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Optical transitions probabilities of Dy^{3+} ions in fluoroindate glass

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Abstract

Fluoroindate glasses of the following compositions: $(40-x)InF_3$–$20ZnF_2$–$20SrF_2$–$2GdF_3$–2NaF–$16BaF_2$–$xDyF_3$ with $x=1.0$, 2.0, 3.0 and 4.0 mol% were prepared in air atmosphere using ammonium process. Absorptions spectra of these glasses at room temperature in the spectral range 300–2500 nm were obtained. Each spectra obtained show identical characteristics and only a change in the intensity of the different bands as the concentration of Dy^{3+} is changed. The oscillator strength is obtained from the area under the absorption band. Using the Judd–Ofelt theory, intensity parameters $\Omega_\lambda(\lambda=2, 4, 6)$ for f–f transitions of Dy^{3+} ions as well as transition probabilities, branching ratios, and radiative lifetimes of each band were determined. The optical properties of the fluoroindate glasses doped with Dy^{3+} are compared with those of other glasses described in the literature.

Keywords: Flouroindate glass; Optical transitions

1. Introduction

Since the discovery of fluoride glass [1], there has been an increasing interest in the determination of the optical properties of heavy metal fluoride glasses doped with rare earths ions. Among the new materials available to date the fluoroindate glasses are emerging as a promising group of halide glasses for optical amplifiers, fibres lasers, etc. [2–4]. These glasses present higher transparency in the mid-infrared range (up to 8 μm) compared to fluorozirconate glasses and are more stable against atmospheric moisture. Studies of their optical properties in the visible region have also attracted attention since rare-earth ions can be easily incorporated in these compounds. It is now well established that the nonradiative relaxation rates of dopant ions levels in fluoroindate glasses are small due to their smaller phonon energies in comparison with other fluoride-based glasses [5]. In this work is used the Judd–Ofelt theory [6,7] for estimating the probability of the forced electric dipole transitions of the Dy^{3+} ion in fluoroindate glass. In the 4f–4f intensity model, the so called intensity parameters $\Omega_{2,4,6}$ are determined from the measurements of absorption spectra and refractive index of the host material. From these parameters, several important optical properties such as oscillator strengths, radiative transition probabilities, branching ratios, spontaneous emission coefficients and peak cross sections for stimulated emission are evaluated.

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2. Theory

The 4f–4f intensity model is described in detail elsewhere [8]. Thus, only a short summary and the most essential formulas will be given.

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

$$f=\frac{4.318\times10^{-9}}{Cl\lambda^2}\int K(\lambda)\,\mathrm{d}\lambda \tag{1}$$

where $K(\lambda)$ is the spectral absorption coefficient, λ (nm) corresponding to the baricentre of each band, C and l are the concentration of Dy^{3+} ions in mol/l and the absorption path length respectively.

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

$$f=\frac{8\pi^2 mc\sigma}{3\hbar(2J+1)}\chi \times\sum_{\lambda=2,4,6}\Omega_\lambda\langle 4f^N(\alpha'S'L')J'\|U^{(\lambda)}\|4f^N(\alpha SL)J\rangle^2 \tag{2}$$

