Optical properties of Nd$^{3+}$:SiO$_2$ Prepared via Sol-Gel

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Abstract

Doped and undoped silicon dioxide was prepared via sol–gel technique under varying conditions. Samples were analyzed by a variety of techniques, including X-ray diffraction, UV-Visible spectroscopy, FTIR spectroscopy and fluorescence spectroscopy to investigate of its optical properties.

A fluorescence spectrum in NIR region was recorded to Nd:SiO$_2$ sample, when the sample was pumping with 795nm laser diode with power equal to 1W. The peak of the fluorescence spectrum was recorded at the wavelength around to 1048nm, which it is close to the fluorescence peaks of Nd:YAG crystal in NIR region.

The conclusions behind this study show that the doped silicate samples have a optical properties close similar to optical properties of Nd:YAG crystal, 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; Neodymium; SiO$_2$; laser active medium.

1. INTRODUCTION

The rare earths have long been a subject of fascination to chemists and physicists. Many research covering a large number of rare-earth active ions in every known glass system [1]. Neodymium Nd$^{3+}$ ion, however, remain the primary rare earth ion of interest for most commercial application of glass lasers. Several methods have been developed to fabricate Lanthanide (rare earth) ions - doped silica, including plasma- enhanced chemical – vapor- deposition, ion implantation, flame hydrolysis, and ion exchange. An alternative technique to prepare rare earth doped silica films or monoliths are by using a sol-gel technique. In recently, a growing interest has been focused on preparation of transparent monoliths, containing Nd$^{3+}$ by using Neodymium (III) acetylacetonate hydrate was demonstrated [3],[4].

The sol-gel process has been widely shown to be a very flexible route for the fabrication of a large variety of photonic materials in various configurations, such as monoliths, coatings, fibers and films for optical device applications [5],[6]. The formation of oxide particles in a liquid phase, and the polymerisation of the particles make the structure of sol-gel materials inherently porous. Silicon alkoxides generally react slowly with water, but the reaction process, hydrolysis and condensation, can be speed up by the use of acid and base catalysts [7],[8].

2. EXPERIMENTAL

2.1 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 reaction was performed at a cooler water jacket (i.e. the solution was cooled by water at temperature (10-15°C). The amount of each chemical in this procedure was TEOS:H$_2$O:EtOH:HCl= 1:1:10:0.1 in molar ratio. All solution was prepared as follows: 1 mole of tetraethylorthosilicate (TEOS) and 1 moles of ethanol (EtOH) were mixed and stirred for 10 min. While stirring, 0.1 M catalysts in water were added dropwise to the solution until water to TEOS molar ratio of $R= 2$ are attained. For dopand samples a neodymium (III) acetylacetonate hydrate was used and solved in ethanol before mixing with TEOS. All solutions were then stirred at room temperature for 2 hours further and aged for 24 hours before use.

After aging for 24 hour, first drying occurred for 2 hour at temperature 60°C. Then samples left in room temperature without covers 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 Snapshots for the prepared doped sample.
2.2 Samples characterization

Structural characterizations of the doped and undoped SiO₂ samples were done by X-ray diffraction (XRD). θ–2θ scans were recorded using ITAL-STRUCTURE diffractometer. While Mid-IR spectra were obtained for the prepared samples using FT-IR spectrometer, Shimadzu, on KBr pellets of the samples.

Absorption spectra were measured at room temperature with TupCen UV-VIS Spectrometer. Emission spectra were measured at room temperature by using SolarLab mono chromatore. As excitation source we used the 795nm 1W Laser diode. Furthermore absorption and emission spectra were measured for Nd:YAG crystal to obtain a standard measurements.

3. Result and Discussion

The doped and undoped samples have amorphous structure and x-ray data show no detectable peaks, as shown in Figure (2) [12]. Fourier transform infrared (FTIR) absorption spectra in the range of 4000–400 cm⁻¹ were taken. The FTIR spectrum of doped and undoped samples was illustrated in Figure (3). The characteristics vibrational bands of silica were found in the FTIR spectra. Where: the absorption bands at about 472 cm⁻¹, 808 cm⁻¹ and 1100 cm⁻¹ which were due to bending, symmetric stretching and asymmetric stretching vibrations of Si-O-Si groups respectively. The band at around 960 cm⁻¹ which is ascribed to stretching vibration of silanol (Si-ON) groups [9], [10], indicates the limited number of these groups in the silica network [9]. For dopant sample the bands around 960 cm⁻¹ is a weak which means that the condensation reaction is nearly complete more than from condensation reaction of pure sample.

