Application of standard and modified Judd–Ofelt theories to thulium doped fluoroindate glass

A. Flórez a,*, M. Flórez A, Y. Messaddeq b, M.A. Aegerter c, P. Porcher d

Universidad Industrial de Santander, Escuela de Física, Departamento de Física-UIS, A.A. 678, Bucaramanga, Colombia
 Instituto de Química, UNESP, CP 355, CEP 14801-970, Araraquara, SP, Brazil
 Institut fur Neue Materialien, INM, Im Stadtwald, Gebäude 43, D-66123 Saarbrücken, Germany
 Laboratoire de Chimic Métallurgique et Spectroscopie des Terres Rares, CNRS, F-92195 Meudon cedéx, France

Abstract

Fluoroindate glasses of the following compositions: $(40-x) InF_3-20 ZnF_2-16BaF_2-20SrF_2-2GdF_3-2NaF-xTmF_3$ with x=1,3 mol% were prepared in a dry box under an argon atmosphere. The absorption spectra at room temperature in the spectral range 350-2200 nm were obtained. The spectra obtained for each sample had similar absorption and only the amplitude of the different bands changed as the concentration of Tm^{3+} . The experimental oscillator strengths were determined from the areas under the absorption bands. Using the standard and modified Judd-Ofelt theory, intensity parameters Ω_i ($\lambda=2,4,6$) and ($\lambda=2,3,4,5,6$), respectively for f-f transitions of Tm^{3+} ions as well as transition probabilities, branching ratios and radiative lifetimes for each band were determined. The results are compared with those of other glasses described in the literature.

1. Introduction

Fluoroindate glasses seem to be particularly useful hosts for rare earth ions due to their optical quality [1–3], chemical stability [4] and phonon cut-off frequency (<500 cm⁻¹) [5]. We have recently described several optical properties of Er³⁺ and Pr³⁺ ions in such glasses [1–3].

The Judd-Ofelt 4f-4f intensity model [6,7] describes the absorption and emission properties of rare earth ions in a number of compounds. However, it has been observed in many cases that this standard theory leads to a negative phenomenological Ω_2 intensity parameter for the Pr^{3+} ion [8], including fluoroindate glasses [2]. These results are in contradiction with the definition of the Ω_{λ} pa-

rameters. Several authors assume that higher order contributions to the forced electric dipole matrix elements might be of considerable importance to solve the problem [9,10]. These introduce additional effective operators of even and odd ranks. Recently, other authors have discussed the problem of the Pr3+ ion in fluoride glasses, including fluorescence measurements of branching ratios [11], and using normalized oscillator strengths [12] to calculate the parameters within the standard Judd-Ofelt theory. In recent papers [13,14] results have been published showing the effect of including higher order contributions to the forced electric dipole matrix elements in Pr³⁺ and Tm³⁺ ions in fluoroindate glasses. Such results show that: Ω_2 for Pr3+ is positive and, for Pr3+ as well as for Tm³⁺ a better fit can be obtained.

In this work we report the results of the application of the standard model [6,7] and modified

^{*}Corresponding author. Tel.: +57-7 644 7248; fax: +57-7 346 149; e-mail: aflorez@uiscol.edu.co

oscillator strengths [14] for the Tm³⁺ ion in fluoroindate glasses to analyze the effect on the optical properties of Tm³⁺ in this host.

2. Theory background

We use the standard 4f-4f intensity model described elsewhere [6,7], and a modified oscillator strength discussed in Ref. [13]. 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 energy (in cm⁻¹) for the transition, $\chi = (n^2 + 2)^2/9n$ 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 measured oscillator strengths, using Eq. (1). It was demonstrated [13] the form of total oscillator strength (modified oscillator strength). It, in its even component, takes into account both contributions of forced electric dipole and of dynamic coupling [15], and the odd component takes into account the contribution due to the odd rank parameters, and is given by

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

where $\Psi = \alpha SL$ and $\xi = \sigma/\overline{\Delta E}$. For Tm³⁺ ion $\overline{\Delta E} \cong 60000$ cm⁻¹ [16,17], which to a first approximation is equal to the energy difference between the baricenters of the ground configuration (f^N) and the first opposite parity excited configuration $(f^{N-1}5d)$.