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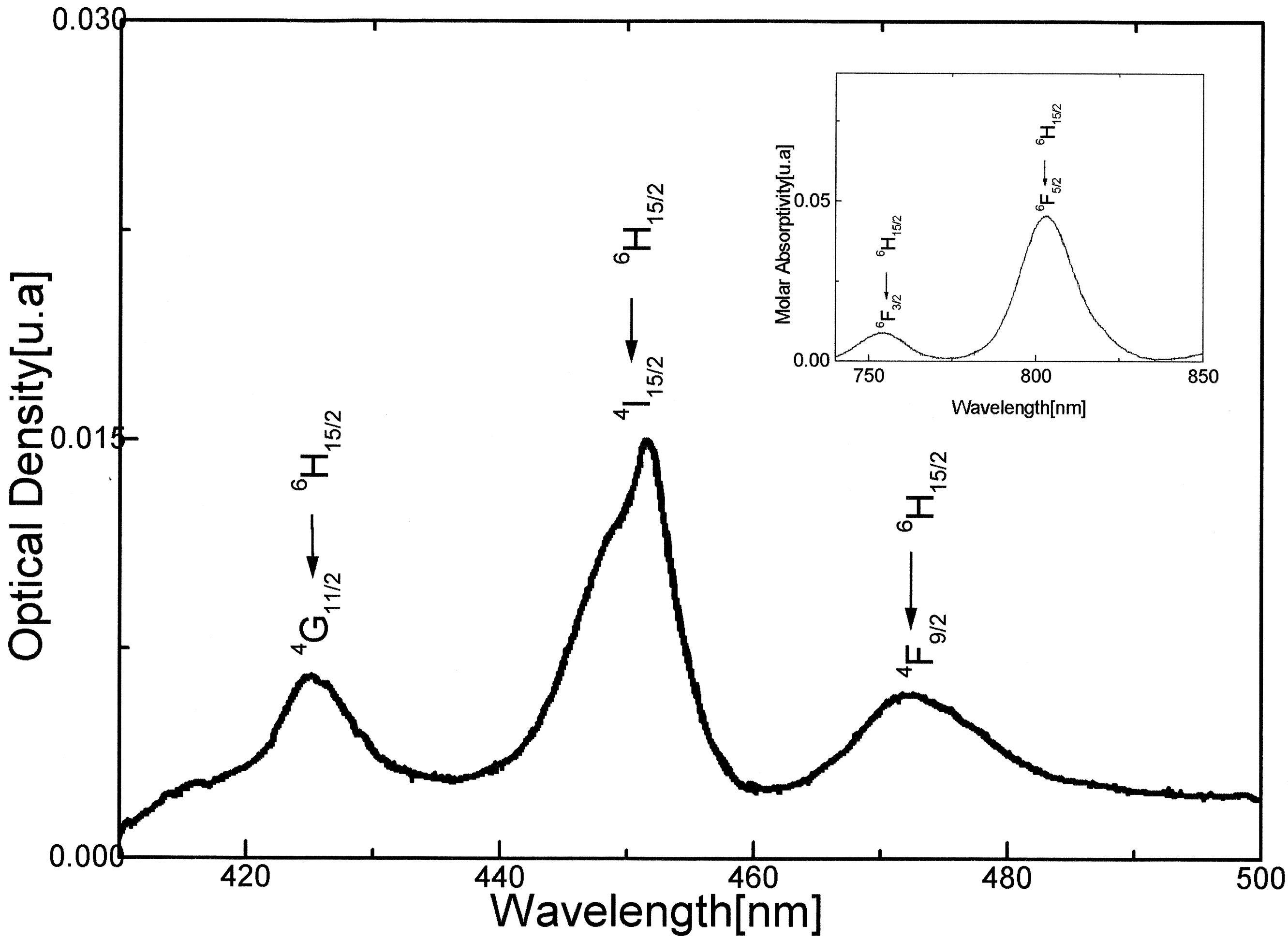

Fig. 1. Absorption spectrum of Dy^{3+} ion in fluoroindate glass containing 1.0 mol% of Dy^{3+}, at room temperature from 400 to 500 nm and inset from 700 to 850 nm.

where m is the mass of the electron, c is velocity of light, h is Planck's constant, σ is the mean frequency for the transition, and $\chi = n(n^2+2)^2/9$ is the effective field corrections at a well-localized centre in a medium of isotropic refractive index n.

The intensity parameters Ω_γ are determined from a least-squares fit to the values of the measured oscillator strengths, using Eq. (2). The quality of the fit can be expressed by the magnitude of the root-mean-square (r.m.s.) deviation, defined by

Table 1

Experimental and calculated oscillator strengths f, ($\times 10^6$) for absorption from the $^6H_{15/2}$ ground state of Dy^{3+} ion in fluoroindate glass, for all concentrations of Dy^{3+} ($x=1.0$, 2.0, 3.0 and 4.0% mol). Also the $\Delta f(\times 10^6)$ between the calculated and experimental oscillator strength and r.m.s. ($\times 10^6$), are included

