



THE RADIATIVE TRANSITION PROBABILITIES AND EMISSION CROSS-SECTION FOR Dy³⁺ DOPED WITH TiO₂

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ABSTRACT

Dysprosium ions Dy³⁺ Doped with nano particular Titanium dioxide was synthesis with help of wet chemical process. Several techniques (like UV- Visible spectroscopy and fluorescence spectroscopy) were used to investigate the spectroscopic properties of of Dy³⁺: TiO₂ sample. By excitation light with wavelength source equal to 360nm, peaks at the wavelength around 478nm and 572nm are clearly observed in fluorescence spectrum. The Judd-Ofelt analysis for the spectroscopic properties of prepared sample showed that peak emission cross-section em have a suitable value. Depending on the suitable emission cross-section em one could suggests to use Dy: TiO₂ as optical material for Laser action.

KEYWORDS: Titanium dioxide, spectroscopic properties, Judd-Ofelt analysis.

INTRODUCTION

Recently, the photonic materials such as monoliths, coatings, fibers and films are widely fabrication by performed sol-gel process. Due to flexible route, high homogeneity, low temperature reaction and formation of oxide particles in a liquid phase, the sol gel process become a favorite process rather than other process^[1-7]. Usually the acid and base are performed as catalysts for sped up the slowly reaction process between Titanium alkoxides with water, these lead to sped up the hydrolysis and condensation of sol gel process. The Titanium dioxide as a host for rare earth ions have great focuses in persistent research. In present work, Sol Gel method is employed to prepare of Titanium dioxide doped with Dysprosium ions. The spectroscopic properties of prepared sample Dy: TiO₂ will be investigated with help of Judd-Ofelt theory.

EXPERIMENTAL

Samples Preparation

The sol-gel method is performed to prepared samples (doped and un-doped) by using

- 1- Titanium iso-propoxide (TTIP) from Aldrich 98%.
- 2-Ethanol EtOH 99.9% from GCC
- 3-hydrochloric acid (HCl, 34.5%) from BDH
- 4-Deionized water H₂O

The molar ratio for the H₂O: TTIP: HCl: EtOH are equal to about 1:1:0.1:10, for doping sample Dysprosium (III) nitrate hydrate (Aldrich) was used to achieved doping rate of samples with Dy³⁺ around to 5% wt. The Disposal of alcohol process is achieved by left samples with covers in room temperature. The Shimadzu UV-VIS Spectrometer and Shimadzu SpectroFluometer RF1501 are performed to

recorded absorption spectrum and emission spectrum, (the light source at wavelength 360nm is used as excitation light to emission spectrum).

RESULTS & DISCUSSION

Several peaks are observed in absorption spectrum of doped sample (absorption spectrum presented in figure (1)), these peaks are electronic transitions caused by the energy level of Dy³⁺ ions. The absorption bands in the range of 300–900 nm are equal to about 388nm, 424nm, 451nm and 475nm which corresponded to the energy level transition of ⁶H_{15/2} → ⁴F_{7/2}, ⁶H_{15/2} → ⁴G_{11/2}, ⁶H_{15/2} → ⁴I_{15/2} and ⁶H_{15/2} → ⁴F_{9/2} [8-10].

The absorption spectrum is well resolved in order to find the integrated absorption cross section Γ for each peak or manifold to Dy³⁺ ions. The Γ can be found by Eq.1 [11]:

$$\Gamma = \int_{\text{manifolds}} \alpha(\lambda) d\lambda \quad \text{--- (1)}$$

Where $\alpha(\lambda)$ is the absorption coefficient as a function of wavelength λ . The values Γ is used to measure the line strength S_{meas} by Eq. 2 [11]:

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

Where J and J' are the total angular momentum of the initial ground and final manifold, the value of J found from the ^{2S+1}L_J designation, ρ_o is the Dy³⁺ ion concentration, n is the refractive indices of the host medium, $\bar{\lambda}$ is mean of wavelength to absorption peak which corresponds to the $J \rightarrow J'$ transition. The values of Γ , $\bar{\lambda}$ and S_{meas} are displayed in Table 1.

