The Judd Ofelt Spectroscopic analysis for Ho$^{3+}$ doped with SiO$_2$

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Abstract
Holmium ions Ho$^{3+}$ Doped with Silicon dioxide was synthesis with help of wet chemical process. Techniques such as UV-Visible spectroscopy and fluorescence spectroscopy were used to investigate the spectroscopic properties of of Ho$^{3+}$:SiO$_2$ sample. The Judd-Ofelt theory is used to achieve of the spectroscopic properties to prepared sample and calculates the three Judd-Ofeltt of parameters; $\Omega_2$, $\Omega_4$ and $\Omega_6$. From the obtained parameters, the $A(J;J')$, $\tau_{rad}$ and $\beta_{J \rightarrow J'}$ are calculated. Depending on the suitable value of $A(J;J')$, $\tau_{rad}$ and $\beta_{J \rightarrow J'}$ it could suggests to use Ho:SiO$_2$ as Laser active medium.

Keywords: Sol- Gel; Spectroscopy; Si O$_2$; Judd-Ofelt

1- Introduction
Glasses doped with rare earth ions are still a target for many research to produced of optical materials. Sol-gel process is widely used to fabrication of optical materials. Sol-gel have several advantage such as 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]. In present work, Sol Gel method is employed to prepare of SiO$_2$ doped with Holmium ions. The spectroscopic properties of prepared sample Ho:SiO$_2$ will be investigated with help of Judd–Ofelt theory.

2- Experimental
2-1 Samples Preparation
The sol–gel method is performed to prepared samples (doped and un-doped) by using
1- Tetra Ethyl Ortho Silicate (TEOS) from Aldrich 97%.
2- Ethanol EtOH 99.9% from GCC
3- hydrochloric acid (HCl, 34.5%) from BDH
4- Deionized water H$_2$O
The molar ratio for the H₂O:TEOS:HCl:EtOH are equal to about 1:1:0.1:10, for doping sample Holmium (III) nitrate hydrate (Aldrich) was used to achieved doping rate of samples with Ho³⁺ around to 5% wt. One mole of TEOS and 1 mole of EtOH are mixed and stirred at 10 min. Through stirring, 0.1 M of catalyst existed in water is added as drop wise to the solution. The molar ratio of water to TEOS is about 2. Holmium (III) is employed with the solution to prepare doped samples. It is solved in ethanol before mixing it with TEOS. Later, an aging operation is applied to the sample at 24 hour. Finally, the sample is putted in a container manufactured from plastic without covers so that to allow solvent evaporation during the drying process (the packing of sample in the container is completed at room temperature).

3- Result and discussion

Figure (1) illustrates the UV-VIS absorption spectrum of Ho³⁺ doped with SiO₂ network; the detectable peaks are obtained due to the electronic transitions between the energy levels of Ho³⁺ ions. These detectable peaks are identified to the energy level transition of 5I₈ → 3G₅ (418nm), 5I₈ → 5F₁ + 3G₆ (448nm), 5I₈ → 3K₈ (467nm), 5I₈ → 3F₃ (486nm), 5I₈ → 5F₄ + 5S₂ (540nm) and 5I₈ → 5F₅ (645nm) [8-12].

The absorption spectrum is well resolved in order to find the integrated absorption cross section \( \Gamma \) for each peak or manifold to Dy³⁺ ions. The \( \Gamma \) can be found by Eq.1[13]:

\[
\Gamma = \int_{\text{manifolds}} \alpha(\lambda) d\lambda
\]

Where \( \alpha(\lambda) \) is the absorption coefficient as a function of wavelength \( \lambda \). The values \( \Gamma \) is used to measure the line strength \( S_{\text{meas}} \) by Eq. 2 [13]:

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

Where \( J \) and \( J' \) are the total angular momentum of the initial ground and final manifold, the value of \( J \) found from the ²⁷S⁶⁻¹L₉ designation, \( \rho_o \) is the Dy³⁺ ion concentration, \( n \) is the refractive indices of the host medium, \( \overline{\lambda} \) is mean of wavelength to absorption peak which corresponds to the \( J \rightarrow J' \) transition. The values of \( \Gamma, \overline{\lambda} \) and \( S_{\text{meas}} \) are listed in Table 1.
Figure (1): Absorption spectrum for Ho3+:SiO2 doped.