The matrix reduced elements in Eq. (2) have been tabulated by Nielson and Koster (1963) [18].

The reduced matrix elements for the Tm^{3+} ion with $\lambda = 1$, 3 and 5, were taken from Ref. [14] and those with $\lambda = 2,4,6$ were taken from Carnall (1977) [19].

The total spontaneous emission probability between the J and J' levels is given by

$$A_{JJ'} = \frac{64\pi^4 \sigma^3}{3h(2J+1)} \chi S_{\rm ed}, \tag{3}$$

where $\chi = n(n^2+2)^2/9$ is the effective field corrections at a well-localized center in a medium of isotropic refractive index n. $S_{\rm ed}$ is the electric dipole line strengths defined by

$$S_{\text{ed}} = e^2 \sum_{\lambda=2,3,4,5,6} \Omega_{\lambda} \langle f^N(\alpha SL) J' || U^{\lambda} || |f^N(\alpha SL) J \rangle^2.$$
(4)

 A_{LP} is related to the radiative lifetime τ_R of an excited state by

$$\tau_{\rm R} = \frac{1}{\sum_{l'} A_{,ll'}}.\tag{5}$$

The branching ratio, $\beta_{JJ'}$, corresponding to the emission from an excited J level to J' is

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}}.\tag{6}$$

The multiphonon relaxation rate between two J levels in glasses may be adequately described by a single phonon frequency model [16] by the formula

$$W_{\rm NR} = B e^{-\alpha \Delta E} (n(\omega, T) + 1)^p, \tag{7}$$

where B and α are constants characteristic of the host material, ΔE is the energy gap between the emitting and the closest lower electronic level, ω is the stretching frequency of the glass-forming groups, and $p = \Delta E/\hbar\omega$ is the number of phonons which must be emitted in order to conserve energy during the transition. The explicit temperature dependence of $W_{\rm NR}$ through the Bose-Einstein occupation number, $n=1/[\exp(\hbar\omega/kT)-1]$, provides a way to determine the number and energy of the phonons involved in the decay processes. These expressions are based on the assumption that phonons of a single energy, $\hbar\omega$, are active in the transition.

3. Experimental procedure

The fluoroindate glasses with batch compositions (mol%) $(40-x) InF_3 - 20 SrF_2 - 20 ZnF_2 - 16 BaF_2 2NaF-2GdF_3-xTmF_3$ (x=1 and 3 mol%) were 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. After the fining process the liquid was poured into a brass mold at 260°C and then cooled to 20°C. The obtained samples were transparent and were non-hygroscopic. The samples were cut and polished into the shape of parallelipipeds. The refractive indices were measured using a Abbé Refractometer and a value of 1.48 ± 0.05 was obtained for two samples (x = 2, 3 mol%). The density was measured by Arquimede's principle using xylene as an immersion liquid and a density of 4.84 g/cm³ was obtained for the sample of 3.0 mol%.

The absorption spectra were recorded in the visible spectral range using a 0.75 m monochromator (Spex) with an AsGa photomultiplier cooled to -30° C, and in the infrared spectral range using a PbS detector at room temperature (Fig. 1). The absorption path length of the sample was 1.30 mm for the sample with 3.0 mol% concentration.

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

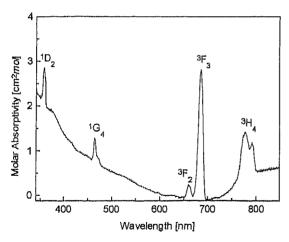


Fig. 1. Absorption spectrum of Tm^{3+} ion in fluoroindate glass, at room temperature in the spectral range from 340 to 850 nm. Sample with x = 3 mol% of Tm^{3+} .

$$f = \frac{4.318 \times 10^{-9}}{Cl\lambda^2} \int k(\lambda) \, \mathrm{d}\lambda,\tag{8}$$

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 cm³ and the absorption path length, respectively.

