Journal of Alloys and Compounds 275–277 (1998) 333–337

4f–4f intensities of the Tm^{3+} ions in fluoroindate glasses: the influence of third-order effects through odd intensity parameters

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Abstract

In this work an analysis of the phenomenological Ω_λ intensity parameters for the Tm^{3+} ion in fluoroindate glass is made using the standard Judd–Ofelt theory, and a modified oscillator strength taking into account odd-order contributions is utilized. Different sets of phenomenological intensity parameters Ω_λ (λ=1,2,3,4,5,6) are discussed. The set of better quality is used to analyze the influence of third-order effects through odd intensity parameters in the new approximation. Fluoroindate glasses of compositions $(40-x)InF_3$–$20ZnF_2$–$20SrF_2$–$16BaF_2$–$2GdF_3$–$2NaF$–$xTmF_3$ with x=1, 2 and 3 mol% were prepared, and the absorption spectra at room temperature in the spectral range from 300 to 2500 nm were obtained. The experimental oscillator strengths determined from the area under the absorption band are compared to the calculated ones. © 1998 Elsevier Science S.A.

Keywords: Intensity parameter; Fluoroindate glass; Judd–Ofelt theory; Absorption spectra

1. Introduction

The understanding of the optical properties of the rare earth ions in inorganic compounds is of great importance due to their potential technological applications as, for example, in optical fibers, optical amplifiers, sensors and lasers.

In this context fluoroindate glasses seem to be a particularly useful host for rare earth ions due to their optical quality, chemical stability and low phonon cut off frequency (<500 cm^{-1}). We have recently described several optical properties of Er^{3+} and Pr^{3+} ions in such glasses [1–3].

The Judd–Ofelt 4f–4f intensity model [4,5] describes the absorption and emission properties of rare earth ions in a great number of compounds. However, it has been observed in many cases that this standard theory leads to a negative value of the phenomenological Ω_2 intensity parameter for the Pr^{3+} ion [6], inclusive in fluoroindate glasses [2]. These results are in contradiction with the definition of the Ω_λ parameters. Several authors believe that higher order contributions to the forced electric dipole matrix elements might be of considerable importance in order to solve the problem [7–9]. These introduce additional effective operators of even and odd ranks. Recently other authors have discussed the problem of the Pr^{3+} ion in fluoride glasses, including fluorescence measurements of branching ratios [10], and using normalized oscillator strengths [11] to calculate the parameters within the standard Judd–Ofelt theory.

In this work we report on the analysis of the absorption intensities of Tm^{3+} ion in fluoroindate glasses taking into account the additional effective operators. Different sets of phenomenological intensity parameters Ω_λ (λ=1,2,3,4,5,6) are obtained and discussed.

2. Theory

We use the standard 4f–4f intensity model described in detail elsewhere [4,5], and a modified oscillator strength

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PII: S0925-8388(98)00334-X

discussed in Ref. [9]. Thus, only a short summary and the most essential formulas will be given.

From the standard 4f–4f intensity model, the oscillator strength of a transition between two multiplets is given by

$$f = \frac{8\pi^2 mc\sigma}{3h(2J+1)}\,\chi \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle f^N\Psi' J' \| U_\lambda \| f^N \Psi J \right\rangle^2 \tag{1}$$

where m is the mass of the electron, c is the velocity of light, h is the Planck's constant, σ is the mean frequency for the transition, and $\chi=(n^2+2)2/9n$ is the Lorentz local field correction (n being the refractive index of the medium) and U_λ is a unit operator of rank λ.

The intensity parameters Ω_λ are determined from a least-squares fit to the values of the measured oscillator strengths, using Eq. (1). The quality of the fit is expressed by the magnitude of the root mean-squares (r.m.s.) deviation, defined by

$$\text{r.m.s.} = \left\{ \sum (f_{\text{cal}} - f_{\text{exp}})^2/(q-p) \right\}^{1/2} \tag{2}$$

where q is the equation number and p the parameter number.

It was demonstrated [9] that the total oscillator strength due to the forced electric dipole mechanism that takes into account the contribution of the odd-order parameters (modified oscillator strength) has the form

$$\begin{aligned} f = \frac{8\pi^2 mc\sigma}{3h(2J+1)}\chi \Bigg(& \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle f^N\Psi' J' \| U_\lambda \| f^N \Psi J \right\rangle^2 \\ & + \xi^2 \sum_{\lambda=1,3,5} \Omega_\lambda \left\langle f^N\Psi' J' \| U_\lambda \| f^N \Psi J \right\rangle^2 \Bigg) \end{aligned} \tag{3}$$

where $\Psi=\alpha SL$ and $\xi=\sigma/\Delta E$.