Table (1): Value of $S_{\text{meas}}$, $\Gamma$ and $\bar{\lambda}$ for each transitions of Ho:SiO$_2$

| Transitions from $^5I_8$ | $\bar{\lambda}$ (nm) | $\Gamma$ (nm cm$^{-1}$) | Line Strength $S_{m'10^{-20}}$ (cm$^{-1}$) |
|-------------------------|---------------------|---------------------|---------------------------------|
| $^5I_8 \rightarrow ^3G_5$ | 418 | 1.053 | 0.977 |
| $^5I_8 \rightarrow ^5F_{1+}^5G_6$ | 448 | 2.292 | 1.993 |
| $^5I_8 \rightarrow ^5K_8$ | 467 | 0.146 | 0.121 |
| $^5I_8 \rightarrow ^3F_3$ | 472 | 0.245 | 0.2 |
| $^5I_8 \rightarrow ^5F_{4+}^5S_2$ | 486 | 0.642 | 0.512 |
| $^5I_8 \rightarrow ^3F_5$ | 540 | 2.922 | 2.098 |
| $^5I_8 \rightarrow ^3G_5$ | 645 | 2.897 | 1.741 |
According to the Judd-Oftel JO theory, the line strength between initial manifold \( J \) and terminal manifold \( J' \) could write in the form [13]:

\[
S^J_J' = \sum_{i=1}^{3} M_{ij} \Omega_i \tag{3}
\]

Where \( \Omega_i \) is the Judd-Oftel parameters which represents components of \([1 \times 3]\) matrix for Judd-Oftel 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 \( N \times 3 \) 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 [14-15].

We have used the values of the \( U^{(2)} \), \( U^{(4)} \) and \( U^{(6)} \) which calculated by Carnall et al. [15-17]. Table (2) involve the value of \( U^{(2)} \), \( U^{(4)} \) and \( U^{(6)} \) to Ho\(^{3+}\) ions for transition from ground state manifold \( ^6H_{15/2} \) to some exited manifolds.

Table (2): Square matrix elements \( U^{(2)} \), \( U^{(4)} \) and \( U^{(6)} \) for Ho\(^{3+}\) ions from ground states \(^5I_8\) to upper manifold [16-17].

| Transitions from \(^5I_8\) | \( U^{(2)} \) | \( U^{(4)} \) | \( U^{(6)} \) |
|---------------------------|--------------|--------------|--------------|
| 3K6 + 3F4                 | 0.0026       | 0.1263       | 0.0073       |
| 3L9 + 5G3                 | 0.0185       | 0.0052       | 0.1169       |
| 3D2 + 3H6 1 5G5           | 0.2155       | 0.1969       | 0.1679       |
| 3K7 + 5G4                 | 0.0058       | 0.0361       | 0.0697       |
| 3G5                       | 0.0000       | 0.5338       | 0.0002       |
| 5F1 + 5G6                 | 1.5201       | 0.8410       | 0.1411       |
| 3K8                       | 0.0208       | 0.0334       | 0.1535       |
| 3F2                       | 0.0000       | 0.0000       | 0.2041       |
| 3F3                       | 0.0000       | 0.0000       | 0.3464       |
The J-O parameters values $\Omega_2$, $\Omega_4$ and $\Omega_6$ are calculated and found equal to 0.112, 1.884 and 1.661 respectfully. The J-O parameters are used with help of Eq.3 to find to their corresponding lower-lying manifold states of Ho$^{3+}$ ions. The values $S_{ed}$ are used to find the radiative transition probabilities $A(J;J')$ for each excited upper manifolds states of Ho$^{3+}$ ions, the $A(J;J')$ is given in Eq. (4) [13]:

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

where $J$ is initial manifold, $J'$ is the final manifold. The radiative lifetime $\tau_{rad}$ is given by [13]:

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

The values for the $S_{ed}, A_{rad}$ and $\beta_{J-J'}$ corresponding to the transition from higher-lying manifold states to lower state of HO$^3$ are listed in table (3) , (4), (5) and (6).