4. Results

4.1. Absorption spectra

Fig. 1 shows the absorption spectrum of Tm³⁺ in fluoroindate glass at room temperature in the spectral range from 350 to 850 nm. The spectrum obtained for each sample have similar bands. There was little difference in the amplitudes of the different bands as the concentration of Tm³⁺ changed. The energy level diagram obtained from the absorption spectra of Tm³⁺ in fluoroindate glass at room temperature is shown in Fig. 2(a).

4.2. Oscillator strengths and spectroscopical parameters

Table 1 gives the oscillator strengths calculated with the standard model Eq. (1), $\lambda = 2.4.6$, and with the modified theory Eq. (3), $\lambda = 2.3.4.5$ and 6. Also, it is included the deviation $\Delta(\Delta = f_{\text{Cal}} - f_{\text{Exp.}})$,

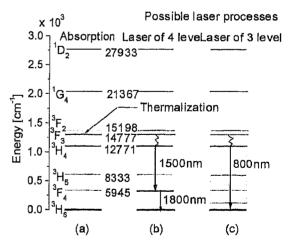


Fig. 2. (a) Energy level of Tm³⁺ ion in fluoroindate glass, obtained from the absorption spectra; (b) one diagram of possible laser transition of 4 levels; (c) diagram of possible laser transition of 3 levels.

Table 1 Experimental oscillator strengths in units of 10^{-6} , $f_{\rm Exp}$, obtained from the absorption spectra at room temperature, and oscillator strengths, $f_{\rm Cal}$, 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 Tm³⁺ ion in fluoroindate glass x = 3 mol%, deviation Δ and RMS (in units of 10^{-6})

S'L'J'	Energy (cm ⁻¹)	$f_{Exp}.$	$f_{\rm Cal}$, $\lambda = 2,4,6$	Δ	f_{Cal} . $\lambda = 2,3,4,5,6$	Δ
³ F ₄	5945	1.65	2.00	0.35	1.69	0.04
$^{3}H_{5}$	8333	1.44	1.67	0.23	1.40	-0.04
$^{3}H_{4}$	12 771	2.61	2.36	-0.25	2.55	-0.06
$^{3}F_{3}$	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
¹ G ₄	21 367	1.23	0.66	-0.57	1.28	0.05
$^{1}D_{2}$	27 933	2.78	2.73	-0.05	2.78	0.00
RMS				0.16		0.03

and the root-mean-square (RMS) deviation of the observed ($f_{\rm Exp.}$) and calculated ($f_{\rm Cal.}$) oscillator strengths [14]. The excited J levels are given in the

column 1, and in the other columns are given f_{lixp} , f_{Cal} and Δ . The average wavelengths were taken to be the baricenters of the absorption bands.

Table 2 Values of the gap energy ΔE , transitions probabilities $A_{M'}$ and branching ratios $\beta_{M'}$, between multipletes J and J' and radiative life time τ_R , and emitting level multiphonon rate W of Tm^{3+} in fluoroindate glass (x = 3 mol%), calculated from the standard theory ($\lambda = 2,4,6$) and modified theory using the better set of fenomenological parameters ($\lambda = 2,3,4,5,6$), obtained in Ref. [12]

