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Synthesis of Nanosilica Glass Activated by Erbium Ions, Spectroscopic studies

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Abstract

Erbium, as optical probe, doped silicate sol-gel glass with different Er concentrations was formed by wet chemical synthesis method using ethanol, water and tetraethaylorthosilicate [$Si(OC_2H_5)_4$] precursor. Erbium ions were incorporated into silica sol-gel matrix via dissolution of Erbium chloride solution into the initial $Si(OC_2H_5)_4$ precursor sol. Aluminum (Al) as a co-dopant was added to the final precursor in the form of Aluminum chloride ($AlCl_3$) solution. The prepared samples were analyzed using atomic absorption analysis, X-ray diffraction and spectroscopic tests. The experimental results concerned with the transmission spectra suggest that the final samples have a good transparency and homogeneity. Also, the X-ray diffraction test showed that they have amorphous structure. The absorption and fluorescence spectra, as a function of Er concentration, were recorded at room temperature. Fluorescence emission of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition at ~ 1.536 µm was observed. In addition, the high values of peak emission cross-section, which were calculated as a function of Er concentration, suggest that the Er in the sol-gel may be favorable as optical material

Keywords
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silica sol-gel

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توليف زجاج النانو سليكا المطعم بايونات الاربيوم، دراسات طيفية

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قسم الفيزياء –كلية العلوم – جامعة بغداد – الجادرية – بغداد – العراق

الخلاصة:

الاربيوم كمجس بصري تم تطعيمه بزجاج السيليكات Sol-gel وبتراكيز مختلفة بأستخدام الطريقة الكيميائية الرطبة بأستعمال كحول الايثانول, الماء و محلول التراثيل اورثو سيليكات [$Si(OC_2H_5)_4$]. ايونات الاربيوم تداخل في مصفوفة السيليكا بواسطة اذابة محلول كلوريد الاربيوم في محلول [$Si(OC_2H_5)_4$] الاولي. الالمنيوم كشائب مشارك قد تم اضافته الى المحلول النهائي بصيغة محلول كلوريد الالمنيوم.

حللت النماذج المحضرة باستخدام تحليل الامتصاص الذري، حيود الاشعة السينية بالاضافة الى الفحوصات الطيفية. اظهرت النتائج التجريبية المتعلقة باطياف النفاذية امتلاك النماذج المحضرة لنفاذية وتجانس جيدين، كذلك اظهرت اطياف حيود الاشعة السينية التركيب العشوائي لهذة النماذج.

سجلت اطياف الامتصاص والفلورة للنماذج كدالة لتركيز ايون الاربيوم عند درجة حرارة الغرفة وقد لوحظ انبعاث الفلورة الخاص بالانتقال $^4I_{13/2}$ $\rightarrow$ $^4I_{15/2}$ ~~عند~~ تقريبا 1.536µm. اضافة الى ذلك فان القيم العالية لذروة المقطع العرضي للانبعاث والتي حسبت كدالة لتركيز ايون الاربيوم بينت أن الاربيوم المطعم بزجاج الـ Sol-gel قد يكون مفضلا كمادة بصرية ليزرية.

Introduction

Over almost 40 years there has been extensive research covering a large number of rare-earth active ions in every known glass system. Neodymium Nd^{3+} ion, however, remain the primary rare earth ion of interest for most commercial application of glass lasers[1]. Only recently, a growing interest has been focused on other rare earth ions such as erbium Er^{3+}. The longer-wavelength luminescence from Er^{3+} ions, which occurs in the near-infrared (NIR) region, show intense transitions that lie in the 1.3-1.6 µm telecommunication window. This makes Er^{3+} ions useful for applications like integrated optical devices such as optical amplifiers and frequency upconvertors[2]. However, all these ions must be doped in a matrix to make them accessible for all these kinds of applications.

The sol-gel technique is a flexible low-temperature preparation method that allows incorporation of rare earths (REs) during the liquid phase of the process [3].

For many applications it is essential that rare earth ions doped nanosilica sol-gel glasses have high fluorescence yields and therefore several mechanisms of fluorescence quenching in these materials must be overcome [4]. Aluminum (Al^{3+}) co-doping improves fluorescence yield remarkably, and the generally accepted explanation is that Al^{3+} disperses RE dopants in the matrix, reducing ion-ion interactions [4, 5, 6].