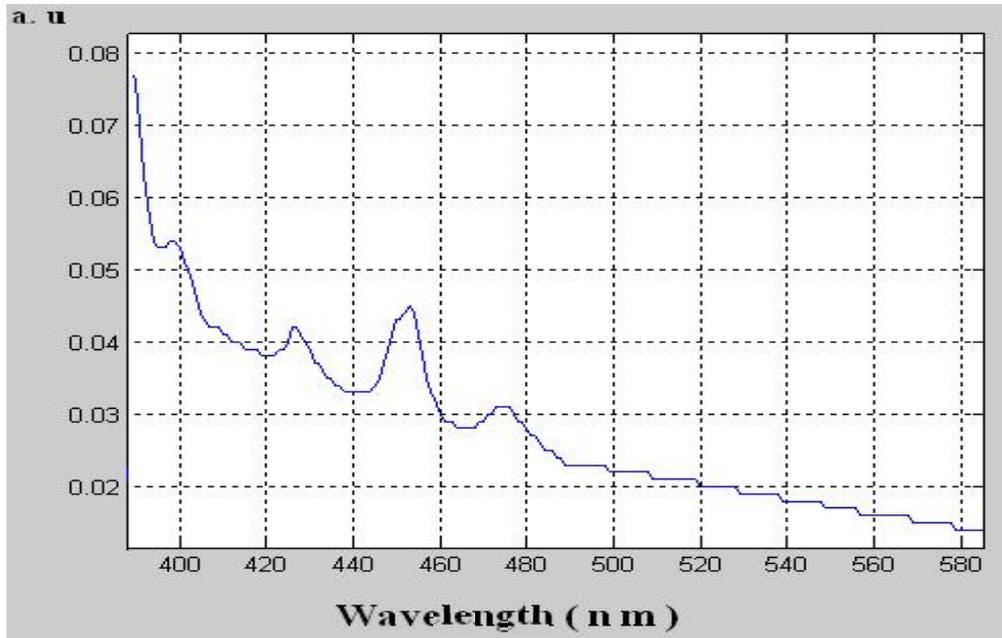


FIGURE 1: Absorption spectrum for Dy³⁺:TiO₂ sample

TABLE 1: Value of S_{meas} , Γ and $\bar{\lambda}$ for each transitions of Dy:TiO₂

Transitions from ⁶ H _{15/2}	Average wavelength $\bar{\lambda}$ (nm)	Absorption cross section Γ (cm ²)	Line Strength $S_m \times 10^{-20}$ (cm ²)
⁴ F _{7/2}	388	0.108	0.36
⁴ G _{11/2}	424	0.108	0.329
⁴ I _{15/2}	451	0.03	0.086
⁴ F _{9/2}	475	0.009	0.024
⁶ F _{3/2}	761	0.026	0.044
⁶ F _{5/2}	810	0.2257	0.36

According to the Judd-Ofelt JO theory, the line strength between initial manifold J and terminal manifold J' could write in the form^[11]:

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

Where Ω_i is the Judd-Ofelt parameters which represents components of [1 x 3] matrix 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 matrix 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 [12-13]. We have used the values of the $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$ which calculated by Carnall *et al.* [14-15], **Table (2)** involve the value of $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$ to Dy³⁺ ions for transition from ground state manifold ⁶H_{15/2} to some exited manifolds.

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

Transitions from ⁶ H _{15/2}	$U^{(2)}$	$U^{(4)}$	$U^{(6)}$
⁴ F _{7/2}	0	0.0695	0.0263
⁴ G _{11/2}	0.0004	0.0145	0.0003
⁴ I _{15/2}	0.0073	0.0003	0.0654
⁴ F _{9/2}	0	0.0047	0.0295
⁶ F _{3/2}	0	0	0.061
⁶ F _{5/2}	0	0	0.3452

The parameters S_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 (3). Then values of the three parameters; S_2 , S_4 and S_6 performed to find transition line strengths for absorption bands by using Eq.3. The values of the measured, S_{meas} , S_{calc} , JO parameters and ROOT MEAN SQUARE (rms deviation) are tabulated in Table (3).

