Judd–Ofelt analysis of Pr^{3+} ions in fluoroindate glasses: influence of odd third order intensity parameters

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Abstract

In this work an analysis of the Judd–Ofelt phenomenological Ω_λ intensity parameters for the Pr^{3+} ion in fluoroindate glass is made. Different Pr^{3+} concentrations, namely 1, 2, 3 and 4 mol% are used. The experimental oscillator strengths have been determined from the absorption spectra. A consistent set of parameters is obtained only with the inclusion of odd rank third order intensity parameters and if the band at 21 470 cm^{-1} is assigned to the $^3H_4 \rightarrow {}^3P_1$ transition and the $^1I_6$ component is incorporated in the $^3H_4 \rightarrow {}^3P_2$ transition at 22 700 cm^{-1}.

1. Introduction

The understanding of the optical properties of the Pr^{3+} ion in inorganic compounds is of great importance due to its potential technological applications as, for example, in optical fibers, optical amplifiers 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+} ion in these glasses [1,2]. In the present paper we report on the optical absorption of Pr^{3+} ion in fluroindate glasses and on the analysis of the data through a modified Judd–Ofelt theory.

The 4f–4f intensity model [3,4] 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 the standard theory [3,4] leads to a negative value of the phenomenological Ω_2 intensity parameter for the Pr^{3+} ion [5,6]. This negative value is also observed for the Pr^{3+} ion in fluoroindate glasses, as shown below. These results are in contradiction to the definition of the Ω_λ parameters. It has been argued [5] that this value is due to the fact that, in Pr^{3+}, the first opposite parity excited configuration ($4f^15d^1$) lies very close to the $4f^2$ ground configuration (~ 1500 cm^{-1}), causing a breakdown in the energy differences approximation used to determine the absorption and emission coefficients in the standard Judd–Ofelt model [3,4]. Therefore higher order contributions to the forced

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PII S0022-3093(97)00014-8

electric dipole matrix elements might be of considerable importance [7,8]. These introduce additional effective operators of even and odd rank.

In the present analysis of the Pr^{3+} absorption intensities these additional effective operators are considered. Different sets of phenomenological intensity parameters Ω_λ ($\lambda = 1, 2, 3, 4, 5, 6$) are obtained and discussed. It is also shown that a better quality set of parameters is obtained if the band at 22 700 cm^{-1} is the ${}^3H_4 \rightarrow {}^3P_2$, ${}^1I_6$ transitions and that at 21 470 cm^{-1} is the ${}^3H_4 \rightarrow {}^3P_1$.

2. Theory

2.1. Odd rank intensity parameter

The standard Judd–Ofelt calculations of the forced electric dipole mechanisms [3,4] involves intermediate states belonging to an excited configuration $4f^{N-1}5d$(B) which has opposite parity to the ground $4f^N$ configuration (A) and differs from it by a one-particle excitation. Both electronic configurations are assumed to be totally degenerate. This procedure leads to transition probabilities which depend on the so-called even rank intensity parameters, Ω_λ, and the total oscillator strength of a transition between two manifolds, with the total angular momentum, J, given by [5,9]

$$f = \chi \frac{8\pi^2 mc\sigma}{3h(2J+1)} \times \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N\psi'J' \| U^{(\lambda)} \| 4f^N\psi J\rangle^2, \qquad (1)$$

where σ is the transition energy (in wavenumbers), $\chi = (n^2+2)^2/9n$ is the Lorentz local field correction (n being the refractive index of the medium) and $U^{(\lambda)}$ is a unit tensor operator of rank λ.

The dynamic coupling mechanism [10] known to be of importance for 4f–4f intensities leads to an oscillator strength expression which has the same form as Eq. (1), so that the experimental even rank Ω_λ parameters absorb both mechanisms. Since for Pr^{3+} ion the barycenters of both configurations (A $= 4f^2$, B $\equiv 4f^1 5d^1$) are separated by a small energy difference, $\Delta E = E_A - E_B \approx 15\,000$ cm^{-1}, the approximation used to derive Eq. (1), $E_{A\alpha} - E_{B\beta} \simeq E_{A\alpha'} - E_{B\beta} \simeq E_A - E_B$, is less valid. It is therefore conceivable that additional even and, mainly, odd rank effective operators may be of importance to determine the correct intensities.