Along-term goal of this research is the synthesis of materials with properties comparable to a melt glass: optical clarity, homogeneity and high fluorescence yield.

Materials and Methods

The following chemical materials were used in this work; Tetraethoxysilane (TEOS) (Purity> 98%) supplied by Schuchardt, Hohenbrunn, Germany; Ethanol was of Analytical grade. (Purity 99.9%) supplied by Gainland Chemical Company, U.K.; N,N-dimethylformamide, hydrochloric acid(0.15 M HCl 37٪) supplied by Aldrich company, Deionized water, Aluminum chloride(AlCl3) supplied by Fluka Garantie; for analytical grade and erbium oxide (Er2O3) of spectroscopy standard and supplied by Johnson Matthy Chemicals limited (JMC), England. The preparation steps of erbium chloride (ErCl3.6H2O) are described in figure (1).

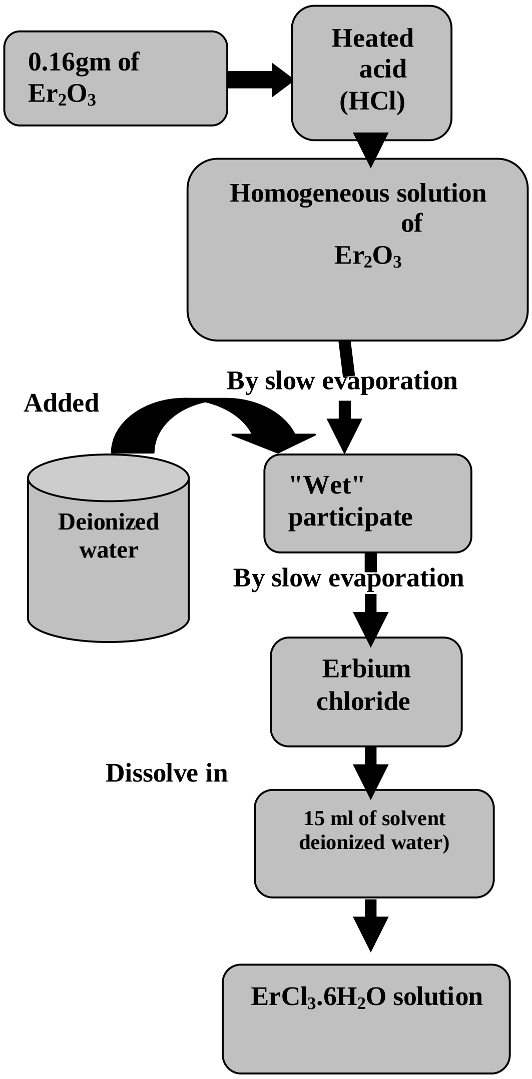

Figure 1: Preparation steps of erbium chloride solutions

The sol-gel glass rod samples were prepared under selected reaction conditions: pH 1 (pH value of solution), R =2 (H_2O/ TEOS) molar ratio, T =60 ºC (reaction temperature) 7; by following the sequence on the scheme given in figure (2-4). TEOS and absolute EthOH were mixed together in a 1:2 volume ratio. For Er^{3+} doping, a 1ml of $ErCl_3.6H_2O$ solution, with different Er^{3+} concentrations, was added to the mixture of TEOS and absolute EthOH before the hydrolysis and denoted as sol(I), then left for (15 min.) under magnetic stirrer to be homogenized. For the Al^{3+} co-doping, aluminum chloride was first dissolved in absolute EthOH, then a 1ml of this solution was added to the mixture of 1ml deionized water and 1ml absolute EthOH. This mixture was denoted as sol(Π) and slowly added to the sol(I) for the hydrolysis. The final solution was left for (1 hour) under magnetic stirrer, after this step, 0.5 ml of N,N-dimethylformamide was added. The resultant solution was poured in a closed glass tube and kept under 60 ºC reaction temperature. After the aging and drying processes that described in (section 2.4.1), the xerogel bulk rod samples was sintered at 500 ºC by increasing the temperature from 110 ºC to 500 ºC within (30 min.), and kept them at 500 ºC for (1 hour). The Al: Er^{3+} concentration ratio has been taken 10: 1. The described procedure allowed us to produce glass rod samples with good transparency of diameter of 0.38-0.4 cm, measured by micrometer, length of 1.4-1.5 cm and weight of 0.1993-0.3438 gm. Figure(2) illustrates some of the final prepared samples.