Transitions		ΔE (cm ⁻¹)	$\lambda = 2,4,6$			$\lambda = 2,3,4,5,6$			Emitting level
			$A_{JJ'}$	$\beta_{JJ'}$	$\tau_{\rm R}$ (ms)	$A_{JJ'}$	$\beta_{JJ'}$	τ _R (ms)	multi-phonon rate W (s ⁻¹)
$^{3}F_{+} \rightarrow$	³ H ₆	5945	150.89	1.0000	6.63	127.53	1.0000	7.84	1.96×10^{-3}
$^{3}H_{5} \rightarrow$	$^{3}F_{4}$	2388	4.75	0.0230	4.84	3.10	0.0230	5.75	1.04×10^{5}
	$^{3}H_{6}$	8333	201.84	0.9770		169.91	0.9770		8.09×10^{-9}
$_{3}\mathrm{H}^{4}\rightarrow$	${}^{3}H_{5}$	4438	34.46	0.0351	1.02	37.13	0.0351	0.94	2.31
	$^3\mathrm{F}_4$	6826	125.39	0.1278		135.09	0.1278		1.50×10^{-5}
	$^{3}H_{o}$	12 771	821.16	0.8370		884.71	0.8370		1.87×10^{-18}
$^{3}F_{3} \rightarrow$	$^{3}H_{4}$	2006	5.28	0.0019	0.36	5.32	0.0019	0.36	4.39×10^{5}
	${}^{3}H_{5}$	6444	175.04	0.0638		176.28	0.0638		1.02×10^{-4}
	3 F ₄	8832	450.65	0.1644		453.86	0.1643		6.66×10^{-10}
	$^{3}H_{6}$	14 777	2110.69	0.7698		2125.71	0.7698		8.24×10^{-23}
$^{3}F_{2} \rightarrow$	3F_3	421	0.01	0.0	1.17	0.01	0.0	1.32	0.19×10^{16}
	3H. ₄	2427	2.62	0.0031		2.32	0.0031		5.38×10^{4}
	$^3\mathrm{H}_5$	6865	59.39	0.0697		52.60	0.0697		1.24×10^{-5}
	$^{3}F_{4}$	9253	145.44	0.1707		128.80	0.1707		8.13×10^{-11}
	$^{3}H_{6}$	15 198	644.45	0.7564		570,72	0.7564		1.00×10^{-23}
$^{1}G_{4} \rightarrow$	$^{3}F_{2}$	6169	15.48	0.0140	0.90	30.18	0.0140	0.46	4.03×10^{-4}
	$^{3}F_{3}$	6590	18.87	0.0170		36.79	0.0170		4.91×10^{-5}
	3 H. ₄	8596	41,88	0.0378		81.65	0.0378		2.17×10^{-9}
	$^{3}\mathrm{H}_{5}$	13 034	146.01	0.1318		284.64	0.1318		5.02×10^{-19}
	$^3\mathrm{F}_4$	15 429	242.20	0.2186		472.15	0.2186		3.17×10^{-24}
	$^{3}H_{6}$	21 367	643.27	0.5807		1253.99	0.5807		4.05×10^{-37}
$^{1}D_{2} \rightarrow$	$^{1}G_{+}$	6566	106.37	0.0059	0.05	108.02	0.0059	0.05	5.53×10^{-5}
	$^{3}F_{2}$	12 735	776.11	0.0429		788,16	0.0429		2.24×10^{-18}
	$^{3}F_{3}$	13 156	855.65	0.0473		868.94	0.0473		2.73×10^{-19}
	$^{3}\mathrm{H}_{4}$	15 162	1309.77	0.0725		1330.11	0.0725		1.20×10^{-23}
	$^3\mathrm{H}_5$	19 600	2829.39	0.1566		2873.34	0.1566		2.78×10^{-33}
	$^{3}F_{4}$	21 988	3994.68	0.2211		4056.73	0.2211		1.82×10^{-38}
	³ H ₆	27 933	8189.88	0.4534		8317.09	0.4534		2.25×10^{-51}

The phenomenological intensity parameters, Ω_{λ} (in unit of 10^{-20} cm²), used in this work [14] are

$$\Omega_2 = 1.77$$
, $\Omega_4 = 2.30$, $\Omega_6 = 1.69$,

$$\Omega_2 = 1.15$$
, $\Omega_3 = 25.24$, $\Omega_4 = 1.79$, $\Omega_5 = 2.49$, $\Omega_6 = 1.48$.

Table 2 gives the energies of the possible $J \leftrightarrow J'$ transitions involving the seven J levels obtained from the absorption spectrum of the sample with a concentration of 3 mol%. The quantities $A_{JJ'}$, $\beta_{JJ'}$ and τ_R and W, were calculated on the basis of Eqs. (3)–(7), respectively, and the results are included in Table 2.

