Preparations of Nd:TiO₂ as Laser active medium by Sol-Gel method

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ABSTRACT
Nd³⁺ doped Nanotitania are successfully prepared by wet chemical synthesis method. Samples were analyzed by a variety of techniques, including X-ray diffraction, FTIR, absorption and emission spectrometer to investigate the optical properties of doped samples. Emission spectrum shows that energy levels manifolds ⁴I₁₁/₂ and ⁴I₁₉/₂ of Nd³⁺ are affected by crystal field of TiO₂ and split into energy sublevels which it quietly difference to the known energy sublevels of Nd³⁺ in YAG or glass. The absorbance and emission spectra to Nd:TiO₂ sample are close similar to absorption and emission spectra of Nd:YAG crystal. This give a good indication in direction of preparation of Nd:TiO₂ as solid state Laser active medium via Sol-Gel technique.

Keywords: Sol-Gel; TiO₂; laser active medium.

1. INTRODUCTION
Nanostructured materials are currently receiving wide attention due to their special optical, electronic, magnetic, chemical, physical and mechanical properties [1]-[5]. Semiconductor nanocrystals have been widely studied for their fundamental properties, especially titanium dioxide (TiO₂). Nanosized titanium dioxide materials have been the focus of great interest because they exhibit modified physical-chemical properties in comparison with its bulk. Inexpensiveness, excellent chemical stability, nontoxicity, high photo-catalytic property, a wide band gap and high refractive index of TiO₂ make it attractive for practical applications [6],[7]. In particular, doping with lanthanide metal ions, such as neodymium (Nd³⁺), has been shown to increase the photocatalytic efficiency for selected reactions [8]-[11]. Therefore, it is critical to assess the effects of lanthanide-ion doping on the structure of titania which will allow greater control over the desired properties. The effective ionic radii of Ti³⁺ and Nd³⁺ are 0.605 and 0.983 Å, respectively [12]. Therefore, any substitution of an neodymium ion for a titanium ion in the TiO₂ lattice would introduce a distortion. Burn et al [11] show that a distortion occurs only along the c-axis of anatase TiO₂ with a maximal distortion at 0.1 mol% Nd³⁺ and no further response at higher concentration. This is due to a combination of interstitial and substitutional accommodation of the dopant ions. The interstitial neodymium does not affect the charge balance in the anatase lattice, as a substitutional neodymium does. Thus, interstitial dopants do not affect the photocatalytic properties of the nanoparticles since they cannot act directly as trapping sites to enhance the carrier lifetime.

Figure 1 depicts the energy level diagram of Nd:YAG. Stark splitting of the manifolds are shown on the right-hand side. Each of the 2S+1L J manifolds is split by the crystal field into J + 1/2 sublevels. The actual laser transitions occur between these individual Stark levels. The heavy line in Fig. 1 indicates the main laser transition in Nd:YAG having a wavelength of 1064 nm. The dashed lines represent transitions leading to 1.3 μm and 946 nm radiations [13].

Figure 2 shows the fluorescence spectrum of Nd³⁺ in YAG near the region or the laser output with the corresponding energy levels for the various transitions.

Unlike many crystals, the concentration of the active ions can be very high in glass. The practical limit is determined by the fact that the fluorescence lifetime and, therefore the efficiency of stimulated emission, decreases with higher concentrations. In silicate glass, this decrease becomes noticeable at a concentration of 5% Nd₂O₃. Figure 3 shows a simplified energy level diagram of Nd:glass. The Nd³⁺ ion in glass represents a four-level system. The upper laser level indicated in Fig.3 is the lower-lying component of the ⁴F₃/₂ pair with a several hundred microsecond spontaneous emission lifetime. The terminal laser level is the lower-lying level of the pair in the ⁴I₁₉/₂ multiplet. The ⁴I₁₁/₂ group empties spontaneously by a radiationless phonon transition to the ⁴I₉/₂ ground state about 1950 cm⁻¹ below [13].
Figure (1): Energy level diagram of Nd:YAG. The solid line represents the major transition at 1064 nm, and the dashed lines are the transitions at 1319, 1338, and 946nm [13].

