Judd–Ofelt analysis of Spectroscopic properties of Nd^{+3}:SiO_2 Prepared via Sol-Gel

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Abstract

Doped and undoped nano particular silicate dioxide was prepared via sol–gel method under varying conditions. The optical properties of prepared samples were investigated by a variety of techniques, including X-ray diffraction, UV- Visible spectroscopy, FTIR spectroscopy and fluorescence spectroscopy. The peak of the fluorescence spectrum was recorded at the wavelength around to 1048nm, which it is close to known fluorescence peaks of Nd:YAG crystal in NIR region. A Judd-Ofelt analysis is performed to calculate the spectroscopic properties of Nd^{3+} ions embedded in SiO_2 and compare it with spectroscopic properties of Nd:YAG crystal. The conclusions behind this study show that the doped silicate samples have a high peak emission cross-section σ_p , which gives an acceptable indication in the direction of using Sol-Gel technique to prepare Nd:SiO_2 as a solid state laser active medium.
Keywords: Sol-Gel; Nano technology; SiO_2; laser active medium.

دراسة تحليلية بأستخدام نظرية Judd – Ofelt للخصائص البصرية لنماذج Nd:SiO2 المحضرة باستخدام طريقة الـ Sol –Gel .

الخلاصة:

تم استخدام تقنية السول-جل Sol-Gel لتحضير عينات من مادة SiO_2 النقية والمشوبة بايون النديميوم الثلاثي Nd^{+3} وتحت ظروف تحضير مختلفة . تم التحقق من الخصائص البصرية للعينات المحضرة من خلال اجراء فحوصات حيود الاشعة السينية، فحوصات النفاذية والامتصاصية، فحص FTIR وفحص طيف التألق. بينت فحوصات الفلورة على وجود قمة مميزة قريبه من الطول الموجي 1048nm وهي أيضاً قريبة من القمة المعروفة للبلورة Nd:YAG. أجريت دراسة تحليلية باستخدام نظرية Judd-Ofelt من اجل ايجاد الخصائص البصرية للايون Nd^{3+} المشاب في SiO_2 ومقارنة هذه الخصائص البصرية مع تلك الخصائص العائدة للبلورة Nd:YG . أشارت نتائج هذا البحث إلى ان عينات Nd:SiO_2 تمتلك لـ *high peak emission cross-section* σ_p ذو قيمة مناسبه بالمقارنة مع قيمته للبلورة Nd:YG ، وهذا يعطي مؤشراً لإمكانية استخدام عينات Nd:SiO_2 المحضرة بطريقة السول-جل، كوسط ليزري فعال.

الكلمات المفتاحية: السول- جل، التقانة النانوّييه، ثاني أوكسيد السيليكون، وسط ليزري فعال.

INTRODUCTION

For more than 50 years, so many research is covered a large number of rare-earth active ions doped with glass as a host material. Neodymium Nd^{3+} ion, is one of an interest primary rare earth ion of for most commercial application of glass lasers [1]. So many methods have been developed to synthesis Nd^{3+} doped with silica, including plasma- enhanced chemical – vapor- deposition, ion implantation, flame hydrolysis, and ion exchange. In recently, a growing interest has been focused on a wet chemical process to prepare of transparent monoliths which containing Nd^{3+} (using Neodymium (III) acetylacetonate hydrat [2-4]).

The sol-gel process has been widely shown to be a suitable process to fabrication of a optical materials with various configurations, such as monoliths, coatings, fibbers and films for optical device applications [5,6]. The formation of oxide particles in a liquid phase, leads to make the structure of sol-gel materials inherently porous. Silicon alkoxides generally react slowly with water, using of acid and base catalysts makes the reaction process (hydrolysis and condensation) to become faster [7,8].

Experimental

Samples Preparation

The doped and un-doped samples were synthesized by sol–gel method from tetraethylorthosilicate (TEOS) (Aldrich 98%), Ethanol (EtOH 99.9%) from GCC, hydrochloric acid (HCl, 34.5%) from BDH and neodymium (III) acetylacetonate hydrate (Aldrich). Deionized water was used for the hydrolysis of (TEOS) and preparation of pure and doped SiO_2 sol. The performed of reaction process was done at a cooler water jacket (the solution was cooled by a cooled water (10-15°C)). The amount of each chemical in this procedure was TEOS:H_2O:EtOH:HCl= 1:1:10:0.1 in molar ratio. All solution was prepared as follows: 1 mole of tetraethylorthosilicate (TEOS) 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 TEOS molar ratio of R= 2 are attained. A neodymium (III) acetylacetonate hydrate was solved in ethanol and used to mixing with TEOS. All solutions were then leaved to stir for about 2 hours further at room temperature aged for 24 hours before use.

