Emission Cross Sections of Eu3+ doped TiO2 Prepared via Sol-Gel

Mohammed H Alwan 1, Hanna M Yaseen 1, Khawla J Tahir 2,* and Basma A Jabar 2

1Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq
2Department of Physics, College of Science, University of Kerbala, Kerbala-56001, Iraq
* Khawla.taher@uokerbala.edu.iq

Abstract. Titanium dioxide nanoparticle doped with Europium ions Eu3+ was synthesis by performing of sol gel technique, the UV-Visible spectroscopy and fluorescence spectroscopy were used to investigate the spectroscopic properties of prepared doped sample. Two peaks at wavelength around 590nm and 612nm are recorded in fluorescence spectrum (wavelength of excitation light source equal to 390nm). The UV-Visible and fluorescence spectra are analyzed to determined peak emission cross-section $\sigma_{em}$. Depending on the suitable value of $\sigma_{em}$, it could strongly suggest to use Eu:TiO2 as optical material for laser action.

1. Introduction

Recently, many research has been focused on using Titanium dioxide as a host for rare earth ions. The Titanium dioxide have a great interest due to a wide band gap, high chemical stability and high refractive index [1-2]. Several methods could be used to prepare TiO2, but for Lab scale, the sol gel is strongly recommended with high homogeneity. Many advantages could be achieved with sol-gel process such as flexible route to synthesis of oxide particles, low cost and easy of fabrication metal oxide with high doping rate. Sol gel involves two major step hydrolysis and condensation. The two-step could be sped up by using acid or base as catalysts. The catalysts sped up the slowly reaction process between water and Titanium alkoxides. Drying process is the final step done in sol gel technique [3,4].

Europium Eu3+ is one of rare earth elements, which still have great interest to study of its spectroscopic properties in various matrices [5], figure (1) show a diagram of partial energy levels of Eu3+:borate glass. The Absorption spectrum analysis is a useful method to determined some of important parameter such as refractive index $n(\lambda)$, absorption coefficients $a(\lambda)$ and absorption cross-sections $\sigma(\lambda)$. In the absence of radiation of frequency $\nu$, the probability of radiative transition from higher state $J$ to the lower state $J'$ is given by:

$$A(J;J') = 1/\tau_{rad}$$ (1)

where $\tau_{rad}$ is radiative lifetime (which refers to light spontaneous emission), $\tau_{rad}$ could be found with help of empirical formula given by Bowen and Wokes [6]:
\[ \frac{1}{\tau_{\text{rad}}} = 2900 \, n^2 \, \dot{\nu}^2 \int \varepsilon(\dot{\nu}) \, d\dot{\nu} \]  

(2)

where \( \dot{\nu} \) (in \( \mu m^{-1} \)) is the wave number at the peak of absorption band, \( \int \varepsilon(\dot{\nu}) \, d\dot{\nu} \) is the area under the peak of absorption band, \( n \) refractive index and \( \varepsilon(\dot{\nu}) \) is molecular extinction coefficient which founds by [6]:

\[ \varepsilon(\dot{\nu}) = \frac{\alpha(\dot{\nu})}{[M]} \]  

(3)

where \( \alpha(\dot{\nu}) \) is absorption coefficients and \([M]\) is the molar concentration (mol liter\(^{-1}\)).

In present work, the Sol Gel method is employed to prepare Titanium dioxide doped with Europium ions, then the spectroscopic properties of Eu:TiO\(_2\) prepared sample will be investigated

![Energy level diagram](image)

**Figure (1).** Energy level diagram for excitation and emission transitions of Eu\(^{3+}\) in borate glass[5].

2. Experimental part

The hydrochloric acid (HCl, 34.5%) from BDH ,Titanium (IV)- iso–propoxide (TTIP), Deionized water H\(_2\)O and Ethanol EtOH 99.9% from GCC are used to prepared samples (doped and un-doped) by using sol–gel method. The molar ratio for the HCl:TTIP:H\(_2\)O:EtOH  are equal to about 0.1:1:1:10. The doping with Europium Eu\(^{3+}\) ions is achieved by using Europium (III) nitrate hydrate from Aldrich Company (Eu\(^{3+}\) doping rate around to 0.7%, 1.1%, 1.9% and 2.3% molar ratio). Aging process for 24 hour is done after finishing of hydrolysis and condensation process, and then sample drying is done by left samples with covers in room temperature.

The surface morphology and nanoparticles average dimension of the samples were characterized by using Atomic Force Microscopy AFM (model AA3000 scanning probe microscope). While Shimadzu Spectrofluorometer type RF1501 and Shimadzu UV-VIS Spectrometer are used to record the emission and absorption spectra respectfully, (for emission spectrum, light source at wavelength 390m is used as excitation light).
3. Result and discussion

The AFM measurement for TiO$_2$ samples (doped with different rate of Europium ions Eu$^{3+}$) are shown in the figures (2), the average grain size and the surface roughness values for each doped sample were listed in Table (1). The results of table (1) shows that TiO$_2$ doped samples are nanoparticle with average grain size equal to 72.74, 65.96, 54.98, 64.35 and 72.89 for the TiO$_2$ samples with 0.7%, 1.1%, 1.9% and 2.3% doped molar ratio of Eu$^{3+}$. The sample surface roughness decreases with increasing of Eu$^{3+}$ concentration of doped rate. While the sample average grain size is reduced at the low Eu$^{3+}$ doping concentration till to the 1.1% doping rate then average grain increased with the higher Eu$^{3+}$ doping concentration.