Figure (2): Fluorescence spectrum of Nd\(^{3+}\) in YAG at 300 K in the region of 1.06 μm [13].

2. EXPERIMENTAL

2.1 Samples Preparation

Sol-gel process was used for preparing Titanium dioxide nanostructures bulk because it is capable of producing highly homogeneous metal oxide nanoparticles as well as its facility for dopant addition [1]-[5]. The doped and un-doped titania nanoparticles were synthesized from Titanium (IV)-iso-propoxide (TTIP) (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 (TTIP) and preparation of pure and doped TiO\(_2\) sol. The final solution was left for 30 minutes under magnetic stirring. 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 TTIP:H\(_2\)O:EtOH:HCl=1:1:10:0.1 in molar ratio. The gelation of monoliths was achieved by pouring the sol into covered glass tube at room temperature. After aging for 24 hour, first drying occurred for 1 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 with Nd\(^{3+}\) was equal to 5% wt.
2.2 Samples characterization

Structural characterizations of the doped and un-doped TiO$_2$ samples were done by X-ray diffraction (XRD). $\theta$–$2\theta$ scans were recorded using ITAL-STRUCURE diffractometer equipped. While Mid-IR spectra were obtained for the prepared samples using FT-IR spectrometer, Shimadzu, on KBr pellets of the samples.

Absorbance 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 Absorbance and emission spectra were measured for Nd:YAG crystal to obtain a standard measurements.

3. RESULT AND DISCUSSION

X-ray diffraction analyses show that doped and undoped prepared samples have amorphous structure [11]. The FTIR spectra for the sample were illustrated in figure (4). The peaks at 667 cm$^{-1}$, 505 cm$^{-1}$ and 447 cm$^{-1}$ are attributed to Ti–O bond. The peak at 667 cm$^{-1}$ refers to symmetric O–Ti–O stretch while peak at 447 cm$^{-1}$ and 505 cm$^{-1}$ are due to the vibration of Ti–O bond [14]. Another two bands were appeared at about 1600 cm$^{-1}$ and 3400 cm$^{-1}$. These two absorption bands are attributed to the characteristics vibration of O–H bond in water molecules [15], and indicating that the drying process at 60ºC does not completely trap the water molecules from the pores of titania network.

UV/Vis Absorbance spectrum, at room temperature, of Nd$^{3+}$ doped monoliths are presented in figure (5). 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 Absorbance spectrum of rare earth ions was due to electronic transitions caused by the energy level. For the Nd:YAG, the absorption bands in the range of 500–850 nm corresponded to the energy level transition of $^4$I$_{9/2}$→$^2$G$_{9/2}$ (513 nm), $^4$I$_{11/2}$→$^2$G$_{7/2}$, (530 nm), $^4$I$_{9/2}$→$^2$G$_{5/2}$, (588 nm), $^4$I$_{9/2}$→$^4$F$_{5/2}$ (680 nm), $^4$I$_{9/2}$→($^4$F$_{7/2}$, $^2$S$_{1/2}$) (735nm, 747nm) and $^4$I$_{11/2}$→($^4$F$_{5/2}$, $^2$H$_{5/2}$) (795, 807nm), respectively[13],[16]. For Nd$^{3+}$:TiO$_2$ sample, the Absorbance bands in the range of 500–850 nm corresponded to the energy level transition of $^4$I$_{9/2}$→$^2$G$_{9/2}$ (509nm), $^4$I$_{9/2}$→$^2$G$_{7/2}$ (530nm), $^4$I$_{9/2}$→$^2$G$_{5/2}$ (580nm), $^4$I$_{11/2}$→$^4$F$_{5/2}$ (680nm), $^4$I$_{9/2}$→$^4$F$_{7/2}$ (747nm) and $^4$I$_{9/2}$→$^4$F$_{5/2}$ (793nm)[16].