A first drying occurred (at temperature 60^{o}C and for about 2 hour) after aging for 24 hour. Then samples without covers left in room temperature in order to permit solvent evaporation through the drying process. The doping rate of samples with Nd^{3+} is equal to 5% wt. figure (1) show Snapshot for some prepared doped samples with different shape.

Samples characterization

Structural characterizations of the doped and un-doped SiO_2 samples were done by X-ray diffraction (XRD). θ–2θ scans were recorded using ITAL-STRUCTURE diffractometer equipped. Shimadzu FTIR spectrometer was used to obtain the Mid IR spectra for the prepared samples (using KBr pellets of the samples).

Absorption spectra at room temperature were obtained with TupCen UV-VIS Spectrometer. SolarLab mono chromatore equipment has been used to obtain the emission spectra (at room temperature). As excitation source we used the 808nm 1W Laser diode. Furthermore standard measurements were obtained via measuring the absorption and emission spectra were to the Nd:YAG crystal.

Results

X-ray diffraction analyses show that both of prepared samples (doped and undoped) have amorphous structure [9]. The FTIR spectrum of doped and un-doped samples was in the range of 4000–400 cm^{-1} illustrated in figure (2). The characteristics vibrational bands of silica were found in the FTIR spectra. Where; the absorption bands at about 1100 cm^{-1}, 472 cm^{-1} and 808 cm^{-1} which attribute to bending, asymmetric stretching and symmetric stretching vibrations of Si-O-Si groups respectively. The band at around 960 cm^{-1} could be attribute to stretching vibration of silanol (Si-OH) groups [10,11], indicates the limited number of these groups in the silica network [10]. The band at around 960cm^{-1} for dopant sample is weak when it compare with the same band for pure sample that means the condensation reaction of doped sample is nearly complete more than from condensation reaction of pure sample. Two other bands at around 1600 $cm^{-1}$and 3400 cm^{-1}were appeared and attribute to the characteristics vibration of O-H bond in water molecules [12]. These two bands are indicating that the drying process does not completely trap the water molecules from the prepared samples (silica Xerogel network). Therefore, the drying process of sample needs to be done at temperatures higher than 500 ºC to obtain sol-gel silica glass [9].

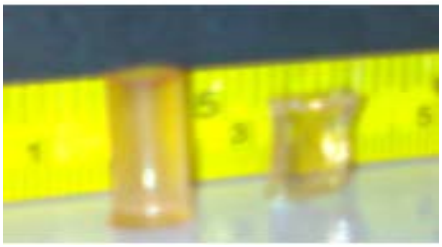

Figure (1) Snapshot for some prepared doped samples with different shape.

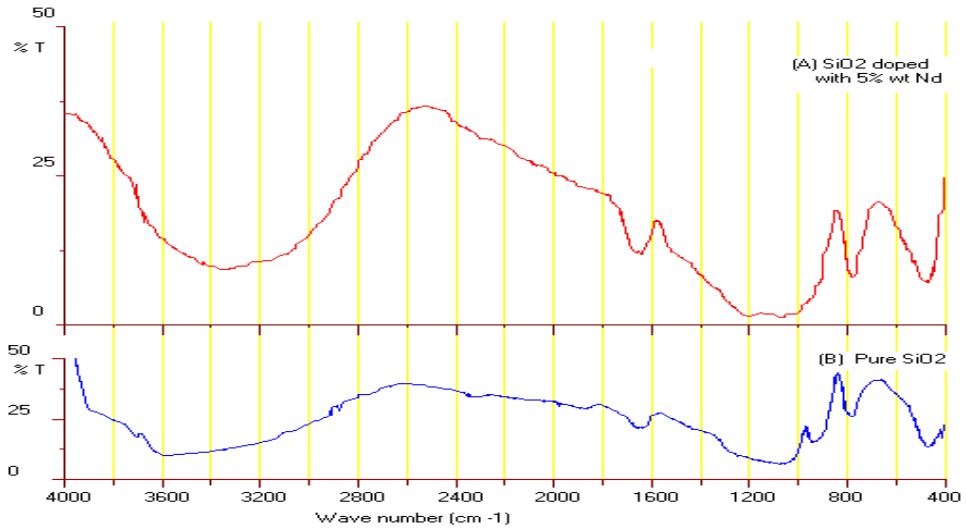

Figure (2) FTIR spectrums for samples: (A)SiO_2 doped with 5%wt Nd^{+3}.(B) Pure SiO_2.