Figure 2: Some of the prepared sol-gel glass rod samples doped with Er^{3+} and Al co-doping.

Results and discussion

The room temperature absorption spectra of the prepared erbium chloride solutions at different concentrations are presented in figure (3). These spectra give principle evidence of the transformation process from erbium oxides to erbium chloride solutions. The intensity of absorption bands for Er^{3+} ions has increased with increasing of their molar concentrations, and this is due to the increasing of ions contribution in the absorption process so much as the increasing of their concentrations, but no observed shifting has been noticed.

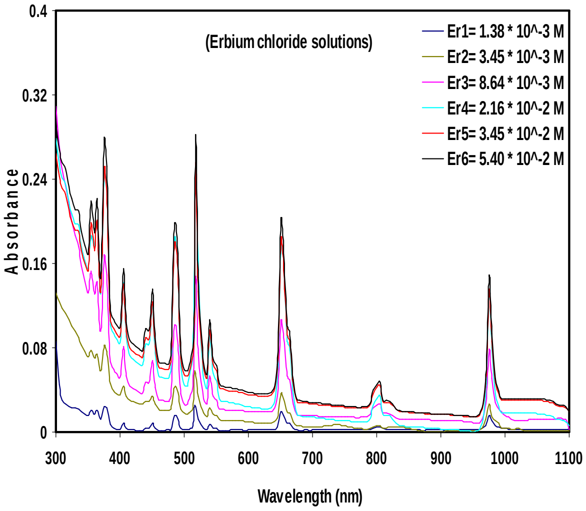

Figure 3: The absorption spectra of Er^{3+} in erbium chloride solutions at different

Table 1: Results of the atomic absorption analysis for (Er^{3+}: sol-gel glass: with Al co-doping) system. All samples derived from the molar concentration ratio Al: Er of 10: 1.

Sample no.	**Practical Concentrations**		**Er ion density × 10^{20} cm^{-3}**			
	Er ion density × 10^{20} cm^{-3}	Al^{3+} ion density ×10^{21} cm^{-3}	%Er ion	%Al^{3+}	%Er ion	%Al^{3+}
SER1	0.0498	0.0499	0.110	0.179	0.115	0.186
SER2	0.1254	0.1260	0.248	0.402	0.274	0.438
SER3	0.3151	0.3148	0.613	0.989	0.622	1.003
SER4	0.7604	0.7607	1.264	2.040	1.351	2.180
SER5	1.1307	1.1410	1.657	2.682	1.839	2.966
SER6	1.7582	1.7583	2.547	4.110	2.632	4.246
SER1	0.0498	0.0499	0.110	0.179	0.115	0.186

Figure (4) illustrate the absorption spectra of erbium chloride solutions and doped samples in sol and bulk phases at maximum concentration of RE3+ ions obtained in the present study.

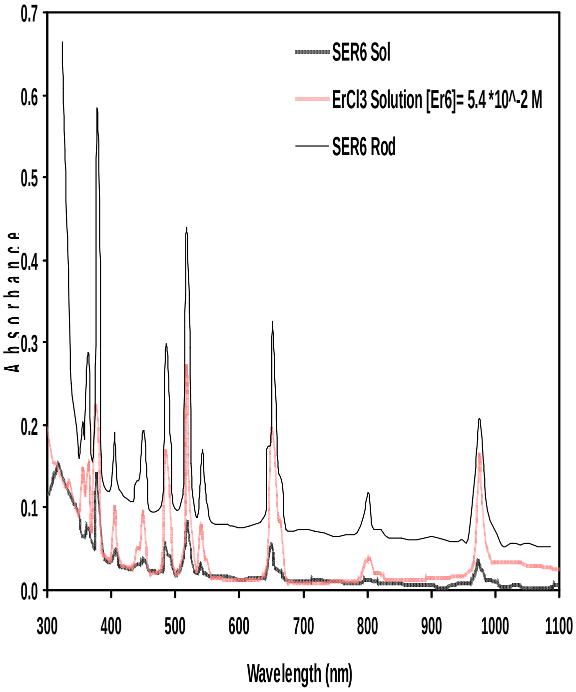

Figure 4: The absorption spectra of Er^{3+} ion in three cases; Er -chloride solution, sol and bulk phases