Another two bands were appeared at around 1600 cm⁻¹ and 3400 cm⁻¹. These two bands were the characteristics vibration of O-H bond in water molecules [11], and indicating that the drying process at 60°C does not completely trap the water molecules from the pores of silica Xerogel network. Therefore, the sample needs heating at temperatures higher than 500 °C to obtain sol-gel silica glass [12].

UV/Vis absorption spectra, at room temperature, of Nd³⁺ doped monoliths are presented in Figure (4). The spectrum of Nd:YAG is given for comparison. The enhanced absorption properties were mainly determined by the energy level structure of rare earth. The absorption spectrum of rare earth ions was due to electronic transitions caused by the energy level. For Nd:YAG, the absorption bands in the range of 500–850 nm corresponded to the energy level transition of ⁴I₉/₂→₂G₇/₂ (513 nm), ⁴I₉/₂→⁴G₇/₂ (530nm), ⁴I₉/₂→⁴G₅/₂ (588nm), ⁴I₉/₂→⁴F₄/₂ (680nm), ⁴I₉/₂→⁴F₇/₂, ⁴S₅/₂ (735nm, 747nm) and ⁴I₉/₂→⁴F₅/₂, ⁴H₉/₂ (795, 807nm), respectively [13]-[15].

For the Nd³⁺:SiO₂, the absorption bands in the range of 500–850 nm corresponded to the energy level transition of ⁴I₉/₂→²G₇/₂ (509nm), ⁴I₉/₂→²G₅/₂ (518nm), ⁴I₉/₂→²G₅/₂ (580nm), ⁴I₉/₂→²F₄/₂ (680nm), ⁴I₉/₂→²F₇/₂ (747nm) and ⁴I₉/₂→²F₅/₂ (797nm) [16],[17].
By comparison between two absorption spectra, it can be noted that some peaks of silica dopant sample are matching with the peaks of Nd:YAG. That’s main the silica medium affect on the energy level of Nd$^{3+}$ and forced the energy level to divided into a sublevel difference from known sublevel of Nd:YAG. It’s clearly seen that the absorption peaks band width of ND:SiO$_2$ are widely while ND:YAG have a narrow absorption peaks. That’s because of amorphous structure of SiO$_2$. The important result from the absorption spectra is that the silica dopant sample could be optically pumped in similar way of Nd:YAG optical pumping.

![Figure 3](image3.png)

**Figure 3** FTIR spectra for samples, (a) SiO$_2$ doped with 5%wt Nd$^{3+}$; (b) Pure SiO$_2$.

An important performance indicator for the sample to be useful for glass laser applications is its fluorescence properties. To determine the optical characteristics of the samples, photoluminescence measurements were carried out using the 795nm Laser Diode for excitation. The obtained spectrum is shown in Figure (5) for both of Nd:SiO$_2$ and Nd:YAG crystal. From Nd:YAG fluorescence spectrum it could be 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 1047nm 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].

![Figure 4](image4.png)

**Figure 4** Absorption spectra for, (a) SiO$_2$ doped with 5%wt Nd$^{3+}$; (b) Nd:YAG Crystal.

Absorption spectra are fundamental to determine the factors governing several optical properties, such as absorption coefficients $\alpha(\lambda)$, absorption cross-sections $\sigma(\lambda)$, and refractive index $n(\lambda)$. $\sigma(\lambda)$ can be calculated from the absorption spectra of Nd$^{3+}$:YAG and ND$^{3+}$:SiO$_2$ sample using the formula[12]:

$$\sigma(\lambda) = \frac{\alpha(\lambda)}{\rho} \quad \text{------(1)}$$

Where $\rho$ is the ion density (cm$^{-3}$). Bowen and Wokes [18] gave empirical formula to get a sufficient accurate value of radiative lifetime $\tau_{\text{rad}}$ (in seconds):

$$\frac{1}{\tau_{\text{rad}}} = 2900 \cdot n^2 \cdot \bar{v}^2 \cdot \int \varepsilon(\bar{v}) \, d\bar{v} \quad \text{------(2)}$$