There are alternative ways to take these additional effective operators into account. The one used in this work is to consider that all but the ground $4f^2$ configuration are degenerate and to take the expansions

$$\frac{1}{(E_{A\alpha} - E_B)} \simeq \frac{1}{(E_A - E_B)} - \frac{\varepsilon_\alpha}{(E_A - E_B)^2}$$

(with similar expressions for $E_{A\alpha'}$ and $\varepsilon_{\alpha'}$),

where

$$E_{A\alpha} = E_A + \varepsilon_\alpha, \qquad E_{A\alpha'} = E_A + \varepsilon_{\alpha'}$$

and assuming

$$\left|\frac{\varepsilon_\alpha}{(E_A - E_B)}\right|, \left|\frac{\varepsilon_{\alpha'}}{(E_A - E_B)}\right| < 1. \qquad (2)$$

It is also convenient to use the average energy denominator method (AEDM) [11], where all energy differences, $(E_A - E_B)$, are replaced by a single average energy, $\overline{\Delta E}$, which to a first approximation is equal to the energy difference between the ground ($4f^N$) and the first opposite parity excited configuration ($4f^{N-1}5d$). Thus, substituting $1/(E_A - E_B)$ in Eq. (1) by the expansions given in Eq. (2) and following the same procedure as in the standard Judd–Ofelt theory, the total oscillator strength due to the forced electric dipole mechanism can be rewritten as

$$f = \frac{8\pi^2 mc\sigma\chi}{3h(2J+1)} \times \left[(1-\xi_1)^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N\psi'J' \| U^{(\lambda)} \| 4f^N\psi J\rangle^2 + \xi_2^2 \sum_{\lambda=1,3,5} \Omega_\lambda \langle 4f^N\Psi'J' \| U^{(\lambda)} \| 4f^N\Psi J\rangle^2\right], \qquad (3)$$

where

$$\xi_1 = \frac{\varepsilon_{J'} + \varepsilon_J}{\overline{\Delta E}}, \qquad \xi_2 = \frac{\varepsilon_{J'} - \varepsilon_J}{\overline{\Delta E}} = \frac{\sigma}{\overline{\Delta E}}.$$

The modulus of the quantities, ξ_1 and ξ_2, are less than 1. The additional contribution associated with

Table 1
Values in the intermediate coupling for the matrix elements $[U^{(\lambda)}]^2 = \langle f^N\psi' J' \| U^{(\lambda)} \| f^N\psi J\rangle^2$. Those for $\lambda = 1, 3, 5$ are taken from Ref. [12] and include the factor ξ_2^2 and those for $\lambda = 2, 4, 6$ from Ref. [13]. $\langle \psi J| = {}^3H_4$ [9]

	$[U_1]^2$	$[U_2]^2$	$[U_3]^2$	$[U_4]^2$	$[U_5]^2$	$[U_6]^2$
$^3H_5$	0.0002	0.1095	0.0000	0.2034	0.0013	0.6106
$^3H_6, {}^3F_2$	0.0000	0.5080	0.0000	0.4369	0.0010	0.2603
$^3F_3, {}^3F_4$	0.0043	0.0820	0.0077	0.4015	0.0000	1.1904
$^1G_4$	0.0000	0.0019	0.0000	0.0044	0.0000	0.0119
$^1D_2$	0.0000	0.0020	0.0000	0.0165	0.0133	0.0493
$^3P_0$	0.0000	0.0000	0.0000	0.1713	0.0000	0.0000
$^3P_1$	0.0000	0.0000	0.0000	0.1721	0.0919	0.0000
$^1I_6, {}^3P_2$	0.0000	0.0081	0.0066	0.0809	0.0620	0.1576

ξ_1 is also modulated by the contribution due to the dynamic coupling mechanism [11]. This contribution is not formally included in Eq. (3), but its effect is expected to be considerably attenuated. Therefore, in a phenomenological treatment, for fitting purposes, the quantity $(1 - \xi_1)^2$ may be taken as a constant which is absorbed by the $\Omega_\lambda(\lambda = 2, 4, 6)$ parameters.

2.2. *Reduced matrix elements*

The matrix elements of odd order calculated with the new approximation using the wavefunctions supplied by Dr M. Porcher (private communication) are included in the Table 1.