### Table (3) The $A(J;J')$ and $\beta_{J-J'}$ for upper state 5F4 to lower state of HO$^{3+}$ ions.

| from | To    | Sed  | $A_{rad}$ (sec$^{-1}$) | $\beta_{J-J'}$ | $\tau_{rad}$ |
|------|-------|------|------------------------|----------------|-------------|
| 5F4  | 5S2   | 0.0867 | 0                      | 0              | 0.2998 |
|      | 5F5   | 1.6885 | 13.602                 | 0.00182        |             |
|      | 5I4   | 1.0027 | 38.406                 | 0.00516        |             |
|      | 5I5   | 2.2379 | 247.019                | 0.0332         |             |
Table (4) The $A(J;J')$ and $\beta_{J \rightarrow J'}$ for upper state $5S_2$ to lower state of HO$^{3+}$ ions.

| from  | To    | Sed  | $A_{\text{rad}}$ (sec$^{-1}$) | $\beta_{J \rightarrow J'}$ | $\tau_{\text{rad}}$ |
|-------|-------|------|-------------------------------|---------------------------|---------------------|
| $5S_2$ | $5F_5$ | 0.053 | 0.809 | 0.00018 | 0.4824 |
|       | $5I_4$ | 1.0832 | 69.787 | 0.01619 |
|       | $5I_5$ | 0.388 | 72.076 | 0.01672 |
|       | $5I_6$ | 0.6158 | 291.141 | 0.06756 |
|       | $5I_7$ | 1.4355 | 1574.432 | 0.3654 |
|       | $5I_8$ | 0.7955 | 2300.515 | 0.53391 |

Table (5) The $A(J;J')$ and $\beta_{J \rightarrow J'}$ for upper state $5F_5$ to lower state of HO$^{3+}$ ions.

| from | To    | Sed  | $A_{\text{rad}}$ (sec$^{-1}$) | $\beta_{J \rightarrow J'}$ | $\tau_{\text{rad}}$ |
|------|-------|------|-------------------------------|---------------------------|---------------------|
| $5F_5$ | $5I_4$ | 0.0177 | 0.037 | 0.00002 | 0.5634 |
|       | $5I_5$ | 0.3258 | 5.772 | 0.00325 |
|       | $5I_6$ | 1.0596 | 76.296 | 0.04299 |
|       | $5I_7$ | 1.3444 | 318.964 | 0.17973 |
|       | $5I_8$ | 1.7505 | 1373.603 | 0.774 |
Table (6) The $A(J;J')$ and $\beta_J - J'$ for upper state $5I4, 5I5, 5I6$ and $5I7$ to lower state of $Ho^{3+}$ ions.

| from | To  | Sed     | $A_{\text{rad}}$ (sec$^{-1}$) | $\beta_J - J'$ | $\tau_{\text{rad}}$ |
|------|-----|---------|-------------------------------|----------------|-----------------|
| $5I4$ | $5I5$ | 1.7484  | 5.03                          | 0.05893        | 11.7144         |
|      | $5I6$ | 1.1564  | 33.846                        | 0.39648        |                 |
|      | $5I7$ | 0.2667  | 38.652                        | 0.45279        |                 |
|      | $5I8$ | 0.0127  | 7.835                         | 0.09178        |                 |
| $5I5$ | $5I6$ | 1.278   | 4.786                         | 0.0383         | 8.0033          |
|      | $5I7$ | 1.5195  | 69.689                        | 0.55774        |                 |
|      | $5I8$ | 0.1741  | 50.473                        | 0.40395        |                 |
| $5I6$ | $5I7$ | 1.8018  | 12.71                         | 0.08647        | 6.8038          |
|      | $5I8$ | 1.7484  | 5.03                          | 0.05893        |                 |
| $5I7$ | $5I8$ | 1.1564  | 33.846                        | 0.39648        | 17.513          |

According to the results of present work (Table (3)-(6)), the $A(J;J')$ values for energy transitions $5F4 \rightarrow 5I8$, $5S2 \rightarrow 5I8$, $5F5 \rightarrow 5I8$, $5I4 \rightarrow 5I7$, $5I6 \rightarrow 5I7$, $5I7 \rightarrow 5I8$ 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.

4- Conclusion

The sol-gel glass of SiO2 doped with Ho3+ is successfully prepared using wet chemical synthesis technique. The radiative transition probabilities $A(J;J')$ for energy transitions $5F4 \rightarrow 5I8$, $5S2 \rightarrow 5I8$, $5F5 \rightarrow 5I8$, $5I4 \rightarrow 5I7$, $5I6 \rightarrow 5I7$, $5I7 \rightarrow 5I8$ are larger than values to others transitions, which indication to the higher intensity of luminescence to these transitions than others. The suitable spectroscopic properties of Ho3+:SiO2 doped give an indication to use Sol-Gel method to prepare Ho3+:SiO2 doped as optical active materials.

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