Upper state	Energy (cm^{-1})	1% mol			2% mol			3% mol			4% mol		
		f_{Exp}	f_{Cal}	Δ	f_{Exp}	f_{Cal}	Δ	f_{Exp}	f_{Cal}	Δ	f_{Exp}	f_{Cal}	Δ
$^6H_{13/2}$	3533	0.95	0.74	−0.21	1.00	0.75	−0.25	0.97	0.74	−0.23	1.01	0.86	−0.15
$^6H_{11/2}$	5845	1.08	0.74	−0.34	1.00	0.75	−0.25	1.01	0.75	−0.26	1.09	0.81	−0.28
$^6H_{7/2}$, $^6F_{11/2}$	7745	2.52	2.58	0.06	2.42	2.46	0.04	2.45	2.49	0.04	2.97	3.00	0.03
$^6F_{7/2}$, $^6H_{5/2}$	11086	1.52	1.52	0.00	1.77	1.64	−0.13	1.63	1.57	−0.06	1.93	1.75	−0.18
$^6F_{5/2}$	12458	0.99	0.72	−0.27	1.02	0.78	−0.24	1.01	0.74	−0.27	0.97	0.79	−0.18
$^4F_{3/2}$	13282	0.16	0.76	0.60	0.19	0.83	0.64	0.17	0.78	0.61	0.16	0.84	0.68
$^4I_{15/2}$	22143	0.33	0.27	−0.06	0.30	0.29	−0.01	0.34	0.27	−0.07	0.29	0.29	0.00
$^4G_{11/2}$	23521	0.09	0.04	−0.05	0.07	0.04	−0.03	0.08	0.05	−0.03	0.07	0.07	0.00
r.m.s.			0.29			0.29			0.29			0.30	