3. Experimental

The fluoroindate glasses with batch compositions (mol%) $34InF_3$–$20ZnF_2$–$20SrF_2$–$6GaF_3$–$2NaF$–$(18 - x)BaF_2$–$xPrF_3$ ($x = 1$, 2, 3 and 4 mol%) have been prepared by melting ultrapure powders (Merck, Fluortran) in a platinum crucible at 800°C for 1 h and then at 850°C for fining, in a dry box under Ar atmosphere. The liquid was cast into a preheated mold at 260°C and then cooled to 20°C.

The absorption spectra have been recorded at 300 K using a spectrophotometer (Cary 17) in the spectral range 400 to 2500 nm and an IR spectrophotometer (Bomen) in order to measure the band at 4280 nm (Fig. 1).

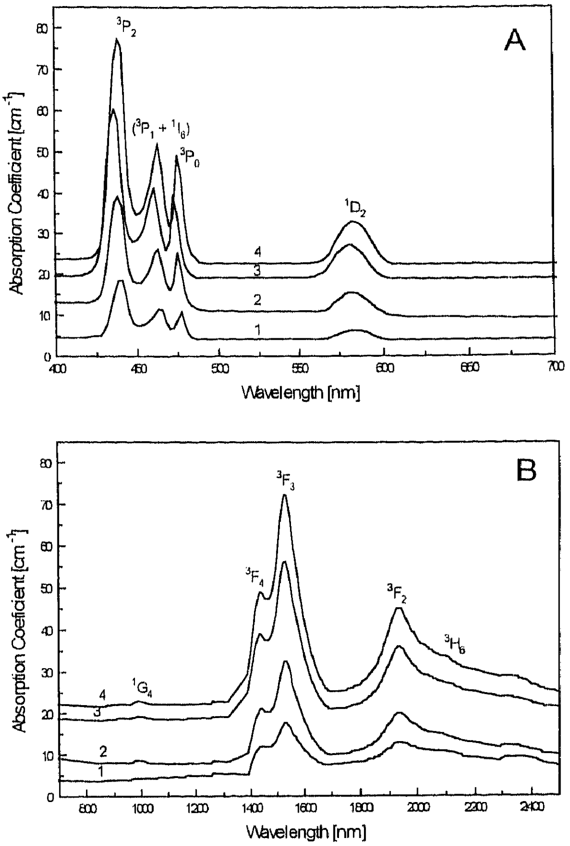

Fig. 1. Absorption spectrum of Pr^{3+} in fluoroindate glasses, at room temperature in the spectral range (A) from 400 to 700 nm and (B) from 700 to 2500 nm. Samples with $x = 1$, 2, 3, 4 mol% of Pr^{3+}.

Table 2
Experimental oscillator strengths f, $(\times 10^{+6})$ obtained from the absorption spectra for Pr^{3+} ion in fluoroindate glasses with different concentrations. $T = 300$ K

	C (mol%)				Energy (cm^{-1})
	1.0	2.0	3.0	4.0	
$^3H_4 \rightarrow {}^3P_2$	6.29	6.74	6.44	6.60	22700
$\rightarrow {}^3P_1, {}^1I_6$	2.19	2.48	2.23	2.47	21470
$\rightarrow {}^3P_0$	0.96	1.09	1.01	1.08	20867
$\rightarrow {}^1D_2$	1.77	2.02	2.11	2.38	17014
$\rightarrow {}^1G_4$	0.25	0.22	0.22	0.28	10000
$\rightarrow {}^3F_4, {}^3F_3$	6.49	7.13	8.21	7.16	6556
$\rightarrow {}^3H_6, {}^3F_2$	1.49	1.50	1.80	1.27	5094
$\rightarrow {}^3H_5$	1.43	1.51	1.61	1.53	2336

Table 3
Values of the oscillator strength calculated using Eq. (3), f_{Cal} ($\times 10^{+6}$), and residuals values Δ ($\times 10^{+6}$) corresponding to Table 2

f_{Cal}				Δ			
1.0	2.0	3.0	4.0	1.0	2.0	3.0	4.0
6.23	6.69	6.39	6.54	−0.06	−0.05	−0.05	−0.06
2.33	2.63	2.38	2.66	0.14	0.15	0.15	0.19
0.83	0.88	0.86	0.75	−0.13	−0.21	−0.15	−0.33
0.81	0.90	1.01	0.93	−0.96	−0.90	−1.10	−1.45
0.09	0.10	0.12	0.10	−0.16	−0.12	−0.10	−0.18
6.73	7.30	8.37	7.35	0.24	0.17	0.16	0.19
1.45	1.59	1.79	1.54	−0.04	−0.09	−0.01	−0.27
1.10	1.23	1.45	1.24	−0.33	−0.28	−0.16	−0.29