4.3. Thermalization

In Tm^{3+} – doped fluoroindate glass the 3F_3 and 3F_2 level separation, ΔE , as obtained from the absorption spectra (Fig. 1), is 421 cm⁻¹. Thus, at room temperature thermalization of the two levels occurs and the effective radiation transition probability of the two levels has to be calculated using the formula

$$A_{\text{eff}} = \frac{12 \exp(-\Delta E/kT) \sum A(^{3}F_{2}) + 4 \sum A(^{3}F_{3})}{12 \exp(-\Delta E/kT) + 4},$$
(9)

where $kT = 209 \text{ cm}^{-1}$ (at room temperature), for $\Omega_{2,4,6}$, $\sum A(^3F_2) = 851.91 \text{ s}^{-1}$, $\sum A(^3F_3) = 2741 \text{ s}^{-1}$ the $A_{\text{eff}} = 2199 \text{ s}^{-1}$ and for $\Omega_{2,3,4,5,6}$, $\sum A(^3F_2) = 754.45 \text{ s}^{-1}$, $\sum A(^3F_3) = 2761.17 \text{ s}^{-1}$ the $A_{\text{eff}} = 2184.98 \text{ s}^{-1}$.

From Eq. (8), assuming that the stretching frequencies for the fluoroindate glasses are similar to that of fluoride glasses, $\hbar\omega = 500$ cm⁻¹ and $B = 1.59 \times 10^{10}$ s⁻¹ and $\alpha = 5.19 \times 10^{-3}$ cm [5], the multiphonon relaxation rate, $W_{\rm NR}$, from the $^{3}F_{2}$ level calculated in this work was 1.9×10^{-9} s⁻¹. From these results, owing to the multiphonon relaxation rate from the $^{3}F_{2}$ level, one eventual laser transition can be expected mainly from the $^{3}F_{3}$ level. The parameters, α and B, are dependent on the host material but approximately independent of the specific J level of a given lanthanide. To illustrate this situation, Fig. 2 shows the energy

levels obtained from the absorption spectra of Tm³⁺ in fluoroindate glass.

5. Discussion

From Fig. 1 the intensity of the hypersensitive transitions ${}^{3}H_{6} \rightarrow {}^{3}F_{4}$, ${}^{3}H_{6} \rightarrow {}^{3}H_{4}$ and ${}^{3}H_{6} \rightarrow {}^{1}G_{4}$ of the Tm³⁺ ion [8] are approximately equal to the intensities of the other transitions (${}^{3}H_{6} \rightarrow {}^{3}H_{5}$, ${}^{3}H_{6} \rightarrow {}^{3}F_{3}$, ${}^{3}H_{6} \rightarrow {}^{1}D_{2}$). This similarity is opposite to the absorption observed for this type of transition for the Er³⁺ and Pr³⁺ ions in glasses of the same composition.

From Table 1 the oscillator strengths for Tm³⁺ in fluoroindate glasses are similar to those in other fluoride glasses [20], but are smaller than in borate, phosphate, germanite and tellurite glasses [21,22]. This fact is due to the lower phonon frequency in the fluoroindate glass. Consequently, for concentrations <5.0 mol% rare earth ions, these results confirm the suitability of fluoride glasses, with respect to multiphonon losses, as hosts for laser operation in the infrared.

From Table 2, the transitions that have greater contribution from the odd rank parameters to the oscillator strengths ${}^{3}H_{6} \rightarrow {}^{3}F_{4}$, ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$, ${}^{3}\mathrm{H}_{6} \rightarrow {}^{3}\mathrm{H}_{4}$ and ${}^{3}\mathrm{H}_{6} \rightarrow {}^{1}\mathrm{G}_{4}$, show the greater differences between the transition probabilities, $A_{II'}$, calculated with the 4f-4f standard and the modified models, the greatest differences being in the transitions from the ¹G₄ level. The magnetic-dipole contribution to the transition ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$ is not taken into account. These results show that there are various potential laser transitions that may be predicted based on the transition probabilities, branching ratio, radiative lifetimes, and multiphonon relaxation rates for Tm³⁺ in fluoroindate glasses. These transitions are included in Table 3. Diagrams 2(b) and (c) in Fig. 2 show possible processes to obtain a four-level laser system and a three-level laser system, respectively. Also, there are transitions at 1200, 1500 and 1800 nm that may be of interest as sources for optical waveguides.