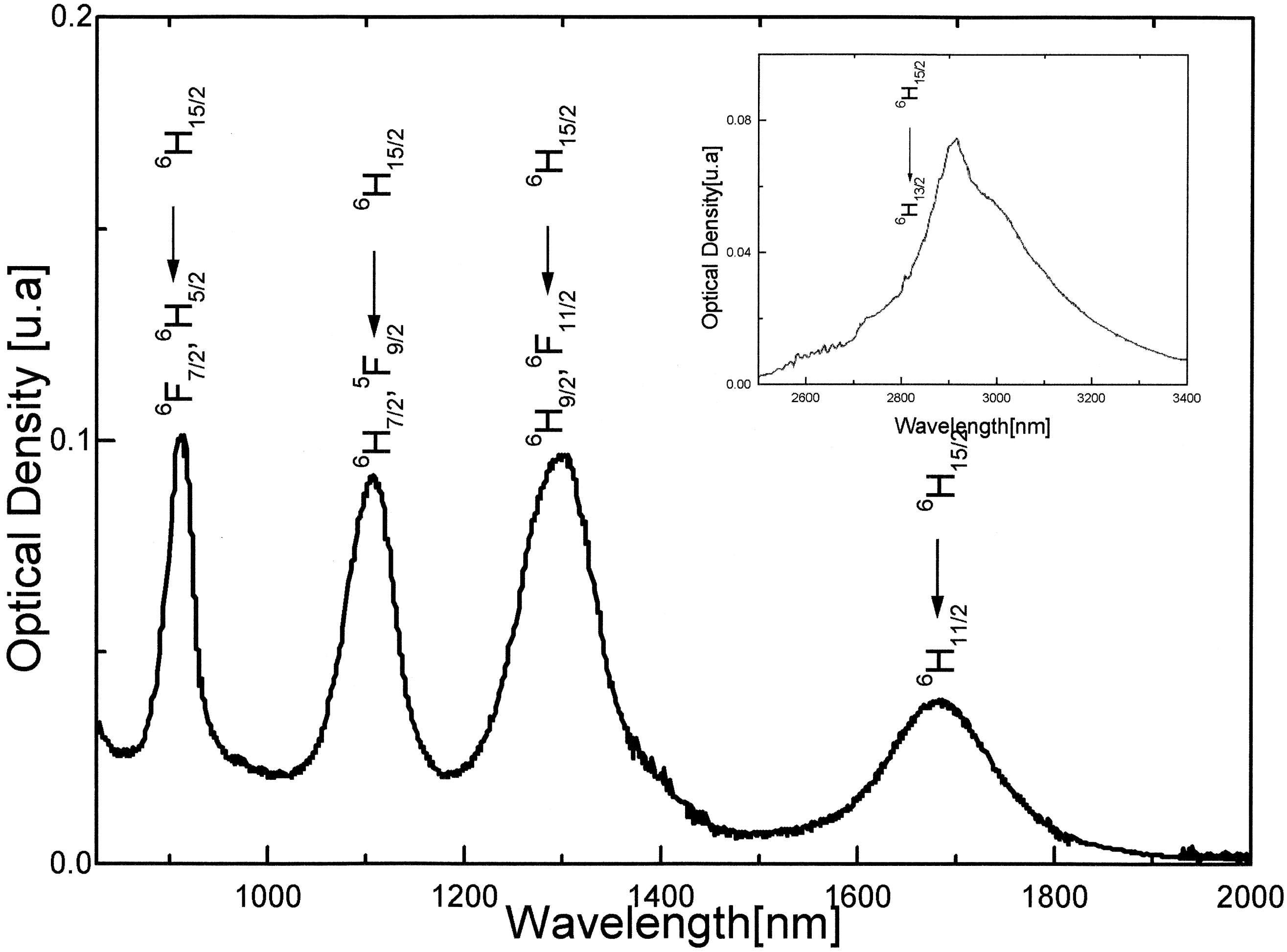

Fig. 2. Absorption spectrum of Dy^{3+} ion in fluoroindate glass containing 1.0 mol% of Dy^{3+}, at room temperature from 850 to 2000 nm and inset from 2500 to 3400 nm.

$$r.m.s = \left\{ \sum \frac{(f_{\mathrm{Cal}} - f_{\mathrm{Exp}})^2}{p-3} \right\}^{1/2} \tag{3}$$

where p is the number of levels fit.

Assuming only electric-dipole transition, the total spontaneous emission probability between the J and J' levels is given by

$$A_{JJ'} = \frac{64\pi^4\sigma^3}{3\hbar(2J+1)} \chi S \tag{4}$$

where S, the linestrength of the electric-dipole transition between manifold J and J' is defined by

$$S = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle f^N(\alpha SL)J' \| U_\lambda \| f^N(\alpha SL)J \rangle^2 \tag{5}$$

The matrix elements $\langle \| U_\lambda \| \rangle$ were obtained from Ref. [8]

$A_{JJ'}$ is related to the radiative lifetime τ_R of an excited state by

$$\tau_R = \frac{1}{\sum_{J'} A_{JJ'}} \tag{6}$$

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

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} \tag{7}$$

3. Experimental

The fluoroindate glasses with nominally compositions (mol%) of $(40-x)InF_3$–$20ZnF_2$–$20SrF_2$–$16BaF_2$–$2GdF_3$–$2NaF$–$xDyF_3$ with $x=1$, 2, 3 and 4 were prepared. The mixtures were heated in a platinum crucible at 800°C

Table 2
Intensity parameters Ω_λ, $\lambda=2$, 4, 6 (in units of 10^{20} cm^2) of the Dy^{3+} ion in fluoroindate glass for different Dy^{3+} concentrations

	Ω_2	Ω_4	Ω_6
1.0	1.78	1.48	1.84
2.0	1.59	1.41	2.01
3.0	1.59	1.52	1.90
4.0	1.72	2.17	2.02

for 1 h for melting and 850°C for finish. Both heatings were performed in a dry box under argon atmosphere. The melt was cast into a preheated mold at 260°C and slowly cooled down to room temperature. The samples were cut and polished into the shape of parallelipipeds.

The absorption spectra were recorder at room tempera-

Table 3
Values of energy, radiative transition probabilities, branching ratios, radiative lifetimes and peak cross-section of Dy^{3+} ion in fluoroindate glass at room temperature, $x=1.0$ mol%