Generally, the positions of the absorption bands in sol and bulk phases are similar to that of erbium chloride solutions, indicating the presence of Er3+ ions and its spectroscopic activity within the sample structure. It can be noticed from figure (1) that the absorbance at sol phase is too low because the concentration of Er3+ ions is diluted, while noticeable absorbance is achieved at bulk phase which is due to the effect of solvent evaporation that leads to concentrate the Er3+ ions in a smaller volume than that of sol volume. Also, the absorption bands in bulk phase have a little red shift in comparison with the erbium chloride solution and sol phase. This may be explained as follows; when solid host is used, the RE3+ ions are located inside the pores of sol-gel glass structure5.So that there is an interaction between these ions as well as with its host environment and this may perturb its energy levels. Therefore the lowest 4f level may be shifted to lower energy. At low concentration, the Er3+ ions become more relaxed and at relatively large separation distance. These conditions will, therefore, reduce the perturbation processes and lead to decreasing this red shift more as observed in our results at lower Er3+ concentrations.

Figure (5) shows the absorption coefficient vs. wavelength of bulk samples doped with different concentrations of Er3+ ions and at Al: Er of 10: 1 molar concentration ratio.

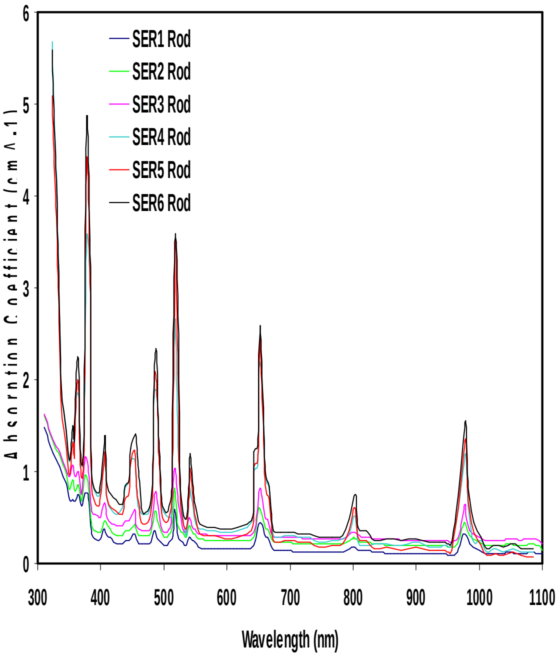

Figure 5: The absorption spectra of Er^{3+}

The present results show that the absorption coefficient α (λ), at the peak of each band, is increased as a result of a corresponding increase of concentration. For example, the α (λ) is increased from 0.581 cm-1 to 3.593 cm-1 for the ($^4I_{15/2}$→ $^2H_{11/2}$, ~ 518 nm) transition of Er3+ ion.

It has been noted that the present absorption spectra show inhomogeneous broadening which may be attributed to the amorphous character of sol-gel glass host. The X-ray diagrams did not display patterns arising from the crystalline phases as shown in figure (6)

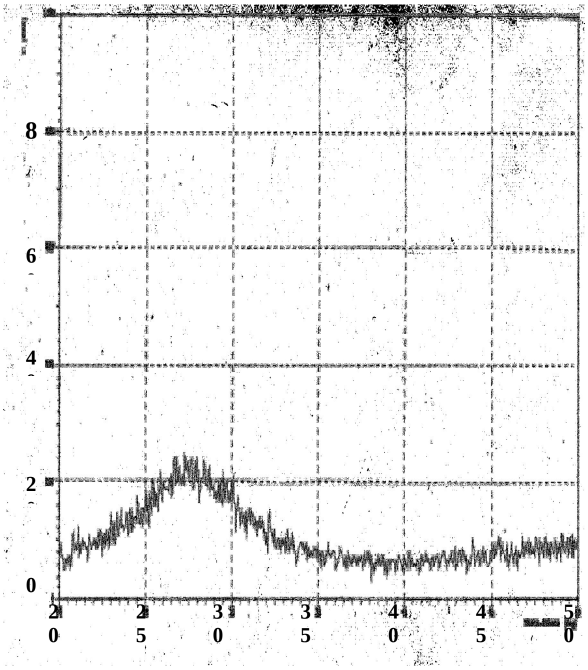

Figure 6: X-ray diffraction spectra of SER6 Rod samples.