For Tm^{3+} ion $\Delta E \cong 60\,000$ cm^{-1} [12,13], which to a first approximation is equal to the difference between the ground configuration (f^N) and the first opposite parity excited configuration ($f^{N-1}5d$).

The matrix elements of Eq. (3) are calculated in the SL basis using the relation [14]

$$\begin{aligned} & \left\langle f^N\Psi' J' \| U_\lambda \| f^N \Psi J \right\rangle = \\ & \quad \delta(S,S')(-1)^{S+L'+J+\lambda}[(2J+1)(2J'+1)]^{1/2} \\ & \quad \times \begin{Bmatrix} J J' \lambda \\ L' L S \end{Bmatrix} \left\langle f^N\Psi'' J' \| U_\lambda \| f^N \Psi J \right\rangle \end{aligned} \tag{4}$$

The matrix elements of Eq. (4) have been tabulated by Nielson and Koster [15]. The 6-j symbols may be obtained from tables of Rotemberg et al. [16].

The intermediate-coupling eigenvectors, $|f^N \psi J\rangle$, are expressed in terms of SL basis states, $|f^N \alpha SLJ\rangle$, as

$$|f^N \Psi J\rangle = \sum_{\alpha,S,L} c(\alpha,S,L)|f^N \alpha SLJ\rangle \tag{5}$$

where $c(\alpha,S,L)$ are the numerical coefficients resulting from the simultaneous diagonalization of the atomic parts of the Hamiltonian [14]. The wave functions of free ion for Tm^{3+} in intermediate coupling used in this work are included in Table 1.

Table 1
Free-ion wave functions for trivalent thulium ion (Tm^{3+}) in intermediate coupling

Energy (cm^{-1})	Wave functions
0.0	$\lvert ^3H_6\rangle = 0.99564\lvert ^3H_6\rangle + 0.09328\lvert ^1I_6\rangle$
5650	$\lvert ^3F_4\rangle = -0.79275\lvert ^3F_4\rangle + 0.28157\lvert ^3H_4\rangle - 0.54062\lvert ^1G_4\rangle$
8213	$\lvert ^3H_5\rangle = -1.00000\lvert ^3H_5\rangle$
12 558	$\lvert ^3H_4\rangle = -0.77161\lvert ^3H_4\rangle - 0.52198\lvert ^3F_4\rangle + 0.36353\lvert ^1G_4\rangle$
14 416	$\lvert ^3F_3\rangle = 1.00000 \mid {}^3F_3\rangle$
15 021	$\lvert ^3F_2\rangle = -0.87560\lvert ^3F_2\rangle + 0.46211\lvert ^1D_2\rangle + 0.14063\lvert ^3P_2\rangle$
21 146	$\lvert ^1G_4\rangle = 0.75867\lvert ^1G_3\rangle + 0.57038\lvert ^3H_4\rangle - 0.31479\lvert ^3F_4\rangle$
27 837	$\lvert ^1D_2\rangle = 0.64015\lvert ^1D_2\rangle + 0.63040\lvert ^3P_2\rangle + 0.43909\lvert ^3F_2\rangle$

The matrix elements for Tm^{3+} ion with $\lambda=1$, 3 and 5, calculated in this work from Eq. (4) and with $\lambda=2,4,6$ taken from Carnall et al. [14] are included in Table 2.

3. Experimental

The fluoroindate glasses with batch compositions (mol%) $(40-x)InF_3$–$20SrF_2$–$20ZnF_2$–$16BaF_2$–$2NaF$–$2GdF_3$-$xTmF_3$ ($x=1$, 2 and 3 mol%) have been prepared in a dry box under Ar atmosphere by melting ultrapure powders (Merck, Fluortran) in a platinum crucible at 800°C for 1 h and then at 850°C for fining. The liquid was cast into a preheated mold at 260°C and then cooled to 20°C.

The absorption spectra have been recorded in the visible spectral range using a 0.75-m Spex monochromator with an AsGa photomultiplier cooled at −30°C, and in the infrared spectral range using a PbS detector at room temperature (Fig. 1).

