

Absorption Spectrum Analysis to Predicted and Calculated the Spectroscopic Properties of Pr:SiO₂

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Abstract: Spectroscopic properties of Pr:SiO₂ samples have been investigated at room temperature, the samples are prepared by using Sol Gel method. Theory of Judd-Ofeltt is used to analysis the UV- Visible spectra (in range of 400-900nm) and to calculate the three Judd-Ofeltt of parameters; Ω_2 , Ω_4 and Ω_6 . From the obtained parameters, the radiative transition probabilities $A(J;J')$, radiative lifetime τ_{rad} and branching ratio $\beta_{J \rightarrow J'}$ are calculated. The suitable values of $A(J;J')$, τ_{rad} and $\beta_{J \rightarrow J'}$ could be lead to suggests Pr : SiO₂ as optical material for Laser action

Keywords: Sol- Gel; Spectroscopy; SiO₂; Judd-Ofelt

1. Introduction

Several methods were developed to synthesis of host medium doped with lanthanides ions. For laboratory scale and room temperature sol gel is the favour technique to syntheses of transparent host medium containing an active ions such as lanthanides ions [1-6]. The first major advantage of the sol gel technique is that doping process could be done with high homogeneity, the second advantage is the flexibility of this process to fabricate optical materials such as thin films, coatings monoliths and fibbers etc. The hydrolysis and condensation reactions of sol gel process become faster by using of acid or base catalysts [7-10]. Judd-Ofelt theory have used in present work to analyzes of absorption spectrum for Pr³⁺:SiO₂ to calculate the spectroscopic properties, especially the transition probabilities $A(J;J')$, radiative lifetime τ_{rad} and branching ration $\beta_{J \rightarrow J'}$ of Pr³⁺ ion.

2. Experimental

Several materials is used for sol gel reaction to prepare SiO₂ as a host medium for Pr ions, the Ethanol is used as solvent

while tetraethylorthosilicate TEOS from Aldrich and HCl are used as precursor and catalysed respectively.

The H₂O is used for TEOS hydrolysis process. The molar ratio is equal to 10:1:0.1:1 for EtOH : TEOS: HCl: H₂O. Presidium (III) nitrate pentahydrate is used for doping process (doping rates ~ 5%wt.). The samples drying are achieved by left sample without cover for about 2 week.

Shimdzu UV-VIS Spectrophotometer is used to obtain Absorption spectrum.

3. Results

Figure (1) illustrated the FTIR spectrum for SiO₂ sample doped with Pr³⁺ ions. The characteristics vibration bands (water molecules of O-H bond) are recorded at about 3400 cm⁻¹ and 1600 cm⁻¹. The asymmetric stretching vibrations, bending and symmetric stretching for Si-O-Si groups were found at about 1100 cm⁻¹, 470 cm⁻¹ and 800 cm⁻¹ respectfully, while the stretching vibration of Si - O H groups is found at about 960 cm⁻¹[5].