Transition	ΔE (cm^{-1})	A^{ed}_{JJ} (s^{-1})	$\beta_{JJ'}$	τ_R (ms)
$^6H_{13/2}\rightarrow{}^6H_{15/2}$	3533	17.83	1.0000	56.08
$^6H_{11/2}\rightarrow{}^6H_{13/2}$	2312	4.01	0.0583	14.53
$^6H_{15/2}$ +	5945	64.80	0.9417	
$^6H_{9/2}$, $^6F_{11/2}{}^a\rightarrow{}^6H_{11/2}$	1900	4.62	0.0124	2.69
$^6H_{13/2}$	4212	50.79	0. 1368	
$^6H_{15/2}$	7745	315.77	0.8507	
$^6H_{9/2}{}^a$, $^6F_{7/2}\rightarrow{}^6H_{9/2}$, $^6F_{11/2}$	1323	1.25	0.0024	1.94
$^6H_{11/2}$	3223	18.11	0.0352	
$^6H_{13/2}$	5535	91.40	0. 1778	
$^6H_{15/2}$	9068	403.35	0.7845	
$^6F_{7/2}\rightarrow{}^6F_{9/2}{}^a$, $^6H_{7/2}{}^a$	2018	4.23	0.0041	0.98
$^6H_{9/2}$, $^6F_{11/2}{}^a$	3341	19.21	0.0188	
$^6H_{11/2}$	5241	74.25	0.0726	
$^6H_{13/2}$	7553	222.30	0.2173	
$^6H_{15/2}$	11086	702.90	0.6872	
$^6H_{5/2}\rightarrow{}^6H_{7/2}$	2372	0.78	0.0008	1.06
$^6H_{9/2}{}^a$, $^6H_{7/2}$	3390	11.93	0.0126	
$^6H_{9/2}$, $^6H_{11/2}{}^a$	4713	32.06	0.0340	
$^6H_{11/2}$	6613	88.57	0.0939	
$^6H_{13/2}$	8925	217.77	0.2308	
$^6H_{15/2}$	12458	592.18	0.6278	
$^6H_{3/2}\rightarrow{}^6H_{5/2}$	824	0.045	0.0001	3.13
$^6H_{7/2}$	2196	0.86	0.0027	
$^6H_{9/2}{}^a$, $^6H_{7/2}$	4214	6.05	0.0189	
$^6H_{9/2}$, $^6F_{11/2}{}^a$	5537	13.77	0.043 1	
$^6H_{11/2}$	7437	33.38	0. 1045	
$^6H_{13/2}$	9749	75.19	0.2353	
$^6H_{15/2}$	13282	190.17	0.5953	
$^6H_{9/2}\rightarrow{}^6H_{3/2}$	7879	8.20	0.0196	2.39
$^6H_{5/2}$	8703	11.05	0.0264	
$^6H_{7/2}$	10075	17.16	0.0410	
$^6H_{9/2}{}^a$, $^6H_{7/2}$	12093	29.68	0.0710	
$^6H_{9/2}$, $^6H_{11/2}$	13416	40.51	0.0969	
$^6H_{11/2}$	15316	60.30	0. 1443	
$^6H_{13/2}$	17628	91.94	0.2200	
$^6H_{15/2}$	21161	159.03	0.3805	
$^4H_{15/2}\rightarrow{}^4H_{9/2}$	982	0.02	0.0	1.41
$^6H_{3/2}$	8861	16.52	0.0233	
$^6F_{5/2}$	9685	21.57	0.0305	
$^6F_{7/2}$	11057	32.08	0. 0453	
$^6F_{9/2}$, $^6H_{7/2}$	13075	53.03	0.0749	
$^6H_{9/2}$, $^6F_{11/2}{}^a$	14398	70.83	0.1001	
$^6H_{11/2}$	16298	102.71	0.1452	
$^6H_{13/2}$	18610	152.93	0.2162	
$^6H_{15/2}$	22143	257.63	0.3642	
$^4G_{11/2}\rightarrow{}^4I_{15/2}$	1378	0.0082	0.0	8.44
$^4F_{9/2}$	2360	0.041	0.0003	
$^6F_{3/2}$	10239	3.36	0.0283	
$^6F_{5/2}$	11063	4.24	0.0357	
$^6F_{7/2}$	12435	6.02	0. 0508	
$^6F_{9/2}{}^a$, $^6H_{7/2}$	14453	9.46	0.0798	
$^6F_{9/2}$, $^6F_{11/2}$	15776	12.30	0. 1038	
$^6H_{11/2}$	17676	17.30	0. 1459	
$^6H_{13/2}$	19988	25.02	0.2111	
$^6H_{15/2}$	23521	40.77	0.3440	