The oscillator strength is obtained from the area under the absorption band with the wavelength (λ) corresponding to the band baricenter, using

$$f = \frac{4.318 \times 10^{-9}}{Cl\lambda^2} \int K(\lambda)\, \mathrm{d}\lambda \tag{6}$$

Table 2
Values in the intermediate coupling of the matrix elements $[U_\lambda]^2 = \langle f^N \Psi \acute{J} \| U_\lambda \| f^N \Psi J\rangle^2$. The values for $\lambda=1,3,5$ were calculated in this work and include the factor ξ^2, and those for $\lambda=2,4,6$ were taken from Carnall et al. [14] ($|\Psi J\rangle = {}^3H_6$)

$S'L'J'$	U_1^2	U_2^2	U_3^2	U_4^4	U_5^2	U_6^2
$^3F_4$	0.0000	0.5395	0.0113	0.7261	0.0003	0.2421
$^3H_5$	0.0024	0.1074	0.0000	0.2314	0.0135	0.6385
$^3H_4$	0.0000	0.2357	0.0176	0.1081	0.0041	0.5916
$^3F_3$	0.0000	0.0000	0.0140	0.3164	0.0000	0.8413
$^3F_2$	0.0000	0.0000	0.0000	0.0000	0.0017	0.2550
$^1G_4$	0.0000	0.0483	0.0132	0.0748	0.0008	0.0125
$^1D_2$	0.0000	0.0000	0.0000	0.3131	0.0777	0.0958

where $K(\lambda)$ is the spectral absorption coefficient, λ is in nm, and C and l are the concentration of Tm^{3+} ions in mol/1000 cm^3 and the absorption path length, respectively.

4. Results and discussion

Fig. 1 shows the absorption spectrum of Tm^{3+} ion in fluoroindate glass at room temperature in the spectral ranges from 350 to 850 nm and from 1150 to 2200 nm.

The intensity of the hypersensitive transitions $^3H_6 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3H_4$ and $^3H_6 \rightarrow {}^1G_4$ of the Tm^{3+} ion [6] is comparable with the intensity of the other transitions ($^3H_6 \rightarrow {}^3H_5$, $^3H_6 \rightarrow {}^3F_3$, $^3H_6 \rightarrow {}^1D_2$). This behavior is opposite to that observed for this type of transition with Er^{3+} and Pr^{3+} ion in the same fluoroindate glasses [1–3].

The effect of the odd-order parameters $\Omega_{1,3,5}$ on those of even-order analyzed within the Judd–Ofelt standard theory, is shown by the different sets of parameters of Table 3.

In all sets where Ω_1 appears (sets 4, 5, 6, 7, 11, 12, 13 and 14), this parameter takes large positive or negative values, except for set 6, compared to the values of the others parameters, $\Omega_{2,3,4,5,6}$. A negative value for any Ω_λ is in contradiction with the definition of the intensity parameter. The larger values may come from the fact that almost all matrix elements of Ω_λ are very small or zero. Ω_1 may be associated with the sites occupied by the Tm^{3+} ion which may be different from C_n, C_{2v} and C_{3v}.

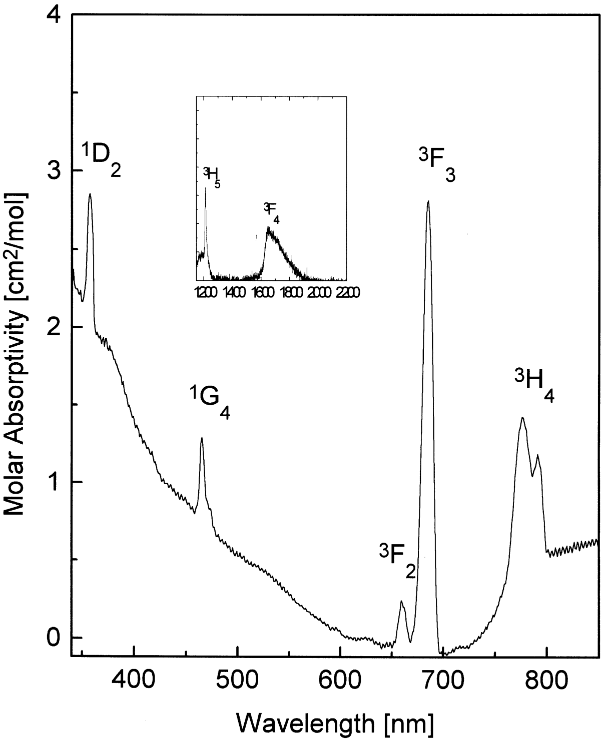

Fig. 1. Absorption spectrum of Tm^{3+} in fluoroindate glass, at room temperature, in the spectral range from 340 to 850 nm and from 1150 to 2200 nm. Sample with $x=3$ mol% of Tm^{3+}.