Table 1. Average Grain Size and the Surface Roughness of Eu$^{3+}$TiO$_2$ Samples at Different Doping Rates.

| Eu$^{3+}$ Doping rate % wt | Average grain size (nm) | Roughness(nm) |
|---------------------------|-------------------------|---------------|
| 0% Eu$^{3+}$              | 72.74                   | 1.28          |
| 0.7% Eu$^{3+}$            | 65.96                   | 0.75          |
| 1.1% Eu$^{3+}$            | 54.98                   | 0.264         |
| 1.9% Eu$^{3+}$            | 64.35                   | 0.413         |
| 2.3% Eu$^{3+}$            | 72.89                   | 0.409         |

Figure 2. AFM for TiO$_2$ Nanoparticle Doped with different molar ratio of Eu$^{3+}$ ions in concretion: (1) =0.0%, (2)= 0.7%, (3) =1.1%, (4) =1.9% and (5) =2.3%
Figure (3) present absorption spectra for Eu$^{3+}$:TiO$_2$ samples at different doping rates, two peaks caused by electronic transitions of energy level of Eu$^{3+}$ ions are recorded in absorption spectrum of doped sample, the wavelengths to these two peaks are equal to about 394nm and 464nm. The two peaks correspond to the energy level transition $^{7}F_0 \rightarrow ^{5}L_6$ (393 nm) and $^{7}F0 \rightarrow ^{5}D_2$ (465nm) [7,8].

![Absorption spectra for Eu:TiO$_2$ sample.](image)

**Figure 3.** Absorption spectra for Eu:TiO$_2$ sample.

Figure (4) present fluorescence spectra recorded for Eu$^{3+}$:TiO$_2$, two peaks caused by electronic transitions of energy level of Eu$^{3+}$ ions are observed recorded in range 400 nm – 700nm. First peak is for electronic transitions between the levels $^5D_0$ and level $^7F_1$ (peak wavelength around 590nm), while the second peak is for electronic transitions between the levels $^5D_0$ and level $^7F_2$ (peak wavelength around 612nm [8-10].

Based on Fuchtbauer–Ladenburg equation, the peak emission cross-section ($\sigma_{em}$) between any two transitions is given by [11,12]:

$$\sigma_{em} = \frac{\lambda_p^4}{8 \pi c \bar{n}^2 \Delta\lambda_{eff} \tau_{rad}} \quad (4)$$

where $\Delta\lambda_{eff}$ is the effective fluorescence line width line width at the FWHM, $\lambda_p$ is the wavelength of the fluorescence peak and $\bar{n}$ is founded by [12]:

4
\[ \hat{n} = \left[ \left( n^2(\lambda) + 2 \right)^2 / 9 n(\lambda) \right] \]  

(5)

where \( n(\lambda) \) is Refractive index. For the asymmetry of fluorescence emission peaks, the \( \Delta \lambda_{\text{eff}} \) can be determined by [13]:

\[ \Delta \lambda_{\text{eff}} = \int \frac{I(\lambda)}{I_{\text{max}}} \]  

(6)

where \( I_{\text{max}} \) is the maximum intensity at the fluorescence emission peaks.

The spectroscopic parameter such as radiative lifetime \( \tau_{\text{rad}} \) and emission cross-section \( \sigma_{\text{em}} \) are calculated with help of eq.(2) and eq.(4), the obtained results are listed in Table (2). In comparable with other results, it’s could noted that Eu:TiO\(_2\) sample have good suitable spectroscopic properties.

**Figure 4.** Fluorescence spectrum for Eu\(^{3+}\):TiO\(_2\) doped.
Table 2. Spectroscopic properties parameters for Eu$^{3+}$ doped with different Host Matrixes.

| Host Matrix | $\lambda_p$ (nm) | $\sigma_{em}$ x $10^{-22}$ cm$^2$ | $\tau_{rad}$ (mS) |
|-------------|-----------------|---------------------------------|-------------------|
| Eu:TiO$_2$ with 0.7% molar ratio [this work] | 590 | 2.311 | 1.13 |
| Eu:TiO$_2$ with 1.1% molar ratio [this work] | 591 | 2.232 | 1.17 |
| Eu:TiO$_2$ with 1.9% molar ratio [this work] | 590 | 1.892 | 1.38 |
| Eu:TiO$_2$ with 2.3% molar ratio [this work] | 591 | 1.865 | 1.4 |
| Eu$^{3+}$:PbF$_2$–SiO$_2$ glass [14] [this work] | 590 | --- | 2.4 |
| Eu$^{3+}$:PbF$_2$–SiO$_2$ glass [14] [this work] | 611 | --- | 2.4 |
| Eu$^{3+}$:PbF$_2$–SiO$_2$ glass [15] | 593 | 3.28 | 2.9 |
| Eu$^{3+}$:PbF$_2$–SiO$_2$ glass [15] | 614 | 5.19 | 2.9 |
| Eu$^{3+}$:tellurite glass [16-18] [this work] | 592 | 2.63 | 1.72 |
| Eu$^{3+}$:tellurite glass [16-18] [this work] | 612 | 16.7 | 1.72 |

