

## Judd–Ofelt Analysis of Spectroscopic Properties of $\text{Er}^{3+}:\text{TiO}_2$ Prepared Via Sol-Gel

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**Abstract :**  $\text{Er}^{3+}$  ions Doped nano particular titanium dioxide was prepared via sol–gel method under varying conditions. The optical properties of prepared doped samples investigate by UV- Visible spectroscopy and fluorescence spectroscopy. A fluorescence peaks recorded at the wavelength around 498 and 533 nm (The excitation source was laser diode 470nm / 1W), The Fluorescence lifetime for these peaks are calculated from recording of fluorescence spectra (with absent of excitation source). A Judd-Ofelt analysis performed to calculate the spectroscopic properties of  $\text{Er}^{3+}$  ions embedded in  $\text{TiO}_2$ .

This study show that the doped titania samples have a suitable peak emission cross-section  $\sigma_{em}$ , which suggests that it could be use Sol-Gel technique to prepare of  $\text{Er}:\text{TiO}_2$  as solid state Laser active medium.

**Keywords:** Sol-Gel; Spectroscopy;  $\text{TiO}_2$ ; laser active medium.

### I. Introduction

Over the past five decades, so many researches are covered a large number of rare-earth active ions doped with a varying host material [1-3], the erbium ion is one of an important ions to synthesis sensitizer of large number of solid-state lasers, especially in Laser eye saving device. Several methods have been developed to synthesis rare earth ions doped with different host medium. Recently, a growing interest has been focused on a wet chemical process to prepare transparent monoliths containing rare earth ions as active ions [4-6].

The sol-gel process has been widely considered a suitable process to fabricate optical materials with various configurations, such as monoliths, coatings, fibbers and films for optical device applications. The formation of oxide particles in a liquid phase, leads to make the structure of sol-gel materials inherently porous. Using of acid and base catalysts makes the reaction process (hydrolysis and condensation) to become faster [7-10]. In the present study, we have performed the Judd–Ofelt theory to analyzes the spectroscopic properties of  $\text{Er}^{3+}$  ion doped with  $\text{TiO}_2$  prepared by sol gel technique.

### II. Experimental

The doped and un-doped samples were synthesized by sol–gel method from Titanium (IV)- iso–propoxide (TTIP) (Aldrich 98%), hydrochloric acid HCl 34.5% from BDH, Ethanol (EtOH 99.9%) from GCC, and Erbium(III) nitrate pentahydrate (Aldrich). Deionized water was used for the hydrolysis of (TTIP) and preparation of pure and doped  $\text{TiO}_2$  sol. The reaction process was conducted at room temperature. The amount of each chemical in this procedure was TEIP:H<sub>2</sub>O:EtOH:HCl= 1:1:10:0.1 in molar ratio. All solution was prepared as follows: 1 mole of Titanium (IV)- iso–propoxide (TTIP) and ethanol (EtOH) were mixed and stirred for 10 min. At the stirring time, 0.1 M catalysts in water were added drop wise to the solution until water to TTIP molar ratio of  $R= 2$  are attained. Erbium(III) nitrate pentahydrate was solved in ethanol and used for mixing with TTIP . All solutions leaved to stir for about 2 hours further at room temperature before use.

Samples with covers left to aged for 24 hours in room temperature in order to complete the hydrolysis process and permit solvent evaporation through the drying process. The doping rate of samples with  $\text{Er}^{3+}$  is equal to 5% wt. Absorption spectra at room temperature were obtained with Shimdzu UV-VIS Spectrophotometer. Suwrit monochromatore device been used to obtain both emission spectrum at room temperature (The excitation source was laser diode 470nm / 1W)

### III. Results

Room temperature UV-VIS-NIR absorption spectra of the  $\text{Er}^{3+}$  doped sample are presented in Figure (1). The absorption spectrum is well resolved so that almost every peaks or stark components corresponding to different manifold of  $\text{Er}^{3+}$  are observed to measure the integrated absorption cross section for each peak or manifold.

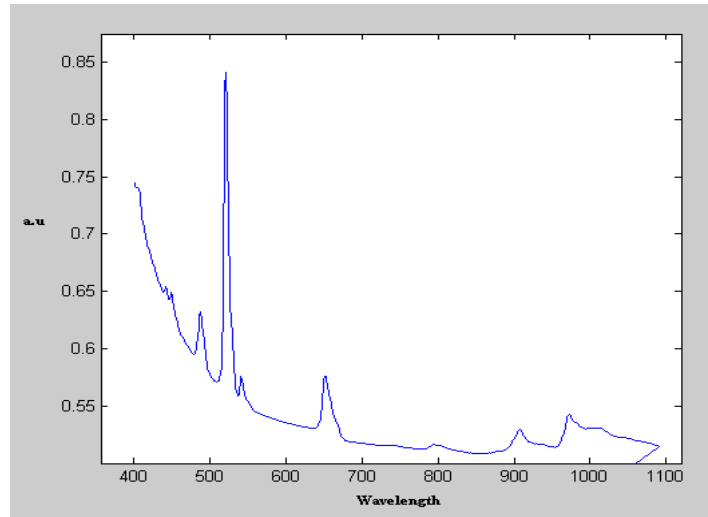


Figure 1: The Absorption spectrum for TiO<sub>2</sub> doped with 5%wt Er<sup>+3</sup>.