From Fig. 2, due to the spread of the energy level structure of Tm³⁺, and the multiphonon transition losses, virtually all the transitions,

Table 3
Selected possible laser transitions of Tm³⁺ in fluoroindate glasses

Transitions		$\Delta E \text{ (cm}^{-1})$	$\lambda = 2,4,6$			$\lambda = 2,3,4,5,6$			Emitting level
			$\overline{A_{JJ'}}$	$\beta_{J,I'}$	τ _R (ms)	$A_{JJ'}$	β_{JP}	$\tau_{R}(ms)$	multi-phonon rate $W(s^{-1})$
$3F_4 \rightarrow$	³ H ₆	5945	150.89	1.0000	6.63	127.53	1.0000	7.84	1.96×10^{-3}
$^{3}H_{5}\rightarrow$	$^{3}H_{6}$	8333	201.84	0.9770		169.91	0,9770		8.09×10^{-9}
$^{3}H_{+} \rightarrow$	³ F.,	6826	125.39	0.1278		135.09	0.1278		1.50×10^{-5}
	$^{3}H_{0}$	12 771	821.16	0.8370		884.71	0.8370		1.87×10^{-18}
${}^3F_3 \rightarrow$	$^{3}H_{5}$	6444	175.04	0.0638		176.28	0.0638		1.02×10^{-4}
	$^{3}F_{4}$	8832	450.65	0.1644		453.86	0.1643		6.66×10^{-10}
	$^{3}H_{6}$	14 777	2110.69	0.7698		2125.71	0.7698		8.24×10^{-23}
$^{3}F_{2} \rightarrow$	$^{3}F_{4}$	9253	145.44	0.1707		128.80	0.1707		8.13×10^{-11}
	3 I-I ₀	15 198	644.45	0.7564		570.72	0.7564		1.00×10^{-23}
$^{1}G_{4} \rightarrow$	${}^{3}H_{5}$	13 034	146,01	0.1318		284.64	0.1318		5.02×10^{-19}
	$^3\mathrm{F}_4$	15 429	242,20	0.2186		472.15	0.2186		3.17×10^{-24}
	3 H ₆	21 367	643.27	0.5807		1253.99	0.5807		4.05×10^{-37}
$^{1}D_{2} \rightarrow$	3F_2	12 735	776.11	0.0429		788.16	().0429		2.24×10^{-18}
	$^{3}F_{3}$	13 156	855.65	0.0473		868.94	0.0473		2.73×10^{-19}
	³ Н.	15 162	1309.77	0.0725		1330.11	0.0725		1.20×10^{-23}
	$^{3}H_{5}$	19 600	2829.39	0.1566		2873.34	0.1566		2.78×10^{-33}
	$^{3}F_{4}$	21 988	3994.68	0.2211		4056.73	0.2211		1.82×10^{-38}
	3H.	27 933	8189.88	0.4534		8317.09	0.4534		2.25×10^{-51}

except the ${}^3F_2 \rightarrow {}^3F_3$ decay, are radiative, and any as, ${}^3F_4 \rightarrow {}^3H_5$, 3H_6 and ${}^3F_4 \rightarrow {}^3H_4$ have been used in fluorozirconate fiber laser [23]. Transitions from the 3H_4 level at 800, 1500 and 2300 nm, and 3F_4 level at 1800 nm are particularly interesting for practical applications; since they can be brought about by excitation of the 3H_4 level by a semiconductor laser diode at 790 nm.