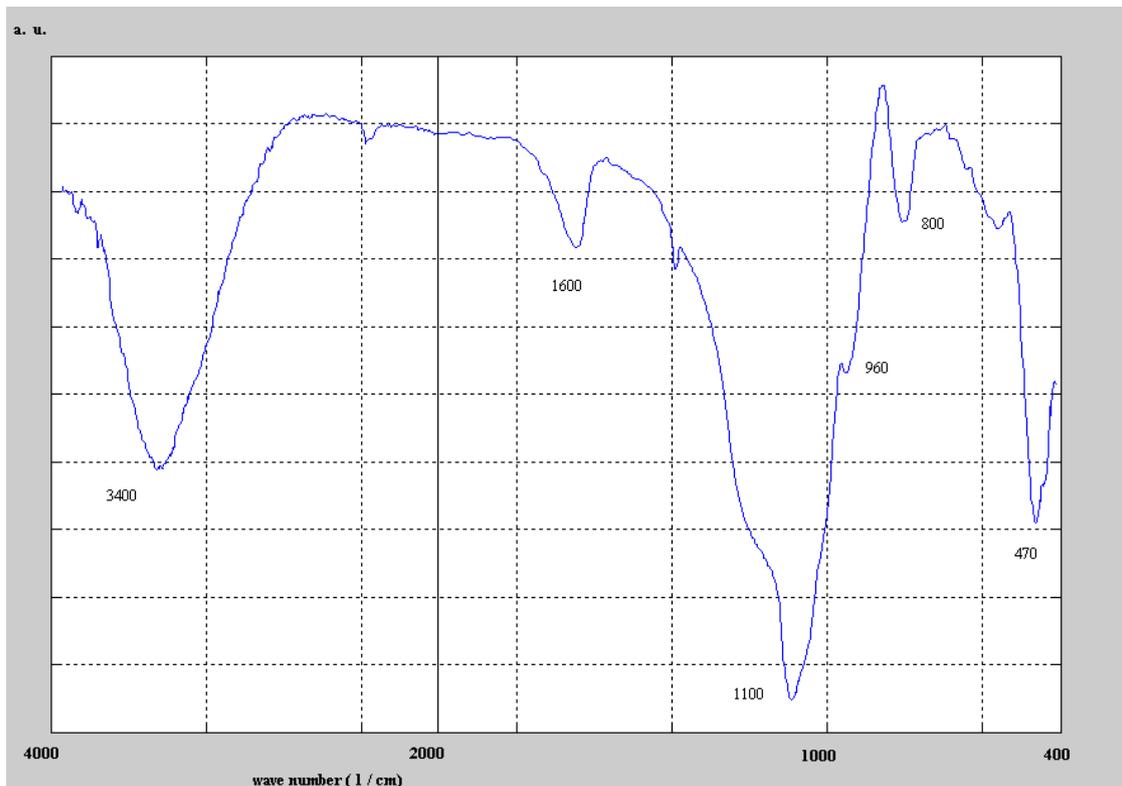


Figure 1: The FTIR spectrum for Pr: SiO₂ sample

The absorption spectrum (in room temperature) for Pr³⁺ doped sample is given in Figure (2). Several peaks caused by electronic transitions for energy level of Pr³⁺ ions are recorded in absorption spectrum, the recording peaks are; ³H₄→³P₂(589nm), ³H₄→³P₁(482nm), ³H₄→³P₀ (468nm) and ³H₄→³D₁ (444nm) [11-13].

The line strength, S_{meas} for each peak is given Eq. 1 [14]:

$$S_{meas}(J \rightarrow J') = \frac{3ch(2J+1)n}{8\pi^3 e^2 \bar{\lambda} \rho_o} \left[\frac{3}{n^2+2} \right]^2 \Gamma \quad (1)$$

Where $\bar{\lambda}$ is the mean to wavelength for the electric transition, J and J' corresponding to total angular momentum of the electric transition, ρ_o is ion concentration for Pr³⁺, Γ is the integrated absorption coefficient [14], n is the host medium refractive indices. The determined values for $\bar{\lambda}$ and S_{meas} are listed in Table (1).

Table 1: Value of $\bar{\lambda}$ and Γ for electric transitions of Pr doped SiO₂

Transitions from ³ H ₄	$\bar{\lambda}$ (nm)	Γ (nm cm ⁻¹)
³ P ₂	589	.0925
³ P ₁	444	.6870
³ P ₀	482	.0351
³ D ₁	468	.2010

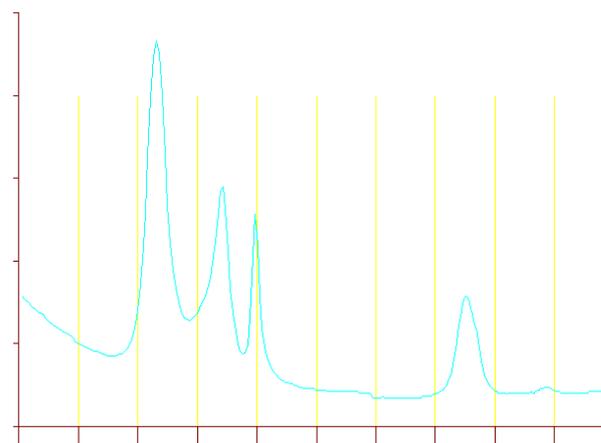


Figure 2: The Pr: SiO₂ Absorption spectrum (doping rate 5wt%)

