength of electronic transitions can be described by the oscillator strength ( $P$ ) that can be determined by two ways: (i) experimentally through the absorption spectrum and (ii) theoretically. The oscillator strength obtained by experimental method is given by Eq. 1.

$$P_{\text{exp}} = \frac{m \cdot c}{\pi \cdot e^2 \cdot N} \int \alpha(\nu) \cdot d\nu \quad (1)$$

where:  $m$  is the electron mass ( $9.11 \times 10^{-28}$  g),  $c$  is the speed of light ( $2.9979 \times 10^{10}$  cm s<sup>-1</sup>),  $e$  is the electron elemental charge ( $4.8063 \times 10^{-10}$  esu; esu<sup>2</sup>=g cm<sup>3</sup> s<sup>-2</sup>),  $\int \alpha(\nu) \cdot d\nu$  is the integrated area in absorption coefficient ( $\alpha$  / cm<sup>-1</sup>) versus frequency ( $\nu$  / s<sup>-1</sup>) plot and  $N$  is the density of lanthanide ions (ion cm<sup>-3</sup>). The  $N$  value can be calculated

**Table 3** Judd-Ofelt intensity parameters of the complexes

| Complexes   | $\Omega_2 / 10^{-20} \text{ cm}^2$ | $\Omega_4 / 10^{-20} \text{ cm}^2$ | $\Omega_6 / 10^{-20} \text{ cm}^2$ | $\Omega_4 / \Omega_6$ | $\partial_{RMS}$ |
|---|------------------------------------|------------------------------------|------------------------------------|-----------------------|------------------|
| [Sm(tta) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ] | 2.0                                | 4.4                                | 2.3                                | 1.9                   | 0.18             |
| [Sm(tta) <sub>3</sub> (tppo) <sub>2</sub> ]             | 2.9                                | 7.9                                | 3.7                                | 2.2                   | 0.33             |
| [Sm(tta) <sub>3</sub> (phen)]                           | 0.63                               | 3.1                                | 2.0                                | 1.5                   | 0.22             |
| [Sm(tta) <sub>3</sub> (bipy)]                           | 4.2                                | 11.2                               | 8.5                                | 1.3                   | 0.24             |

by two ways. First is necessary to calculate the amount of RE<sup>3+</sup> ions. For example the complex [Sm(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]:

In  $849.36 \times 10^{-3} \text{ kg}$  there are  $6.02 \times 10^{23} \text{ RE}^{3+}$  ions, in  $x \text{ kg}$  of complex there will be  $n \text{ RE}^{3+}$  ions. Second is necessary divide  $n$  by the volume of pellet. The volume can be obtained by two ways: the first one is to measure the dimensions of the pellets (width and height), the second one is through the density of KBr. The two ways lead the same result.

On the other hand, the oscillator strength can be theoretically calculated by Eq. 2.

$$P_{calc} = \frac{8 \cdot \pi^2 \cdot m \cdot \nu}{3 \cdot h \cdot (2 \cdot J + 1) \cdot e^2 \cdot n^2} \times [\chi_{ed} \cdot S_{ed} + \chi_{md} \cdot S_{md}] \tag{2}$$

where:  $h$  is the Planck’s constant,  $J$  is the initial state quantum number,  $n$  is the refractive index,  $\chi_{ed}$  and  $\chi_{md}$  are the Lorentz local field correction for the electric and magnetic dipole transitions, respectively, and  $\nu$  is the frequency of transition in  $s^{-1}$ . For the given transitions the magnetic dipole transitions may be negligible and then the Eq. 2 becomes:

$$P_{calc} = \frac{8 \cdot \pi^2 \cdot m \cdot \nu}{3 \cdot h \cdot (2 \cdot J + 1) \cdot e^2 \cdot n^2} \cdot [\chi_{ed} \cdot S_{ed}] \tag{3}$$

where:  $\chi_{ed} = \frac{n(n^2+2)^2}{9}$  is the Lorentz local field correction for electric dipole transitions,  $|\langle aJ || U^{(\lambda)} || bJ' \rangle|^2$  are the squared reduced matrix elements of transitions; their values were calculated by Carnall [26], and  $S_{ed}$  is the strength of electric dipole line, calculated by Eq. 4.

$$S_{ed} = e^2 \cdot \sum_{\lambda}^{2;4;6} \Omega_{\lambda} \left| \langle aJ || U^{(\lambda)} || bJ' \rangle \right|^2 \tag{4}$$