The room temperature UV-VIS-NIR absorption spectra of the Nd^{3+} doped sample are presented in Figure (3). For comparison, other spectrum of Nd:YAG crystal is also given in Figure (3). It is clearly seen that all absorption bands of Nd^{3+} in SiO_2 sample are somehow close similar to absorption bands of Nd^{3+} in YAG crystal hosts [13-17]. The absorption peaks band width of ND:SiO_2 are widely in comparison with absorption peaks ND:YAG. That's because the prepared SiO_2 samples have amorphous structure. One of most important result could be concluded from the absorption spectra is that the optical pumping for prepared dopant sample could be done in similar way of Nd:YAG optical pumping.
The fluorescence property to the prepared sample is one of an important performance indicator for the sample to be useful for glass laser applications. To determine the optical characteristics of the samples, photoluminescence measurements were carried out using the 808nm/1W Laser Diode for excitation. The obtained spectrum is shown in Fig.4 for both of Nd:SiO_2 and Nd:YAG crystal. From Nd:YAG fluorescence spectrum it could observed a weak and broad peak around 1065nm with band width of 11nm at full width half maximum (FWHM). While the Nd:SiO_2 fluorescence spectrum have a weak and broad peak at around 1048nm with band width of 18nm at FWHM. These two peaks correspond to the transition between the levels $^4F_{3/2}$ -$^4I_{11/2}$ of Nd^{3+} ion [13-17].

The absorption and fluorescence spectrums are well resolved so that almost every stark components corresponding to different manifold of Nd^{3+} are observed and tabulated in **Table 1** and **Table 2** for absorption and fluorescence spectra respectively. From the integrated absorption cross section, the so-called line strength, S_m, can be found by Eq. 1 [18]:

$$S_m = \frac{3ch(2J+1)}{8\pi^3 e^2 \bar{\lambda}} n\left(\frac{3}{n^2+2}\right)^2 \int_{manifolds} \sigma(\lambda) d\lambda \qquad \ldots (1)$$

Where J is the total angular momentum of the initial ground manifold, found from the $^{2S+1}L_J$ designation. σ(λ) is the absorption cross section as a function of wavelength λ. The absorption bands were chosen to determine the phenomenological Judd-Ofelt parameters [18-19]. The J-O parameters for Nd:YAG crystals and Nd:SiO_2 are given in Table (1). These phenomenological J-O parameters were subsequently utilized to determine emission line strengths S_{ed} corresponding to the transitions from the upper multiplet manifolds $^{2S+1}L_J$ to the corresponding lower lying multiplet manifolds $^{2S'+1}L_{J'}$ of Nd^{3+} in YAG and TiO2. The S_{ed} are determined by Eq. 2 [18]:

$$S_j^t = \sum_{i=1}^{3} M_{ij}\, \Omega_i \qquad \ldots (2)$$

where M_{ij} are components of a 3 x N matrix for the square matrix elements of $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$. The Ω_i are components of a 1 x 3 matrix for the Judd-Ofelt parameters

Ω_2, Ω_4 and Ω_6. N represents the number of transitions to fit. The square matrix element does not depend on host materials [21-22].