Table 3
Sets of values of the intensity parameters $\Omega_{1,...,6}$ (in units of 10^{-20} cm^2) obtained using different combinations of the matrix elements for the Tm^{3+} ion in fluoroindate glass

Set	Ω_1	Ω_2	Ω_3	Ω_4	Ω_5	Ω_6
1		1.77		2.30		1.69
2			30.08	2.22	0.88	1.41
3		1.89		2.10	0.92	1.73
4	−83.78			3.00	−2.61	1.72
5	−115.12	1.81		2.29		1.74
6	0.88	23.51		2.33		1.39
7	61.37		29.96	2.41		1.33
8		0.26	44.35	3.97	−4.24	
9		2.06	29.42		9.18	1.87
10		1.15	25.24	1.79	2.49	1.48
11	67.10		31.42	2.20	1.01	1.36
12	−119.03	1.96		2.05	1.09	1.79
13	18.57	0.86	23.98	2.34		1.38
14	19.39	1.13	25.73	1.79	2.50	1.47

In all sets where Ω_2 is included (sets 1, 3, 5, 6, 8, 9, 10, 12, 13 and 14), this parameter takes a small value ($\approx 2.0 \times 10^{-20}$ cm^2), except for set 6. This can be an indication for a high local symmetry around the Tm^{3+} ion, associated with the high homogeneity of the glass [17].

In the sets where Ω_4 and Ω_5 or Ω_5 and Ω_6 appear (sets 8 and 9) the value of Ω_5 experiences large variations, compared to the values that it takes in the sets which are included, Ω_4, Ω_5 and Ω_6 (sets 2, 3, 4, 10, 11, 12 and 14). In the same sets, these parameters take small values ($\leq 3.0 \times 10^{-20}$ cm^2). This may indicate some intrinsic relationship among these three parameters. Since Ω_4 and Ω_6 are associated with the viscosity of the material [17], Ω_5, given its apparent relationship with Ω_4 and Ω_6, might be considered as an odd parameter related to the viscosity. In the sets where Ω_4 and Ω_6 are included (all sets, except sets 8 and 9), these parameters show small variation and their values are always Ω_4, $\Omega_6 \leq 3 \times 10^{-20}$ cm^2 with $\Omega_4 > \Omega_6$.

In all the sets where Ω_3 was included, the Ω_3 value was always high and larger than the values of $\Omega_{2,4,6}$. This may indicate an important contribution made by Ω_3 to the oscillator strength determined by the standard Judd–Ofelt theory.

Table 4 gives the values of the oscillator strength calculated with the set of parameters of set 1 (Table 3) with the standard model Eq. (1), and set 10 (Table 3) with the modified theory (Eq. (3)) which gives the best fit. Also included are the deviation Δ ($\Delta = f_{calc} - f_{exp}$), and the root-mean-square (r.m.s.) deviation of the observed (f_{exp}) and calculated (f_{calc}) oscillator strengths.

The r.m.s. values obtained with the modified oscillator strength model are in general smaller than those obtained with the standard theory. The best set of Ω_λ giving the smallest r.m.s. (0.03×10^{-6}) is $\Omega_{2,3,4,5,6}$ (set 10). This is

Table 4
Experimental oscillator strengths in units of 10^{-6}, f_{exp}, obtained from the absorption spectra at room temperature, and oscillator strengths, f_{calc}, calculated from the standard model (Eq. (1)), $\lambda = 2,4,6$, and from (Eq. (3)) modified oscillator strength, $\lambda = 2,3,4,5,6$ for Tm^{3+} ion in fluoroindate glass, $x = 3$ mol%, deviation Δ and r.m.s. (in units of 10^{-6})