The oscillator strength is obtained from the area under the absorption band after transformation of the mean wavelength (λ) corresponding to the band baricenter to a convenient scale, using

$$f=(4.318\times 10^{-9}/C\ell\lambda^2)\int K(\lambda)\,\mathrm{d}\lambda, \qquad (4)$$

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

3.1. Searching a best fit for Pr^{3+} in fluoroindate glasses

The experimental values of the oscillator strengths (Table 2), together with the values of the intermediate coupling coefficient for the matrix elements, $U^{(\lambda)}$ (Table 1), have been used to determine different sets of intensity parameters, Ω_λ, using Eq. (3) and a least square procedure.

Table 4
Comparison of the values of Ω_λ, $\lambda = 3, 4, 5, 6$ of Pr^{3+} ion in fluoroindate glasses with different concentrations. $T = 300$ K (Ω_λ in unit of 10^{-20} cm^2)

C (mol%)	Designation A				Designation B			
	Ω_3	Ω_4	Ω_5	Ω_6	Ω_3	Ω_4	Ω_5	Ω_6
1.0	−13.91	0.81	1.35	9.42	99.63	1.48	4.58	4.13
2.0	−14.62	0.87	1.50	10.05	97.95	1.57	5.40	4.65
3.0	−12.61	0.99	1.19	10.22	66.98	1.51	4.73	5.71
4.0	−13.91	0.69	1.54	9.89	86.39	1.33	5.95	4.82

Table 5
Comparison of the values of Ω_λ, $\lambda = 1, 3, 4, 5, 6$ of Pr^{3+} ion in fluoroindate glasses with different concentrations. $T = 300$ K. (Ω_λ in unit of 10^{-20} cm^2)

C (mol%)	Ω_1	Ω_3	Ω_4	Ω_5	Ω_6
Designation A					
1.0	87.56	−53.36	1.67	3.44	5.73
2.0	107.10	−62.84	1.90	4.07	5.66
3.0	79.15	−47.95	1.76	3.07	6.88
4.0	121.94	−68.38	1.88	4.44	4.74
Designation B					
1.0	−639.58	38.09	1.19	4.87	6.82
2.0	−604.56	39.80	1.30	5.68	7.19
3.0	−903.58	18.13	0.72	1.71	9.45
4.0	−635.18	25.31	1.05	6.24	7.49

The following combinations have been calculated $\Omega_{2,4,6}$, $\Omega_{1,4,5,6}$, $\Omega_{2,3,5,6}$, $\Omega_{3,4,5,6}$, $\Omega_{1,3,4,5,6}$, $\Omega_{2,3,4,5,6}$ and $\Omega_{1,2,3,4,5,6}$ assuming that the absorption bands at 21372 and 22562 cm^{-1} belong either to the transitions $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^3P_1 + {}^1I_6$ (set A) or to the transitions $^3H_4 \rightarrow {}^3P_2 + {}^1I_6$ and $^3H_4 \rightarrow {}^3P_1$ respectively (set B). The results are given in Tables 4–7 for the sets $\Omega_{3,4,5,6}$ (A and B), $\Omega_{1,3,4,5,6}$ (A and B), $\Omega_{2,3,4,5,6}$ (A and B) and $\Omega_{2,4,6}$(A and B).

In order to evaluate the quality of the fit, two criteria have been used:

(1) A set of Ω_λ parameters is acceptable if all its values are positive.

Table 6
Comparison of the values of Ω_λ, $\lambda = 2, 3, 4, 5, 6$ of Pr^{3+} ion in fluoroindate glasses with different concentrations. $T = 300$ K. (Ω_λ in unit of 10^{-20} cm^2)

C (mol%)	Ω_2	Ω_3	Ω_4	Ω_5	Ω_6
Designation A					
1.0	−2.77	−16.38	1.67	1.13	10.05
2.0	−3.32	−17.17	1.89	1.23	10.80
3.0	−2.48	−14.51	1.75	0.99	10.78
4.0	−3.82	−15.85	1.86	1.23	10.75
Designation B					
1.0	0.20	99.55	1.43	4.66	4.13
2.0	−0.21	98.03	1.63	5.31	4.66
3.0	0.08	66.96	1.49	4.76	5.71
4.0	−0.79	86.68	1.53	5.62	4.84