**Table 4** Squared reduced matrix elements for  ${}^4G_{5/2} \rightarrow J'$  transitions

| $J'$           | $ \langle {}^4G_{5/2}    U^{(2)}    J' \rangle ^2$ | $ \langle {}^4G_{5/2}    U^{(4)}    J' \rangle ^2$ | $ \langle {}^4G_{5/2}    U^{(6)}    J' \rangle ^2$ |
|----------------|--|--|--|
| ${}^6H_{7/2}$  | 0  | 0.0078   | 0.0075   |
| ${}^6H_{9/2}$  | 0.0096   | 0.0061   | 0.0019   |
| ${}^6H_{11/2}$ | 0  | 0.0045   | 0.0018   |

The oscillator strength is a dimensionless quantity. From a quick examination of Eqs. 1 and 3, it can be seen that the dimensionally is consistent, as demonstrated below.

$$unit(P) = \frac{g \cdot cm \cdot s^{-1} \cdot cm^{-1} \cdot s^{-1}}{g \cdot cm^3 \cdot s^{-2} \cdot cm^3}$$

$$unit(P) = \frac{g \cdot s^{-1} \cdot cm^2}{g \cdot cm \cdot s^{-2} \cdot cm \cdot s}$$

Therefore, the Judd-Ofelt intensity parameters can be obtained by equalling Eq. 1 with the Eq. 3, obtaining the relation shown in Eq. 5.

$$P_{exp} = P_{calc} \leftrightarrow P_{exp} = C \cdot [(\Omega_2 \left| \langle aJ || U^{(2)} || bJ' \rangle \right|^2) + (\Omega_4 \left| \langle aJ || U^{(4)} || bJ' \rangle \right|^2) + (\Omega_6 \left| \langle aJ || U^{(6)} || bJ' \rangle \right|^2)] \tag{5}$$

where:  $C = \frac{8 \cdot \pi^2 \cdot m \cdot \nu \cdot \chi_{ed}}{3 \cdot h \cdot (2 \cdot J + 1) \cdot n^2}$ .

Some values of the constants are shown in Table 2 and others were already specified for Eq. 1. The frequencies and the areas of each transition were obtained from the NIR absorption spectrum of the complexes.

The Judd-Ofelt intensity parameters ( $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ ) shown on Table 3 can provide a lot of structural and chemical information around the lanthanide ion. The first one,  $\Omega_2$ , is correlated with: symmetry around the lanthanide ion and covalence between ligand and lanthanide. The changes of the  $\Omega_2$  values can be correlated with the changes in rare earth micro symmetry and the covalence degree of the chemical bond of Sm-ligands. The presence of tppo and bipy ligands in [Sm(tta)<sub>3</sub>(tppo)<sub>2</sub>] and [Sm(tta)<sub>3</sub>(bipy)] complexes lead a more assymetrical coordination polyhedra and change the covalence of the system. On the other hand the presence of phen ligand in [Sm(tta)<sub>3</sub>(phen)] decreases the  $\Omega_2$  value, probably due to modifications in the local symmetry around the

**Table 5** Value for efficiency parameters:  $A_{rad}$ ,  $A_{nrads}$ ,  $A_{tot}$  e  $\eta$ 

| Complex   | $A_{rad} / s^{-1}$ | $A_{nrads} / s^{-1}$ | $A_{tot} / s^{-1}$  | $\tau / ms$ | $\eta / \%$ |
|---|--------------------|----------------------|---------------------|-------------|-------------|
| [Sm(tta) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ] | 343.7              | $2.378 \times 10^5$  | $2.381 \times 10^5$ | 0.004       | 0.14        |
| [Sm(tta) <sub>3</sub> (tppo) <sub>2</sub> ]             | 583.9              | $6.820 \times 10^3$  | $7.404 \times 10^3$ | 0.140       | 7.90        |
| [Sm(tta) <sub>3</sub> (bipy)]                           | 915.5              | $1.358 \times 10^4$  | $1.449 \times 10^4$ | 0.069       | 6.30        |
| [Sm(tta) <sub>3</sub> (phen)]                           | 227.7              | $1.284 \times 10^4$  | $1.306 \times 10^4$ | 0.077       | 1.70        |

samarium(III) ion. The  $\Omega_4$  parameter is correlated with: symmetry [27] and long range effects [4]. The increase of the  $\Omega_4$  parameter can be attributed to  $\pi$ - $\pi$  interactions between phenyl rings. The [Sm(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] complex shows a high value of  $\Omega_4$  due to the hydrogen bond between hydrogen from water molecules and fluorine from the CF<sub>3</sub> group. The  $\Omega_6$  parameter can be correlated with the rigidity of system [11]. The complexes [Sm(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] and [Sm(tta)<sub>3</sub>(phen)] show similar values of this parameter. The complexes [Sm(tta)<sub>3</sub>(tppo)<sub>2</sub>] and [Sm(tta)<sub>3</sub>(bipy)] present the highest values among the complexes synthesized in this work, probably due to long range interactions.