By comparison between two absorption spectra, it was noted that some peaks of titania dopant sample are mismatching with the peaks of Nd:YAG. That’s main the titania medium effect on the energy level of Nd$^{3+}$ and forced the energy level to split into a sublevel difference from known sublevel of Nd in YAG. It’s clearly seen that the absorption peaks band width of Nd:TiO$_2$ are widely while Nd:YAG have a narrow absorption peaks. That’s because of amorphous structure of TiO$_2$ prepared sample. The important result from the absorption spectra is that the titania dopant sample could be optically pumped in similar way of Nd:YAG optical pumping.

An important performance indicator for the sample to be useful for laser applications is its fluorescence properties. To determine the optical characteristics of the samples, photoluminescence measurements were carried out using the 795nm/1W Laser Diode for excitation. The obtained fluorescence spectra are shown in Figure 6. The fluorescence peaks location for Nd:YAG and Nd:TiO$_2$ are close with that result given by text books[13] and other researches[17],[18] respectively.

![Diagram](image-url)
According to figure 1 and 3, it can note that Stark components corresponding to manifolds $^4I_{9/2}$ and $^4I_{11/2}$ of Nd$^{3+}$ are strongly changed when the host medium changed, while energy sublevels R2 have a slightly change and its value around 11500 cm$^{-1}$. At room temperature and according to Boltzmann’s law, Lasing takes place only by R2 ions whereby the R2 level population is replenished from R1 by thermal transitions. For Nd:YAG the value of energy sublevel of R2 equal to 11507 cm$^{-1}$[13]. Because of Nd:TiO$_2$ sample have amorphous structure just like Nd:glass, we will assume that R2 for Nd:TiO2 have same value to Nd:glass. The value of energy levels can now calculated to various transitions which corresponding to fluorescence peaks of Nd$^{3+}$ in YAG and TiO$_2$ (figure 6).

Table 1 present wavelength, transitions and energy sublevels which corresponding to fluorescence peaks of Nd$^{3+}$ in YAG and TiO$_2$.

<table>
<thead>
<tr>
<th>Nd:YAG</th>
<th>Nd:TiO$_2$</th>
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<tbody>
<tr>
<td>Wavelength</td>
<td>Energy level</td>
</tr>
<tr>
<td>879nm</td>
<td>130 cm$^{-1}$</td>
</tr>
<tr>
<td>939nm</td>
<td>857 cm$^{-1}$</td>
</tr>
<tr>
<td>1063nm</td>
<td>2099 cm$^{-1}$</td>
</tr>
<tr>
<td>1111nm</td>
<td>2489 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Figure 6: fluorescence spectra for: (A) Nd:TiO$_2$ sample and (B) Nd:YAG Crystal.
The measured and calculated parameters to Nd:YAG are close to known parameters of Nd:YAG crystal [13]. That’s gives a good indication about the accuracy of both of fluorescence spectra and the parameters which measured and calculated to doped prepared sample.

Figure 7 depicts the energy levels diagram to Nd$^{3+}$, the values of energy levels are obtained from figure1, figure3 and table 1 to Nd$^{3+}$ in YAG, Glass and TiO2 respectively.

From table 1, it can noted that Nd:TiO$_2$ parameters dose not matching with Nd:YAG parameters. That’s means the crystal field of TiO$_2$ effect on Stark components corresponding to manifolds $^4$I$_{9/2}$ and $^4$I$_{11/2}$ of Nd$^{3+}$ and forced it to split into energy sublevels which it quietly difference to that known energy sublevels of Nd$^{3+}$ in YAG or glass. Figure 7 prompt this result.

**CONCLUSION**

The Nd$^{3+}$ doped Nanotitania is successfully prepared by wet chemical synthesis method. The doped and undoped prepared Nanotitania samples have amorphous structures. The energy levels manifolds 4I9/2 and 4I11/2 of Nd$^{3+}$ effected by crystal field of TiO2 and split to energy sublevels which it quietly difference to that known energy sublevels of Nd$^{3+}$ in YAG or glass. The absorption and emission spectra of Nd:TiO$_2$ sample are close similar to absorption and emission spectra of Nd:YAG crystal. This suggests that it could use Sol-Gel technique to prepare of Nd:TiO$_2$ 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.