$S'L'J'$	Energy (cm^{-1})	$\lambda = 2,4,6$			$\lambda = 2,3,4,5,6$	
		f_{exp}	f_{calc}	Δ	f_{cal}	Δ
$^3F_4$	5945	1.65	2.00	0.35	1.69	0.04
$^3H_5$	8333	1.44	1.67	0.23	1.40	−0.04
$^3H_4$	12 771	2.61	2.36	−0.25	2.55	−0.06
$^3F_3$	14 777	3.59	3.52	−0.07	3.55	−0.04
$^3F_2$	15 198	0.41	0.72	0.31	0.64	0.23
$^1G_4$	21 367	1.23	0.66	−0.57	1.28	0.05
$^1D_2$	27 933	2.78	2.73	−0.05	2.78	0.00
r.m.s				0.16		0.03

justified by the contribution of odd-order parameters $\Omega_{3,5}$ to the oscillator strength of the $^3H_6 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_3$, $^3H_6 \rightarrow {}^3H_4$, and $^3H_6 \rightarrow {}^1G_4$ transitions (Table 5).

The contribution made by the even- and odd-order parameters to the total oscillator strength of the different transitions and the respective total percentual contributions are included in Tables 5 and 6, respectively.

These results show that, taking into account the contribution of the odd-order parameters in the standard oscillator strength, the contradiction to the definition of the Ω_λ parameters seems less probable, and better fit can be obtained.

Table 5
Contributions of f_{even} and f_{odd} terms in units of 10^{-6} to the oscillator strength calculated with sets 9, 10 and 14 for Tm^{3+} ion in fluoroindate glass, $x = 3$ mol%, $T = 300$ K

$S'L'J'$	Components	$\lambda = 2,3,4,6$	$\lambda = 2,3,4,5,6$	$\lambda = 1,2,3,4,5,6$
$^3F_4$	f_{calc}	1.83	1.69	1.69
	f_{even}	1.71	1.51	1.50
	f_{odd}	0.12	0.18	0.19
$^3H_5$	f_{calc}	1.41	1.40	1.44
	f_{even}	1.40	1.37	1.36
	f_{odd}	0.01	0.03	0.08
$^3H_4$	f_{calc}	2.40	2.55	2.54
	f_{even}	1.82	1.91	1.88
	f_{odd}	0.58	0.64	0.66
$^3F_3$	f_{calc}	3.67	3.55	3.55
	f_{even}	3.12	2.98	2.96
	f_{odd}	0.55	0.57	0.59
$^3F_2$	f_{calc}	0.59	0.64	0.64
	f_{even}	0.59	0.64	0.64
	f_{odd}	0.00	0.00	0.00
$^1G_4$	f_{calc}	1.29	1.28	1.30
	f_{even}	0.55	0.49	0.49
	f_{odd}	0.74	0.79	0.81
$^1D_2$	f_{calc}	2.67	2.78	2.78
	f_{even}	2.67	2.18	2.17
	f_{odd}	0.00	0.60	0.60

Table 6
Percentual average values of the contribution of the even and odd parts to the oscillator strength for the three best fit sets 9, 10 and 14 for Tm^{3+} ion in fluoroindate glass with $x = 3$ mol%

Combinations	f_{even} (%)	f_{odd} (%)
$\lambda = 2,3,4,6$	85	15
$\lambda = 2,3,4,5,6$	80	20
$\lambda = 1,2,3,4,5,6$	79	21

5. Conclusions

A better fit between the theoretical and experimental oscillator strengths of Tm^{3+} ion in fluoroindate glass is obtained when the Judd–Ofelt theory with a modified oscillator strength, that includes odd rank third-order intensity parameters, is used. The parameter Ω_1 can be associated with the symmetry of the sites occupied by the Tm^{3+} ion in this glass. The best fit is obtained with the set $\Omega_{2,3,4,5,6}$ (set 10). This is justified by the important contribution made by the odd-order parameters $\Omega_{3,5}$ to the oscillator strengths of the $^3H_6 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_3$, $^3H_6 \rightarrow {}^3H_4$, and $^3H_6 \rightarrow {}^1G_4$ transitions. The small values taken by Ω_2 may be associated with the micro-structural homogeneity around the Tm^{3+} ions. The r.m.s. deviations obtained are smaller than those reported for similar and other glasses using the standard theory and other approximation methods [17–19].

Acknowledgements

This research was supported by DIF of the Science Faculty of the Universidad Industrial de Santander (UIS)–Colombia, Telebras and Capes–Brazil.

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