Comparing the values obtained in Table 2 with those obtained for samarium(III)-doped glasses [11–14], the parameter  $\Omega_2$  is in the same range of  $(0.50 - 6.0) \times 10^{-20} \text{ cm}^2$ , the values of the  $\Omega_4$  and  $\Omega_6$  parameters are higher than those obtained for glasses, indicating an important influence of the organic ligands compared with an inorganic matrix.

Using the values of the Judd-Ofelt intensity parameters it is possible to calculate the efficiency parameters ( $A_{rad}$ ,  $A_{nrads}$ ,  $A_{tot}$ ,  $\eta$ ). The Einstein's spontaneous emission coefficient ( $A_{rad}$ ) is given by Eq. 7.

$$A = \frac{64 \cdot \pi^3 \cdot \nu^3}{3 \cdot (2 \cdot J + 1) \cdot h \cdot c^3} \cdot [\chi_{ed} \cdot S_{ed} + \chi_{md} \cdot S_{md}] \quad (7)$$

Considering that the contributions of magnetic transitions are negligible the Eq. 8 may be re-written as:

$$A = \frac{64 \cdot \pi^4 \cdot \nu^3}{3 \cdot (2 \cdot J + 1) \cdot h \cdot c^3} \cdot [\chi_{ed} \cdot S_{ed}] \quad (8)$$

The squared reduced elements used in the calculations were taken from Carnall [26] and are shown in Table 4.

The total emission rate and non-radiative emission rate are obtained by Eq. 9.

$$\frac{1}{\tau} = A_{tot} = A_{rad} + A_{nrads} \quad (9)$$

The emission lifetime of the state  $^4G_{5/2}$  was obtained from a luminescence intensity decay curve, with excitation

centered in the ligand band and emission centered in the  $^4G_{5/2} \rightarrow ^6H_{9/2}$  hypersensitive transition of samarium(III). The quantum efficiency was obtained by Eq. 10.

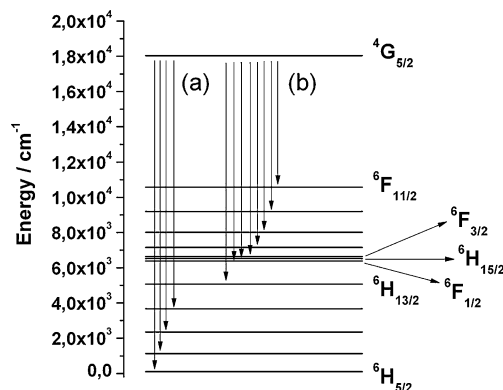
$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrads}} \quad (10)$$

All these quantities ( $A_{rad}$ ,  $A_{nrads}$ ,  $A_{tot}$ ,  $\eta$  and  $\tau$ ) are shown in Table 5.

The samarium(III) complexes show very low quantum efficiency values of the transition in the visible range, as shown in Table 5, when compared with the analogous europium(III) complexes [28]. The low quantum efficiency values may be justified due to the non-radiative transitions from  $^4G_{5/2}$  to  $^6F_J$  ( $J=1/2; 3/2; 5/2; 7/2; 9/2$  and  $11/2$ ) states, Fig. 4, in the near-infrared region [29] that are not included in radiative rates ( $A_{rad}$ ) to calculate the quantum efficiency (Eq. 10) and also because of possible high rate of non-radiative transitions. The increase in the emission lifetime values of the aquo-substituted complexes indicates that the non-radiative process attributed to O-H vibrations diminishes when the ligands tppo, bipy and phen are in the coordination sphere.

## Conclusions

The Judd-Ofelt intensity parameters were determined using the oscillator strengths obtained from NIR absorption spectra. This methodology is very well described for rare earths dispersed in an inorganic matrix or in solution. In



**Fig. 4** Energy levels diagram of the samarium(III) ion. **a** transitions in visible region. **b** transitions in NIR region

this work KBr pellets were used in order to obtain the absorption spectra of complexes and avoid any influence on the optical properties from matrixes or solutions. The intensity parameters were determined with low  $\partial_{RMS}$  values confirming an agreement between experimental and theoretical oscillator strength values. Therefore, the proposed approach may be extended to other rare earth compounds that present spin-allowed electronic transitions.

The increase of the  $\Omega_2$  value for  $[\text{Sm}(\text{tta})_3(\text{tppo})_2]$  and  $[\text{Sm}(\text{tta})_3(\text{bipy})]$ , when compared with  $[\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2]$ , can be justified by the changes in the symmetry and in the covalent degree of the Ln–O bonds. The increase of the  $\Omega_4$  values of the same complexes may be attributed to  $\pi$ - $\pi$  interactions between phenyl rings and the variation of the  $\Omega_6$  values reveals that the organic ligands increase the rigidity of the systems.

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