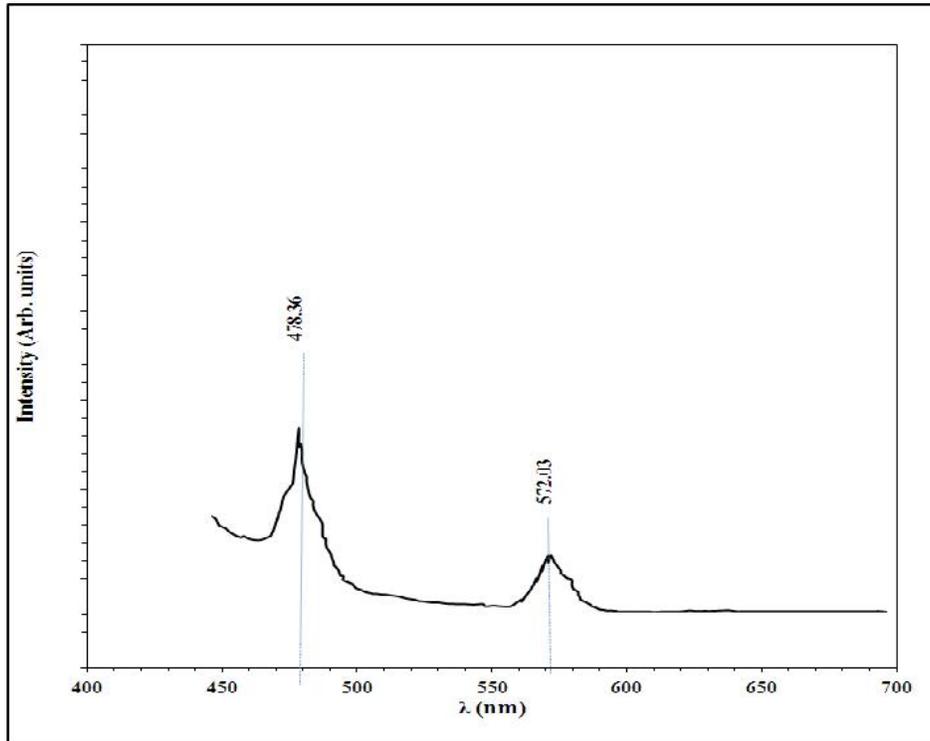


FIGURE 2: Fluorescence spectrum for Dy³⁺:TiO₂ doped sample

Figure (2) show the fluorescence spectrum for Dy:TiO₂ sample, the spectrum is recorded when Dy:TiO₂ sample is excited by light with wavelength 360nm. It could observed two peaks at around 478nm and 572nm, these two peaks correspond to the transition between the levels ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ of Dy³⁺ ions.

The J-O parameters are used with help of Eq.3 to find emission line strengths S_{ed} corresponding to the transitions from the upper multiplet manifolds states ${}^4F_{9/2}$ to their corresponding lower-lying manifold states 6H_J (${}^6H_{15/2}$ and ${}^6H_{13/2}$) of Dy³⁺ ions. The values S_{ed} are used to find the radiative transition probabilities $A(J;J')$ for each excited upper manifolds states ${}^4F_{9/2}$ to the manifold ${}^6H_{15/2}$ and ${}^6H_{13/2}$ of Dy³⁺ ions, the $A(J;J')$ is given in Eq. (4) [11]:

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

Where J is initial manifold, J' is the final manifold.

The radiative lifetime τ_{rad} is given by [11]:

$$\tau_{rad} = 1 / \sum A(J;J') \quad \text{..... (5)}$$

TABLE 3: Value of S_{meas} , S_{calc} and S for each transitions of Dy:TiO₂

Transitions from ${}^6H_{15/2}$	S_{meas}	S_{calc}	S
${}^4F_{7/2}$	0.36	0.409	0.034
${}^4G_{11/2}$	0.329	0.081	0.175
${}^4I_{15/2}$	0.086	0.099	0.009
${}^4F_{9/2}$	0.024	0.055	0.022
${}^6F_{3/2}$	0.044	0.061	0.012
${}^6F_{5/2}$	0.36	0.349	0.008
$S_2=4.376, S_4=5.51$ and $S_6=1.011$			

Stimulated emission cross-section (σ_{em}) give indication about efficiency of a laser transition, and determined by Fuchtbauer–Ladenburg method [16].

$$\sigma_{em} = \frac{\lambda_p^4}{8 \pi c \Delta \lambda_{eff}} \frac{A(J;J')}{(n(\lambda_p))^2} \text{ ----(6)}$$

The results of σ_{em} , σ_{eff} , A_{rad} , τ_{rad} and σ_{em} are listed in Table(4) and Table(5). According to the results of present work one could noted that Dy:TiO₂ have suitable spectroscopic properties in comparable to those results of Dy:LLF [17], Dy:KYF [18], Dy:YAG [19], Dy:CGA [20].

TABLE 4. The σ_{em} , σ_{eff} and A_{rad} for Dy:TiO₂

Transition		σ_{em} (nm)	σ_{eff} (nm)	A_{rad} (sec ⁻¹)
From	To			
⁴ F _{9/2}	⁶ H _{15/2}	478	18	128.347
	⁶ H _{13/2}	572	23	501.047

TABLE 5. The τ_{rad} and σ_{em} for Transsion ⁴F_{9/2} of Dy³⁺ in different host

Transition		$\sigma_{em} * 10^{-20}$ (cm ²)	τ_{rad} (m sec) for ⁴ F _{9/2}
Dy: TiO2 (This work)	⁴ F _{9/2} ⁶ H _{13/2}	0.1292	1.588
	⁴ F _{9/2} ⁶ H _{15/2}	0.0202	
Dy:LLF [17]	⁴ F _{9/2} ⁶ H _{13/2}	-	3.5
Dy:KYF [18]	⁴ F _{9/2} ⁶ H _{13/2}	-	2.700
Dy:YAG [19]	⁴ F _{9/2} ⁶ H _{13/2}	0.3	2.020
Dy:CGA [20]	⁴ F _{9/2} ⁶ H _{13/2}	0.51	0.501

CONCLUSION

The wet chemical synthesis method is strongly successes to syntheses of Dysprosium ions doped Nano_Titania. The spectroscopic properties such as radiative transition probabilities A (J;J'), emission cross-section and radiative lifetime τ_{rad} have suitable values in comparable with other results, the suitable values give strongly indication about using Dy:TiO₂ doped sample as optical material for Laser action.

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