According to the Judd-Ofeltt theory, the line strength between initial manifold J and terminal manifold J' could write in the form [14]:

$$S_j^t = \sum_{i=1}^3 M_{ij} \Omega_i \quad (2)$$

Where Ω_i is the Judd-Ofelt parameters which represents components of [1 x 3] matrices for Judd-Ofelt parameters (include to three parameters; Ω_2 , Ω_4 and Ω_6). M_{ij} is doubly reduced matrix (or square matrix elements) and represented components of [N x 3] matrices for square matrix elements $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$. N represents the number of transitions to fit, which depends on the number of absorption manifolds actually measured. The square matrix element does not depend on host materials [15-17]. We have used the values of the $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$ which calculated by Carnall *et al.* [18-20], Table (2)

involve the value of $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$ to Pr^{3+} ions for transition from ground state manifold 3H_4 to some excited manifolds.

Table 2: Values of the square matrix elements $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$

Transitions from 3H_4	$U^{(2)}$	$U^{(4)}$	$U^{(6)}$
3P_2	0	0.0695	0.0263
3P_1	0.0004	0.0145	0.0003
3P_0	0.0073	0.0003	0.0654
3D_1	0	0.0047	0.0295

The parameters Ω_i determined the transition strength between any two energy levels in these active ions. These parameters could be found using the S_{meas} values (that obtained from equation (1) into equation (2)). Then values of the three parameters; Ω_2 , Ω_4 and Ω_6 performed to find transition line strengths for absorption bands by using Eq.2. The values of the measured, S_{meas} , S_{calc} , the three JO parameters and ROOT MEAN SQUARE (rms deviation) are tabulated in Table (3).

The J-O parameters are used with help of Eq.2 to find emission line strengths S_{ed} corresponding to the transitions from the any upper multiple manifolds states to their corresponding lower-lying manifold states of Pr^{3+} ions. The values S_{ed} are used to find the radiative transition probabilities $A(J;J')$ and could be found by Eq.3 [14]:

$$A(J;J') = \frac{64\pi^4}{3h(2J+1)\lambda^3} \left[\frac{n(n^2+2)^2}{9} \right] S_{ed} \quad \text{--- (3)}$$

Where J is initial manifold, J' is the final manifold. The radiative lifetime τ_{rad} is given by [14]:

$$\tau_{rad} = 1 / \sum A(J;J') \quad \text{..... (4)}$$

Table 3: Value of S_{meas} , S_{calc} and ΔS for each transitions of $Pr: SiO_2$

Transitions from 3H_4	S_{meas}	S_{calc}	ΔS
3P_2	0.086	0.099	0.009
3P_1	0.024	0.055	0.022
3P_0	0.044	0.061	0.012
3D_1	0.360	0.349	0.008
$\Omega_2 = 4.376$, $\Omega_4 = 5.51$ and $\Omega_6 = 1.011$			

where the sum is done for all final lower-lying states J' . The radiative transition probabilities $A(J;J')$ rates for the Pr^{3+} transitions in SiO_2 hosts are determined by using Eq.3; these values are given in Table (4). The values of the $A(J;J')$ are added to obtain the total radiative rates for the $3H_6$, $2F_4$, $3F_3$, $1D_2$, $3F_2$, $3P_0$, $3P_1$ manifold states. The radiative lifetimes of these levels are determined by Eq.(4). These values are given in **Table (4)**. The transitions from the individual excited state to the lower-lying manifolds should have the same measured lifetime because they all originate from the same excited state. Therefore, while the predicting radiative lifetime of an individual upper level, according to the Judd–Ofelt analysis, one should add the all value of $A(J;J')$ for the corresponding transitions from that level to all lower levels and then invert the sum according to the Eq. (4) [21].