4. Conclusion

Sol Gel technique is successfully used to syntheses of Europium ions doped TiO$_2$ nanoparticle. The spectroscopic parameters (such as radiative lifetime $\tau_{rad}$ and emission cross-section $\sigma_{em}$) for Eu:TiO$_2$ doped sample have suitable values in comparable with other research results. Depending on the spectroscopic parameters to doped sample, it could be concluded that Eu:TiO$_2$ has the capability to be an optical material and it could use it for laser action.

References

[1] M. Pal, J. G. Serrano, P. Santiago, et al., “Size-Cont-rolled Synthesis of Spherical TiO$_2$ Nanoparticles: Morphology, Crystallization, and Phase Transition” 2007 The Journal of Physical Chemistry C, Vol. 111, No. 1, (2007), pp. 96-102.

[2] Wu X Wei, Wu D Jian and Liu X Jun , “Silver-Doping In-duced Lattice Istortion in TiO$_2$ Nanoparticles” (2009). J. Chinese Physics Letters, Vol. 26, No. 7, pp. 4

[3] Brinker C Jeffrey and George W Scherer “The Physics and Chemistry of Sol-Gel processing”, SOL-GEL SCIENCE Academic press, (1990).

[4] J Livage, M Henry and C Sanchez, “Sol-Gel Chemistry of Transition Metal Oxides”, (1988) Progress in Solid State Chemistry, Vol. 18, No. 4, pp. 259-342.
[5] J Rajagukguk, J Kaewkhao, M Djamal and Y Reungtaweep, “Structural and optical characteristics of Eu³⁺ ions in sodium-lead-zinc-lithium-borate glass system”, (2016), Journal of Molecular Structure 1121, pp. 180-187

[6] C A Parker, "Photoluminescence of Solutions", (1986), Elsevier, Amsterdam, pp. 25-27.

[7] A Herrmann, S Fibikar and D Ehrt, "Time-resolved fluorescence measurements on Eu³⁺ and Eu²⁺ doped glasses", (2009), Journal of Non-Crystalline Solids 355 pp 2093–2101

[8] E Tomaszewicz, M Guzikb, J Cybin skab and J Legendziewicz, “Spectroscopic Investigation of the Europium³⁺ Ion in a New ZnY4W3O16 Matrix”, (2009), Journal Helvetica Chimica Acta J., Vol. 92, Issue 11, pp. 2274-2290.

[9] P Kumar and Y Dwivedi, “Observation of two-way multichannel interaction among Dy and Eu ions in Bi2SiO5 nanophosphor”, (2018), Journal Dyes and Pigments, Vol. 148, pp. 1-8.

[10] K Binnemans, “Interpretation of europium(III) spectra”, (2015), Journal Coordination Chemistry Reviews 295, pp 1–45.

[11] M Alwan Hamzah, ” Spectroscopic properties of Nd³⁺: TiO₂ synthesis by Sol Gel”, (2015), Journal International Journal of Application or Innovation in Engineering & Management (IJAIEM ) 5 pp. 465-469.

[12] M Mahdi Salih“Spectroscopic Study of Dy³⁺:SiO₂ Prepared via Sol-Gel”, (2017), Diyala Journal for Pure Sciences, Vol. 13, Issue 3 pp. 15-23.

[13] D K Sardar, W M Bradley and J J Perez’Judd–Ofelt analysis of the Er³⁺ . 4f11. absorption intensities in Er³⁺ doped garnets”, (2003), Journal of Applied Physics 93, 2041.

[14] B Szpikowska Sroka et.al, “Long-lived emission from Eu³⁺:PbF₂ nanocrystals distributed into sol–gel silica glass”, (2013) Journal of Sol-Gel Science and Technology, Vol. 68, Issue 2, pp. 278–283.

[15] S Balaji, P Abdul Azeem and R R Reddy “Absorption and emission properties of Eu³⁺ ions in Sodium fluoroborate glasses”, (2007), Physica B: Condensed Mater, Vol 394, Issue 1, pp. 62–68

[16] R K Mohammad, R A Madlol, N M Umran and F I Sharrad, Structure and electronic properties of substitutionally doped cycloheptane molecule using DFT, Results Phys. 6 (2016 ) 1036.

[17] Khodair, Z.T., Al-Jubbori, M.A., Hassan, A.M. et al. Journal of Elec Materi (2019) 48: 669.

[18] M Haouari, F Benslimen, A Maaoui and N Gaumer, “Structural and spectroscopic properties of Eu³⁺ doped tellurite glass containing silver nanoparticles”, (2018), Journal of Alloys and Compounds, Vol 743, pp. 586-596.