[a] Larger contribution

ture using a CARY 17 spectrophotometer in the espectral range from 300 to 2500 nm and Perkin Elmer Spectrophotometer from 2500 to 3600 nm. The CARY spectrophotometer provides a graph of the spectral absorption coefficient, $K(\lambda)$ as a function of wavelength, λ, Fig. 1. The chart speed and scanning rate were in each case selected so that the pen writing speed was well below the maximum allowed and the resulting areas always were large in order to reduce the mistake in the measures. The areas under the experimental spectra curves were measured with a digital planimeter, Planix 5, 6, the results obtained were according with the obtained with a computer program. The refractive indices were measured using a Abbe refractometer of the Edmont Scientific, and a value of 1.48 was obtained for all samples.

4. Results and discussi6n

Figs. 1 and 2 show the absorption spectrum, at room temperature, of the fluoroindate glass doped with the Dy^{3+} ion, with concentration of 1.0 mol% of Dy^{3+}, in the spectral range 300–850 nm (visible range) and 850–3400 nm (infrared range) respectively. The transition $^6H_{15/2} \rightarrow {}^6H_{13/2}$ in 2830 nm may be important for future applications in telecomunications.

The experimental and calculated oscillator strengths for all samples studied are included in Table 1. The excited state J' levels are given in column 1 and the energy corresponding to baricentre in column 2, in the other columns are given the values of f_{exp}, f_{cal} (least squares adjusted values) and Δf for each sample obtained from Eqs. (1) and (2).

From Table. 1, may be noted that in the transitions from $^6H_{15/2}$ to $^6H_{13/2}$; $^6H_{11/2}$; $^6F_{5/2}$ and particularly to $^6F_{3/2}$ the differences between calculated and experimental oscillator strengths are relatively larger. Over this fact is important to attract attention, already that for these transitions, a better fit might be obtained if we take account the odd order contributions intensity parameters [9,10], a analysis over it will be made in the next paper.

Table 2 includes the intensity parameters Ω_λ of Dy^{3+} ion in fluoroindate glasses obtained by the least-squares fitting of the experimental oscillator strengths for all concentrations. The squared reduced matrix elements, $[U^{(\lambda)}]^2$, were taken from [8]. From it is noted relatively small values for all the Ω_λ, (Ω_2, max. 1.78×10^{-20} cm^2; Ω_4, max. 2.17×10^{-20} cm^2 and Ω_6, max. 2.02×10^{-20} cm^2), this fact indicates the high degree of homogeneity of these glasses [5]. Not any important variation in the values of the intensity parameters to appear exist in the range of concentrations studied in this work. The similarity in the behaviour of the Ω_λ parameters may be explained by the fact that the Dy^{3+} ions are surrounded by similar environments, and consequently it can evidence one very good quality of the glasses.

Table 3, gives energies of the possible $J \leftrightarrow J'$ transitions involving the ten levels J' obtained from the absorption spectrum. The quantities $A_{JJ'}$, $\beta_{JJ'}$ and τ_R were calculated on the base of Eqs. (3)–(7) respectively; the results are included in Table 2. From these results is noted that there are several transitions that can be eventually used, as for example for laser emission. Given the low phonon energy in these glasses, (<500 cm^{-1}) [5], there are levels that can be populated by processes of thermalization: $^6F_{3/2} \rightarrow {}^6F_{5/2}$ and $^4I_{15/2} \rightarrow {}^4F_{9/2}$, and eventually can serve as metastable levels for laser emission.

5. Conclusions

This work shows the reliability of the predictions of the f–f intensity model for Dy^{3+} ion doped fluoroindate glass at room temperature in the range of concentrations study in this work (1.0, 2.0, 3.0 and 4.0) mol%. The small value obtained for Ω_2, indicates a high degree of homogeneity of the glass and a manifest covalence effect. This fact coupled with the low phonon cut off frequency energy of the phonon modes in this glass makes of it a promising material for use as a fibre laser or optical amplifier in telecommunications. The spectroscopic properties found from the absorption spectra of the Dy^{3+} ion in these glasses (Table 3) are similar to other Dy^{3+} ion doped glass.

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