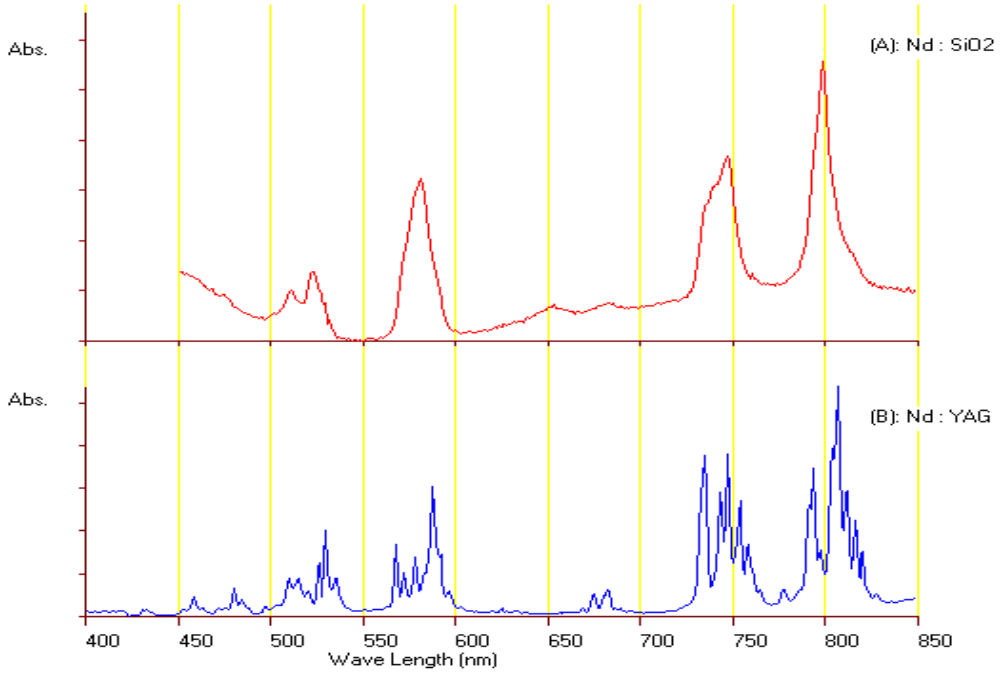

Figure (3) Absorption spectrums for (A) SiO_2 doped with 5%wt Nd^{+3} (B) Nd:YAG Crystal

The radiative transition probabilities *A(J;J')*, are given in Eq. (3) [18], were obtained with the line strength for the excited $^4F3/2$ to $^4I_{J'}$ manifold for Nd^{3+}

$$A(\mathrm{J};\mathrm{J}') = \frac{64\,\pi^4}{3\mathrm{h}\,(2\mathrm{J}+1)\lambda^3}\left[\frac{\mathrm{n}(\mathrm{n}^2+2)^2}{9}\right]\mathrm{S}_{\mathrm{ed}} \qquad \ldots (3)$$

Where

$[n(n^2+2)^2/9]$ is the local field correction for Nd^{3+} in the initial *J* manifold. *J'* is the final manifold. *n* is the refractive index at the wavelength (λ) of the transition.

The efficiency of a laser transition is evaluated by considering stimulated emission cross-section ($\sigma_{em}(\lambda)$). In our case $\sigma_{em}(\lambda)$ between $^4F_3 \rightarrow {}^4I_{J'}$ was determined from the emission spectrum using Fuchtbauer–Ladenburg method [23]:

$$\sigma_{\mathrm{em}} = \frac{\lambda_{\mathrm{p}}^4}{8\,\pi\mathrm{c}\,\Delta\lambda_{\mathrm{eff}}}\,\frac{\mathrm{A}(\mathrm{J};\mathrm{J}')}{(\,\mathrm{n}(\lambda_{\mathrm{p}})\,)^2} \qquad \ldots (4)$$

Where:

λ_p is the wavelength of the peak emission, *c* is the speed of light in vacuums, and $n(\lambda_p)$ is the refractive index at each emission peak wavelength. $\Delta\lambda_{eff}$ is an effective linewidth.

Table (1) Measured absorption Line Strengths of Nd^{3+} in YAG crystal and SiO_2.