Fluorescence measurements for Er3+ samples are performed using the 515 nm line of an Argon ion laser which corresponds to the peak of the absorption band due to the $^4I_{15/2}$→ $^2H_{11/2}$ transition of Er3+ ions

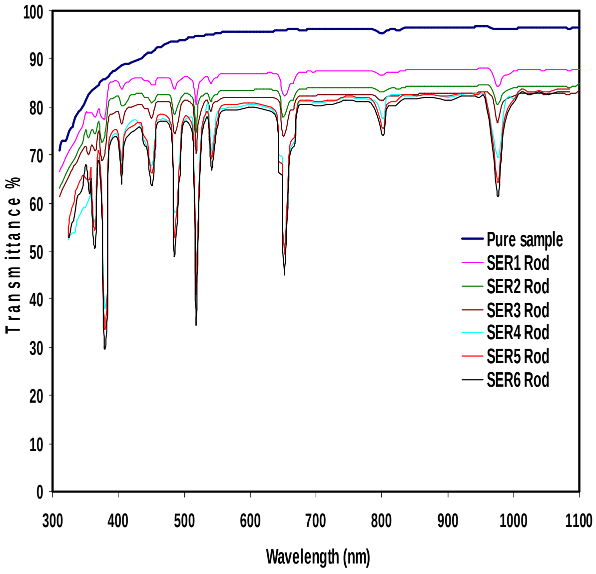

Figure 7: UV-VIS-NIR Transmission of pure sol-gel glass (sample thickness 0.37 cm) and SER Rod samples (thickness of

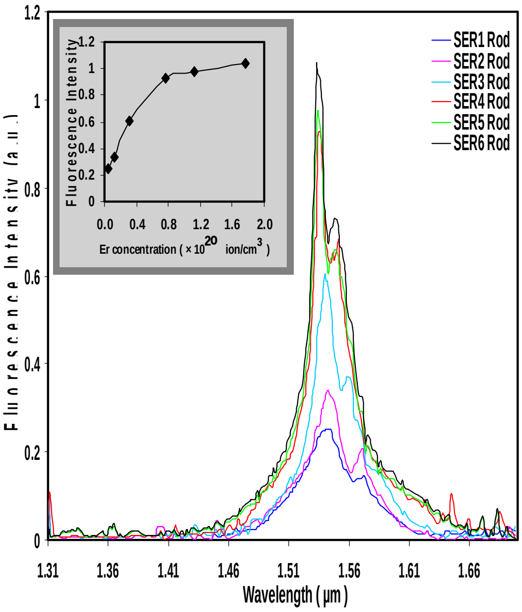

Figure 8: Fluorescence spectra of sol-gel silica glass samples doped with different concentrations of Er^{3+} and Al

The Er^{3+} fluorescence around 1.536 μm is clearly observed, as shown in figure (8), and results from the intra-4f electric dipole transition from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$. The two peaks result from Stark splitting of the Er^{3+} levels and characteristics for Er^{3+} in SiO_2 network[8].

It can be seen from figure (8) that the peak fluorescence intensity increases as the concentration of Er^{3+} ions increases as shown in the inset of figure (8). This can be attributed to the increase of the absorbed intensity (I_a) (i.e. increase the concentration of excited ions) causing corresponding increase of fluorescence intensity (I_f) which is proportional to I_a ($I_f \alpha \eta I_a$), where η is the fluorescence quantum efficiency[9].The corresponding increases of (I_f) can occurre only if the probability of radiative emission is higher than the probability of non-radiative relaxations. This condition is achieved by adding the Al co-doping with optimum ratio of 10 which enhances a good distribution of RE^{3+} ions in the silica network, reducing the tendency of these ions to cluster and subsequently the non-radiative relaxations, then results in
an increase in (I_f) and reduce concentration quenching at high doping levels.

The fluorescence bands corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition exhibited a broad spectral width of around 46 nm at FWHM. This spectral width is due to the thermal distribution over the Stark levels and homogeneous and inhomogeneous broadening[10].