Table 7
Comparison of the values of Ω_λ, $\lambda = 2, 4, 6$ of Pr^{3+} in fluoroindate glasses with different concentrations of Pr^{3+}. $T = 300$ K (Ω_λ in unit of 10^{-20} cm^2)

C (mol%)	Designation A			Designation B		
	Ω_2	Ω_4	Ω_6	Ω_2	Ω_4	Ω_6
1.0	−1.79	2.11	5.71	−1.92	3.09	2.24
2.0	−2.35	2.42	6.25	−2.49	3.48	5.73
3.0	−1.61	2.12	6.92	−1.77	3.10	6.41
4.0	−2.88	2.42	6.27	−3.03	3.44	5.77

(2) The best set is the one for which the root mean square values of the fit (rms) is the smallest.

4. Discussion

Table 7 shows that the standard Judd–Ofelt model gives negative Ω_2 values for both A and B sets for all samples. This fact is in contradiction with the definition of the Ω_λ parameters.

Examination of part A of Tables 4–6 indicates that the best fit is obtained for $\Omega_{3,4,5,6}$ (set B). All Ω_λ for all samples are positive. The large values of Ω_3 may be indicative of the important contribution given to the total oscillator strength by the odd Ω_λ (Table 8), which varies between 18.41% for the 3.0 mol% sample to 22.29% for the 4.0 mol% sample. The larger values may also come from the fact that almost all the matrix elements are zero.

From Tables 4 and 5, set B, we note for all samples a large effect on the values of $\Omega_{3,4,5,6}$ parameters, when Ω_1 is included (Table 5). Meanwhile, when Ω_2 is included (Table 6) the values of $\Omega_{3,4,5,6}$ are almost constant. The effect of the inclusion of Ω_1 and Ω_2 on $\Omega_{3,4,5,6}$ may be seen as the following: (a) Ω_1 has almost zero matrix elements and appears more as a fitting parameter (Table 5B), (b) Ω_2 is associated to the contribution of electric dipole and dynamic coupling mechanism. These contributions may mutually cancel since they have opposite sign. This cancellation can produce small or near zero values for Ω_2 for all concentrations of Pr^{3+} and not affect the values of $\Omega_{3,4,5,6}$ (Table 6B). The small variations of Ω_λ with the concentration of Pr^{3+} in the fluoroindate glasses, may indicate a high microstructural homogeneity of these glass hosts. Among the various combinations of Ω_λ parameters studied in this work only one of them produces positive values for all Ω_λ parameters ($\lambda = 3, 4, 5, 6$) and for all concentrations of Pr^{3+}.

Table 8
Percentual average values of the contribution of the even and odd parts to the oscillator strength for the best set of Ω_λ ($\lambda = 3, 4, 5, 6$) (set B), for different concentration (C) of Pr^{3+}. The r.m.s. values (in unit of 10^{-6}) are also included

C (mol%)	f_{Even} (%)	f_{Odd} (%)	r.m.s
1.0	78.37	21.63	0.59
2.0	78.37	21.63	0.68
3.0	81.59	18.41	0.65
4.0	77.71	22.29	0.89

Also, with the modified oscillator strength Eq. (3), the quality of the fit is better than those reported in the literature for Pr^{3+} in similar glasses [3,4,14,15] and obtained with the standard Judd–Ofelt model.

5. Conclusions

Using the standard Judd–Ofelt theory, no satisfactory set of intensity parameters Ω_λ ($\lambda = 2, 4, 6$) could be obtained for Pr^{3+} doped fluoroindate glasses. However by attributing the bands centered at 21470 cm^{-1} to the $^3H_4 \rightarrow {}^3P_1$ transition and that at 22700 cm^{-1} to the $^3H_4 \rightarrow {}^3P_2, {}^1I_6$ transition and by considering odd third order Ω_λ contributions, a better coherence has been obtained. The best set of Ω_λ, which gives the smallest rms values of the oscillator strength was found for Ω_λ ($\lambda = 3, 4, 5, 6$). This configuration is the only one which gives positive Ω_λ values for all samples studied. The odd factors which were taken into account contribute for about 20% to the oscillator strength.

The best fit does not include any Ω_2 contribution, indicating that the contributions of the electric dipole and the dynamic coupling associated with it, cancel each other.

Acknowledgements

This research was supported by Telebrás, Capes, CNPq program RHAE-New Materials and Fapesp, Brazil.

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