For laser action, branching ratio $\beta_{J \rightarrow J'}$ is an important parameter which gives the possibility of stimulated emission from upper electric transition manifold to any other transition; the branching ratio equal to $A(J;J') / \sum J' A(J;J')$ the result of $\beta_{J \rightarrow J'}$ are listed in **Table (4)**.

Table 4: The $\beta_{J \rightarrow J'}$, $A(J;J')$ and τ_{rad} For $Pr^{3+}: SiO_2$

From	To	$A_{rad} (sec^{-1})$	$\beta_{J \rightarrow J'}$	$\tau_{rad} (msec)$
3P_0	$3F_2$	140000	0.912	0.006
	$1D_2$	98.25	0.001	
	$3H_4$	10358	0.067	
	$3F_4$	1602.8	0.010	
	$3H_6$	1335.7	0.008	
3P_1	$3F_2$	20313	0.315	0.015
	$1D_2$	125.67	0.001	
	$3F_3$	33761	0.525	
	$3H_4$	1804.9	0.028	
	$3F_4$	882.08	0.013	
	$3H_5$	4853	0.075	
3F_2	$3H_6$	2562.3	0.039	0.773
	$3H_4$	1218.9	0.942	
	$3H_5$	73.7	0.056	
1D_2	$3H_6$	0.42	0.002	0.077
	$3F_3$	652.84	0.050	
	$3H_4$	1377.8	0.107	
	$3F_4$	10625	0.825	
	$3H_5$	11.95	0.001	
3F_3	$3H_6$	201.83	0.015	0.48
	$3H_4$	1156.9	0.556	
	$3H_5$	887.44	0.426	
2F_4	$3H_6$	35.48	0.017	0.265
	$3H_5$	278.57	0.073	
3H_6	$3H_6$	3492.3	0.926	10.059
	$3H_5$	50.29	0.505	
	$3H_4$	49.11	0.494	

According to Table (4) the $A(J;J')$ values for energy transitions $^3P_1 \rightarrow ^3F_2$, $^3P_0 \rightarrow ^3H_4$, $^3P_1 \rightarrow ^3F_2$ and $^1D_2 \rightarrow ^3F_4$ are larger than values to others transitions. The higher value of $A(J;J')$ give an indication to the higher intensity of luminescence to these transitions than others. Generally the branching ratio with value more than 50% is powerful for laser emission, so it could select $^3H_6 \rightarrow ^3H_5$, $^3H_6 \rightarrow ^3H_4$, $^2F_4 \rightarrow ^3H_6$, $^3F_3 \rightarrow ^3H_4$, $^1D_2 \rightarrow ^3F_4$, $^3F_2 \rightarrow ^3H_4$, $^3P_1 \rightarrow ^3F_3$ and $^3P_0 \rightarrow ^3F_2$ for laser emission transitions. Especially the $^3H_6 \rightarrow ^3H_5$ and $^3H_6 \rightarrow ^3H_4$ which they have higher radiative lifetimes

4. Conclusion

The wet chemical synthesis method is strongly successes to syntheses of Praseodymium ions doped with Nano_Silica. the $A(J;J')$ values for energy transitions $^3P_1 \rightarrow ^3F_2$, $^3P_0 \rightarrow ^3H_4$, $^3P_1 \rightarrow ^3F_2$ and $^1D_2 \rightarrow ^3F_4$ are larger than values to others transitions. The branching ratio for transitions $^3H_6 \rightarrow ^3H_5$, $^3H_6 \rightarrow ^3H_4$, $^2F_4 \rightarrow ^3H_6$, $^3F_3 \rightarrow ^3H_4$, $^1D_2 \rightarrow ^3F_4$, $^3F_2 \rightarrow ^3H_4$, $^3P_1 \rightarrow ^3F_3$ and $^3P_0 \rightarrow ^3F_2$ have value more than 50%, which strongly recommend these transition to be considered for laser emission transitions especially the $^3H_6 \rightarrow ^3H_5$ and $^3H_6 \rightarrow ^3H_4$ which they have higher radiative lifetimes value.

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