τ_{rad} can be calculated from the absorption spectra of Er^{3+}samples using the formula[11]:

$$1/\tau_{rad} = 2.88 \times 10^{-9} \times n^2 \acute{\upsilon}^2 \int \varepsilon(\acute{\upsilon})\, d\acute{\upsilon} \qquad (1)$$

Where n is the refractive index of the material, $\acute{\upsilon}$ is the wavenumber at the peak of absorption band in cm^{-1} and $\int \varepsilon(\acute{\upsilon})\, d\acute{\upsilon}$ is the area under the absorption band curve. Peak emission cross-section (σ_p) can be determined from the relation[12]:

$$\sigma_p = \lambda_p^4 / 8 \pi \acute{n}^2 \Delta\lambda_{eff.} \tau_{rad.} , \qquad (2$$

where λ_p is the peak wavelength within the fluorescence band, $\Delta\lambda_{eff.}$ is the fluorescence linewidth (effective); which determined by the full width half maximum (FWHM) of the fluorescence band and ń is given by[13]:

$$\acute{n} = [n^2(\lambda) + 2]^2 / 9n(\lambda). \qquad (3)$$

The quantity ń taking in to account the polarizability of active media by the electric field of the electromagnetic radiation.
The results which concerned the samples doped with different Er^{3+} concentrations and at (Al: Er) ratio of 10: 1 are plotted in figures (9 and 10)

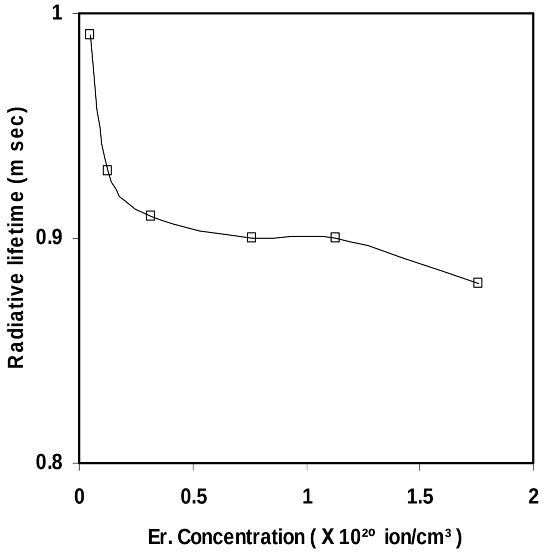

Figure 9: The natural lifetime as a function of Er^{3+}concentration for the prepared samples at Al: Er molar ratio of 10: 1

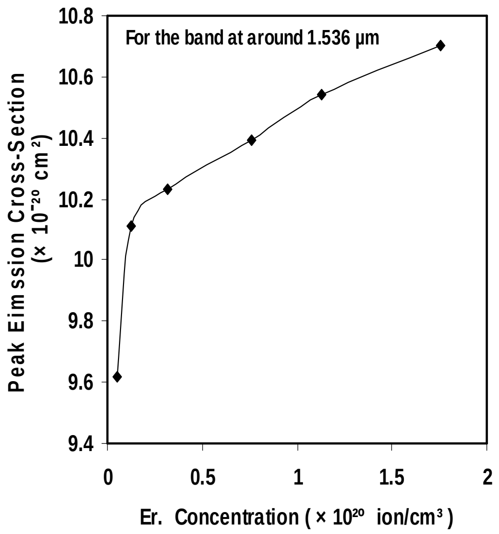

Figure 10: Peak emission cross-section as a function of Er^{3+}concentration for $^4I_{13/2}$→ $^4I_{151/2}$ transition of Er^{3+} ions ***at Al: Er molar ratio of 10: 1***

In this case the values of τ_{rad} have no drastic changes as the Er^{3+} concentration increases. This may give an indication that the Er-Er interactions do not take place significantly because of the presence of Al co-doping, at (Al: Er) molar ratio of 10: 1, in silica network. Therefore, the slight decrease in these values with the Er concentration may be attributed to the inhomogeneous distributions of the vibrational and electrical host field which due to the amorphous character of sol-gel glass. On the other hand, the slight increase in σ_p values with Er concentration, which corresponds with the observed increasing in the fluorescence intensity [see figure (8)] may give a primary evidence of increasing the number of emitting Er^{3+} ions.

Conclusions

The sol-gel glass of Er^{3+} doped Nanosilica is successfully prepared by wet chemical synthesis method. The prepared samples seem to be transparent and unbroken which due to the suitable sol-gel parameters used (i.e. pH 1, *R* =2, T =60 °C). A high peak emission cross-section σ_p is acquired with the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+}. This suggests that the Al^{3+} co-doping is effective, at dispersion Er^{3+}, when the ratio of Al: Er is 10: 1 and the Er in the sol-gel may be more favorable as laser material.

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