6. Conclusions

In this work we present the calculated spectroscopic properties of various Tm^{3+} transitions in multicomponent fluoroindate glass using the standard 4f–4f intensity model and with a better fit obtained with modified Judd–Ofelt theory [11]. The more important effects of odd rank parameters on the spectroscopic parameters appear in the transitions in which there are a greater contribution to the oscillator strengths. Based on spectroscopic parameters, $A_{JJ'}$, $\beta_{JJ'}$, τ_R and W of Tm^{3+} , various transitions suitable for laser action can be suggested. Also in this paper with Tm^{3+} as with Er^{3+} and Pr^{3+} [1–3], the Ω_2 intensity parameters may be

associated with the micro-structural homogeneity (high local symmetry) around the Tm³⁺ ions.

Acknowledgements

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

References

- A. Flórez, O.L. Malta, Y. Messaddeq, M.A. Aegerter, J. Alloys, J. Alloys Compounds 227 (1995) 135.
- [2] A. Flórez, O.L. Malta, Y. Messaddeq, M.A. Aegerter, in: Proceedings of the 17th International Congress on Glasses, vol. 7(supplement), Chinese Ceramic Society, 1995, pp. 129.
- [3] A. Flórez, O.L. Malta, Y. Messaddeq, M.A. Aegerter, in: Proceedings of the 17th International Congress on Glasses, vol. 3, Chinese Ceramic Society, Beijing, 1995, pp. 483.
- [4] J.Y. Carre, G. Maze, Y. Messaddeq, M. Poulain, A. Soufiane, European Pat. 9203568, 1992.
- [5] R. Reisfeld, C.K. Jorgensen, Excited State Phenomena in vitreous materials, in: Handbook on the Physics and

- Chemistry of Rare Earths, ch. 58, Elsevier, Amsterdam, 1977.
- [6] B.R. Judd, Phys. Rev. 127 (1962) 750.
- [7] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
- [8] R.D. Peacock, Struct. Bonding Berlin 22 (1975) 83.
- [9] L. Smentek-Mielczarek, K. Jankowsky, Molec. Phys. 38 (1979) 1459.
- [10] K. Jankowski, L. Smentek-Mielczarek, Molec. Phys. 38 (1979) 1445.
- [11] R.S. Quimby, W.J. Miniscalco, J. Appl. Phys. 75 (1994) 613.
- [12] P. Goldner, F. Auzel, J. Appl. Phys. 79 (1996) 7972.
- [13] A. Flórez, O.L. Malta, Y. Messaddeq, M.A. Aegerter, J. Non-Cryst. Solids 213&214 (1997) 315.
- [14] A. Flórez, M. Flórez, S.A. López-Rivera, J. Martin, P. Porcher, O.L. Malta, Y. Messaddeq, M.A. Aegerter, J. Alloys Compounds 275, 277 (1998) 333.
- [15] O.L. Malta, J.S.L. Riveiro, M. Faucher, P. Porcher, J. Phys. Chem. Solids 52 (1991) 587.

- [16] R. Reisfeld, C.K. Jorgensen, Lasers and Excited States of Rare Earth, Springer, Berlin, 1977.
- [17] G.H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals. John, 1968.
- [18] C.W. Nielson, G.F. Koster, Spectroscopic Coefficients for pⁿ, dⁿ and fⁿ Configurations, MIT, Cambridge, MA, 1964.
- [19] W.T. Carnall, H. Crosswhite and H.M. Crosswhite, Energy level structure and transition probabilities of He trivalent lanthanides in LaF₃, Argone National Laboratory Special Report, 1977.
- [20] C. Guery, J.L. Adam, J. Lucas, J. Lumin, 42 (1988) 181.
- [21] R. Reisfeld, Y. Eckstein, J. Chem. Phys. 63 (9) (1975) 4001.
- [22] Y. Subramanyam, L.R. Moorthy, S.V.J. Lakshman, J. Non-Cryst. Solids 139 (1992) 67.
- [23] J.Y. Allain, M. Monerie, H. Poignant, Electron. Lett. 26 (1990) 166.