The so-called line strength,  $S_{meas}$ , can be found by Eq. 1 [11]:

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

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,  $\rho_o$  is the Er<sup>+3</sup> ion concentration,  $n$  is the refractive indices of the host medium,  $\bar{\lambda}$  is the mean wavelength of the specific absorption peak corresponds to the  $J \rightarrow J'$  transition, while  $e$ ,  $c$  and  $h$  have their usual meaning.  $\Gamma$  is the integrated absorption coefficient and given by [11]:

$$\Gamma = \int_{\text{manifolds}} \alpha(\lambda) d\lambda \quad \text{--- (2)}$$

Where  $\alpha(\lambda)$  is the absorption coefficient as a function of wavelength  $\lambda$ . The  $S_{meas}$ ,  $\bar{\lambda}$  and integrated absorption coefficients are displayed in Table I.

Table (1): Value of  $S_{meas}$ ,  $\Gamma$  and  $\bar{\lambda}$  for each transitions of Er: TiO<sub>2</sub>

Transitions from $^4I_{15/2}$	Average wavelength $\bar{\lambda}$ (nm)	Absorption cross section $\Gamma$ (nm cm <sup>-1</sup> )	Line Strength $S_m \times 10^{-20}$ (cm <sup>-1</sup> )
$^4F_{7/2}$	498	2.346	0.378
$^2H_{11/2}$	523	12.377	1.954
$^4S_{3/2}$	555	.4677	0.071
$^4F_{9/2}$	653	3.8	0.523
$^4I_{9/2}$	802	.6243	0.073

According to the Judd-Ofelt JO theory, the line strength between initial manifold  $J$  and terminal manifold  $J'$  may be written in the form [11]:

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

Where  $\Omega_i$  is the Judd-Ofelt parameters which represents components of [1 x 3] matrix for Judd-Ofelt parameters (include to three parameters;  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ ).  $M_{ij}$  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 [12-14]. We have used the values of the U<sup>(2)</sup>, U<sup>(4)</sup> and U<sup>(6)</sup> which calculated by Carnall *et al.* [15-17], **Table (2)** involve the value of U<sup>(2)</sup>, U<sup>(4)</sup> and U<sup>(6)</sup> to Er<sup>3+</sup> ions for transition from ground state manifold <sup>4</sup>I<sub>15/2</sub> to some exited manifolds.

The parameters Ω<sub>i</sub> determined the transition strength between any two energy levels in these active ions. These parameters could be found using the S<sub>meas</sub> values (that obtained from equation (1)) into equation (3) in addition to the square matrix elements U<sup>(2)</sup>, U<sup>(4)</sup> and U<sup>(6)</sup>. The values of the three parameters; Ω<sub>2</sub>, Ω<sub>4</sub> and Ω<sub>6</sub> can then be used to recalculate the transition line strengths of the absorption bands using Eq.3. The values of the measured absorption line strengths, S<sub>meas</sub>, S<sub>calc</sub> and the three JO parameters are tabulated in Table III. The spectroscopic quality factor, X= Ω<sub>4</sub>/Ω<sub>6</sub>, for the Er<sup>3+</sup> in TiO<sub>2</sub> is found to be 0.942, which fall within the range of 0.22–1.5 for the famous Nd<sup>3+</sup> ions doped in a different hosts [18-19]. The ROOT MEAN SQUARE (rms deviation) applied to measure of the accuracy of the fit of S<sub>meas</sub> to S<sub>calc</sub>, and its values are given in Table (3)

**Table (2) Values of the square matrix elements U<sup>(2)</sup>, U<sup>(4)</sup> and U<sup>(6)</sup>**

Transitions from <sup>4</sup> I <sub>15/2</sub>	U <sup>(2)</sup>	U <sup>(4)</sup>	U <sup>(6)</sup>
<sup>4</sup> F <sub>7/2</sub>	0	0.1469	0.6266
<sup>2</sup> H <sub>11/2</sub>	0.7125	0.4125	0.0925
<sup>4</sup> S <sub>3/2</sub>	0	0	0.2211
<sup>4</sup> F <sub>9/2</sub>	0	0.5354	0.4618
<sup>4</sup> I <sub>9/2</sub>	0	0.1733	0.0099