	Nd : YAG		Nd : SiO_2	
Transitions from $^4I_{9/2}$	$\overline{\lambda}$ (nm)	S_{m*10}^{-20} (cm^{-1})	$\overline{\lambda}$ (nm)	S_{m*10}^{-20} (cm^{-1})
$^2K_{15/2} + {}^2G_{9/2} + {}^4G_{11/2}$	481	0.233	----	----
$^2K_{13/2} + {}^4G_{7/2} + {}^4G_{9/2}$	531	1.330	521	0.3043
$^2G_{7/2} + {}^4G_{5/2}$	588	2.335	580	0.9410
$^4F_{9/2}$	684	0.218	681	0.0831
$^4F_{7/2} + {}^4S_{3/2}$	748	3.072	746	0.7761
$^4F_{5/2} + {}^2H_{9/2}$	808	3.439	799	0.8953
$^4F_{3/2}$	882	0.345	866	0.1783
	Ω_2=0.72, Ω_4=2.208 and Ω_6=4.929		Ω_2=0.4594, Ω_4=0.6903 and Ω_6=1.2227	

According to **Table (1) and (2)**, the measured and calculated parameters to Nd:YAG are close to known parameters of Nd:YAG crystal [13-15]. That's gives a good indication about the accuracy of parameters measurements to doped silica. Also it can see that Nd:SiO_2 parameters are somewhat close to parameters of Nd:YAG. That's means the spectroscopic properties of prepared doped sample are close similar to spectroscopic properties of Nd:YAG crystal. This result gives further more good indication in direction of using Sol-Gel technique to prepare of Nd:SiO_2 samples as solid state Laser active medium.

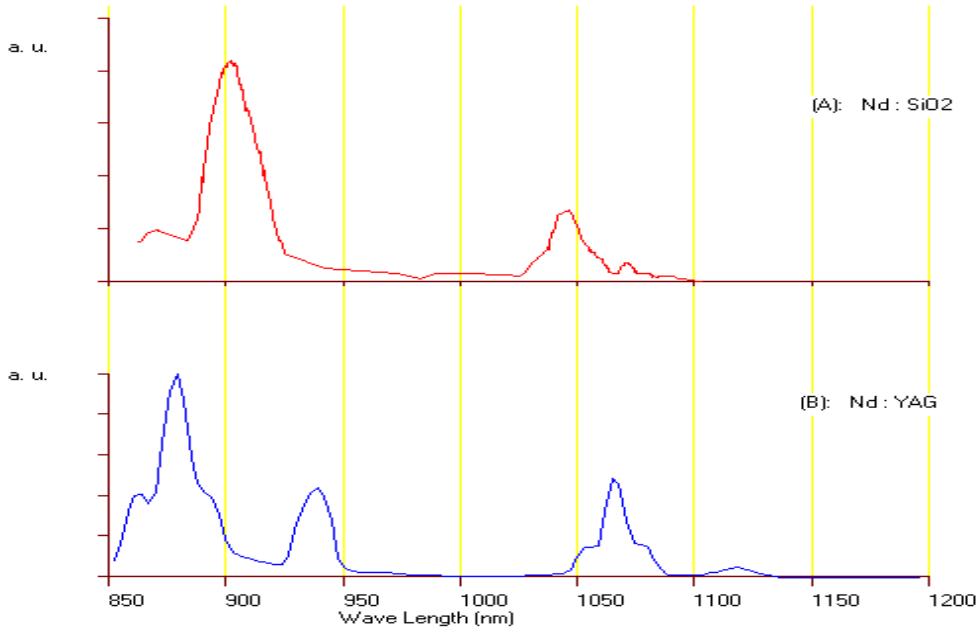

Figure (4) fluorescence spectrums for: (a) SiO_2 doped Nd^{+3}; (b) Nd:YAG Crystal.

Table (2) Spectroscopic properties of Nd:YAG and Nd:SiO_2.

	Transmission	λ_{em} (nm)	$\Delta\lambda_{eff}$ (nm)	A_{rad} (S^{-1})	σ_{em} *10^{-20} (cm^2)
Nd:YAG	$^4F_{3/2}\rightarrow{}^4I_{9/2}$	879	15	4846	10.364
		939	16	3975	10.381
	$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1065	11	1236	7.601
		1109	19	1070	4.617
Nd:SiO_2	$^4F_{3/2}\rightarrow{}^4I_{9/2}$	901	26	1140	1.5605
	$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1048	18	327.5	1.1804
		1071	6	306.04	3.1050

Conclusion

The transparent and unbroken sample of Nd^{3+} doped Nanosilica is successfully prepared by wet chemical synthesis method. The optical properties of prepared doped samples are close similar to optical properties of Nd:YAG crystal. The Nd^{3+} doped Nanosilica network have a high peak emission cross-section σ_p. This suggests that it could be use Sol-Gel technique to prepare of Nd:SiO_2 as solid state Laser active medium.

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