Where $n$ is the refractive index of the material, $\bar{v}$ is the wavenumber at the peak of absorption band in $\mu$m$^{-1}$ and $\int \varepsilon(\bar{v}) \, d\bar{v}$ is the area under the absorption band curve. $\varepsilon(\bar{v})$ is molecular extinction coefficient [18]. The radiative lifetime $\tau_{\text{rad}}$ calculated by eq. (2) refers to the spontaneous emission of light, and corresponds to the probability $A_{\text{em}} (=1/\tau_{\text{rad}})$, that a
molecule will undergo a radiative transition from an upper state \( n \), to a lower state \( m \), in the absence of radiation of frequency \( \nu \) [18].

Peak emission cross-section \( (\sigma_p) \) for lasing transition \( ^4F_{3/2} \rightarrow ^4I_{11/2} \) can be determined from the relation [12], [19]:

\[
\sigma_p = \frac{\lambda_p^4}{8 \pi c} \hat{n}^2 \Delta \lambda_{\text{eff}} \tau_{\text{rad}}. \quad (3)
\]

where \( \lambda_p \) is the peak wavelength within the fluorescence band, \( \Delta \lambda_{\text{eff}} \) is the fluorescence linewidth (effective); which determined by the full width half maximum (FWHM) of the fluorescence band and \( \hat{n} \) is given by:

\[
\hat{n} = \frac{[n^2(\lambda) + 2]^2}{9n(\lambda)}. \quad (4)
\]

Table (1) present some results of measured and calculated parameters for Nd:YAG and Nd:SiO\textsubscript{2} samples. The parameters calculated to absorption band \( ^4I_{9/2} \rightarrow ^4F_{5/2} \) and to fluorescence peak correspond to the transition \( ^4F_{3/2} \rightarrow ^4I_{11/2} \) of Nd\textsuperscript{3+} ion.

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. From table (1), it can see that Nd:SiO\textsubscript{2} parameters are somewhat close to parameters of Nd:YAG. That’s means the optical properties to prepared doped sample are close similar to optical properties of Nd:YAG crystal. This result gives further more good indication in direction of using Sol-Gel technique to prepare of Nd:SiO\textsubscript{2} samples as solid state Laser active medium.

<table>
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<th>Parameters</th>
<th>Nd:YAG</th>
<th>Nd:SiO\textsubscript{2}</th>
</tr>
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<tbody>
<tr>
<td>absorption cross-sections ( \sigma(\lambda) ) (cm\textsuperscript{-1})</td>
<td>7.2*10\textsuperscript{-19}</td>
<td>2.1*10\textsuperscript{-19}</td>
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<tr>
<td>Radiative lifetime ( \tau_{\text{rad}} ) (mS)</td>
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<td>Emission Peak wavelength (nm)</td>
<td>1063</td>
<td>1048</td>
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<tr>
<td>Linewidth FWHM (nm)</td>
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<td>18</td>
</tr>
<tr>
<td>Emission Cross section (( \times 10\textsuperscript{-19} ) cm\textsuperscript{2})</td>
<td>6.7</td>
<td>1.45</td>
</tr>
</tbody>
</table>

**Figure 5:** fluorescence spectra for, (a) SiO\textsubscript{2} doped with 5\%wt Nd\textsuperscript{3+}; Nd:YAG Crystal.

4. CONCLUSION
The sol-gel glass of Nd\textsuperscript{3+} doped silica is successfully prepared via sol-gel technique. Due to the suitable sol-gel parameters; the silica samples have transparent. The doped and undoped prepared silica samples have amorphous structures. The optical properties of doped samples are close similar to the optical properties of Nd:YAG crystal. This suggests that it could use sol-gel technique to prepare of Nd:SiO\textsubscript{2} as solid state Laser active medium.

References

AUTHOR
Mohammed Alwan Hamzah received the B.Sc. and M.Sc. degrees in Physics from Baghdad Uni. (Iraq) in 1986 and 1999, respectively. During 1996-1999, he stayed in college of science to study Optoelectronics, Laser and Digital Image processing. In 2014 he received the Ph.D. degree from Mosul University, (Iraq). He works now at the college of science, Baghdad University.