**Table (3): Value of S<sub>meas</sub>, S<sub>calc</sub> and ΔS for each transitions of Er:TiO<sub>2</sub>**

Transitions from <sup>4</sup> I <sub>15/2</sub>	S <sub>meas</sub>	S <sub>calc</sub>	ΔS
<sup>4</sup> F <sub>7/2</sub>	0.378	0.372	0.003
<sup>2</sup> H <sub>11/2</sub>	1.954	1.954	0
<sup>4</sup> S <sub>3/2</sub>	0.071	0.102	0.021
<sup>4</sup> F <sub>9/2</sub>	0.523	0.515	0.005
<sup>4</sup> I <sub>9/2</sub>	0.073	0.102	0.02

Ω<sub>2</sub>=2.35, Ω<sub>4</sub>=0.563 and Ω<sub>6</sub>=0.462

The phenomenological J-O parameters were subsequently utilized to determine emission line strengths S<sub>ed</sub> corresponding to the transitions from the upper multiplet manifold states <sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>I<sub>11/2</sub>, <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>F<sub>9/2</sub>, <sup>4</sup>S<sub>3/2</sub>, <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>F<sub>7/2</sub> and <sup>2</sup>G<sub>9/2</sub> to their corresponding lower-lying manifold states Er<sup>3+</sup> in TiO<sub>2</sub>, the S<sub>ed</sub> are calculated by using Eq. 3. The values S<sub>ed</sub> are used to find the radiative transition probabilities A(J;J') for each excited upper manifold states to the <sup>4</sup>I<sub>J</sub> and <sup>4</sup>F<sub>J</sub> manifold for Er<sup>3+</sup>, 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 [n(n<sup>2</sup>+2)<sup>2</sup>/9] is the local field correction for Er<sup>3+</sup> in the initial J manifold. J' is the final manifold. n is the refractive index at the wavelength (λ) of the transition. The radiative lifetime τ<sub>rad</sub> is given by [11]:

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

The efficiency of a laser transition is evaluated by considering stimulated emission cross-section (σ<sub>em</sub>(λ)) using Fuchtbauer–Ladenburg method [20]:

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

Where λ<sub>p</sub> is the wavelength of the peak emission, c is the speed of light in vacuums, and n(λ<sub>p</sub>) is the refractive index at each emission peak wavelength. Δλ<sub>eff</sub> is an effective linewidth.

The fluorescence spectrum of Er: TiO<sub>2</sub> spectrum is shown in Fig.2. From fluorescence spectrum it could observed two peaks at around 495nm and 522nm, these two peaks correspond to the transition between the levels <sup>4</sup>F<sub>7/2</sub>–<sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>S<sub>3/2</sub>–<sup>4</sup>I<sub>15/2</sub> of Er<sup>3+</sup> ion.

**Table (4)** involve the spectroscopic properties of Er: TiO<sub>2</sub> sample, the value of peak emission cross-section σ<sub>em</sub> is more suitable which give good indication about using Sol-Gel technique to prepare of Er:TiO<sub>2</sub> as solid state Laser active medium.

**Table 4. Spectroscopic properties of Er:TiO<sub>2</sub>.**

Transition	λ <sub>em</sub> (nm)	Δλ <sub>eff</sub> (nm)	A <sub>rad</sub> (sec <sup>-1</sup> )	σ <sub>em</sub> *10 <sup>-20</sup> (cm <sup>2</sup> )
<sup>4</sup> F <sub>7/2</sub> → <sup>4</sup> I <sub>15/2</sub>	498	19	7407.958	0.603
<sup>2</sup> H <sub>11/2</sub> → <sup>4</sup> S <sub>3/2</sub>	533	18	1667.075	0.188

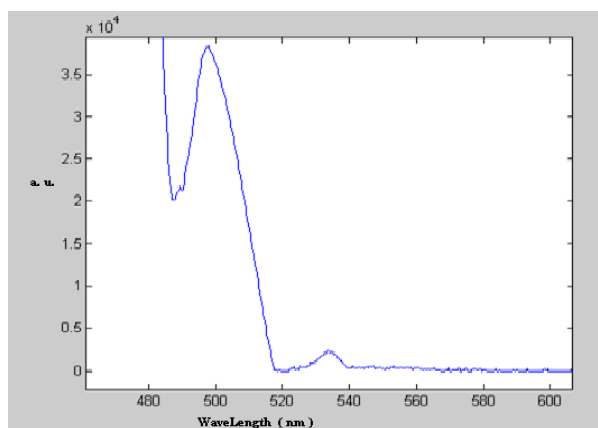


Figure 2: fluorescence spectrum for  $\text{TiO}_2$  doped with  $\text{Er}^{3+}$ .

#### IV. Conclusion

The transparent and unbroken sample of  $\text{Er}^{3+}$  doped NanoTitnia is successfully prepared by wet chemical synthesis method. The optical properties of prepared doped samples are close similar to the known of Er:YAG optical properties. The  $\text{Er}^{3+}$  doped NanoTitnia network have a suitable peak emission cross-section  $\sigma_{em}$ . This suggests that it could be use Sol-Gel technique to prepare of Er: $\text{TiO}_2$  as solid state Laser active medium

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