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Prepared of Nd:TiO_2 via Sol-Gel technique

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ABSTRACT

Nd^{3+} 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 spectroscopic properties of doped samples. A Judd-Ofelt analysis is performed to calculate the optical properties of Nd^{3+} ions embedded in TiO2 and compare it with optical properties of Nd:YAG crystal. The doped prepared sample have a high peak emission cross-section σ_p. This suggests that it could use Sol-Gel technique to prepare of Nd:TiO_2 as solid state Laser active medium.

Keywords: Sol-Gel; TiO_2; 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 (TiO_2). Nanosized titanium dioxide materials have been the focus of great interest because they exhibit modified physical-chemical properties in comparison with its bulk [5,6]. Inexpensiveness, excellent chemical stability nontoxicity, high photo-catalytic property, a wide band gap and high refractive index of TiO_2 make it attractive for practical applications [7,8]. The uses and performance for a given application are strongly influenced by the crystalline structure, the morphology and the size of the particles [5].

The optical and electronic properties of nanostructured TiO_2 can be tailored by a variety of measures, including thermal treatments [9], supported film growth [10], and metal-ion doping [11]. In particular, doping with lanthanide metal ions has been shown to increase the photocatalytic efficiency for selected reactions [12-16]. 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. Doping of TiO_2 with neodymium ion would introduce a distortion in TiO_2 lattice, that's because of the deference in effective ionic radii of Ti^{4+} and Nd^{3+} (0.605 and 0.983 Å, respectively [17]). Burn et [14] show that a distortion occurs only along the *c*-axis of anatase TiO_2 with a maximal distortion at 0.1 mol% Nd^{3+} 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.

Sol-gel process is one of the most successful techniques for preparing nanocrystalline metallic oxide materials due to low cost, easy of fabrication (flexibility) and low processing temperatures [3-6]. Generally, in a typical sol-gel process, a colloidal suspension or a sol is formed due to the hydrolysis and polymerization reactions of the precursors, which on complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. The wet gel can be converted into nanocrystals with further drying and hydrothermal treatment [18-19].

The purpose of this paper is to report a new laser host material based on TiO_2. Major optical properties are determined from the absorption and the emission spectra to evaluate the performance of TiO_2 host material doped with Nd^{3+} for optical amplifier and laser application.

2. EXPERIMENTAL

2.1 Samples Preparation

The doped and un-doped titania nanoparticles were synthesized by sol–gel method 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:H2O: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+} is equal to 1% wt.

2.2 Samples characterization

Structural characterizations for prepared samples were done by X-ray diffraction (XRD). θ–2θ scans were recorded using ITAL-STRUCTURE diffractometer equipped. 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 monochromatore. 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 X-ray diffraction spectrums (XRD) were illustrated in **Figure 1**, and show that doped and undoped prepared samples have amorphous structure [14,19].
FTIR spectrums for the sample were illustrated in **Figure 2**. 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 [20-22]. 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 [22], and indicating that the drying process at 60ºC does not completely trap the water molecules from the pores of titania network.

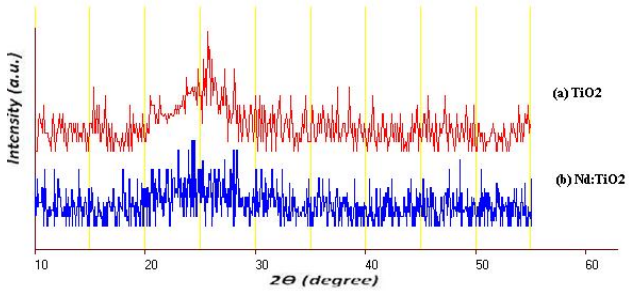

Figure 1: XRD spectrums for prepared samples, (a) TiO2; (b) Nd:TiO2.

The room temperature UV-VIS-NIR absorption spectra of the Nd^{3+} doped monoliths sample are presented in **Figure 3**. The spectrum of Nd:YAG crystal is given for comparison. It was found that all absorption bands of Nd^{3+} in TiO_2 are close similar to absorption bands of Nd^{3+} in YAG crystal hosts [12-13,23,24].
Photoluminescence measurements to Nd:TiO_2 and Nd:YAG crystal were carried out using the 795nm Laser Diode for excitation. The obtained spectrums between 850 and 1150nm are shown in **Figure 4.** The fluorescence spectrum of doped sample is somewhat close similar to Nd:YAG fluorescence spectrum [12-13].

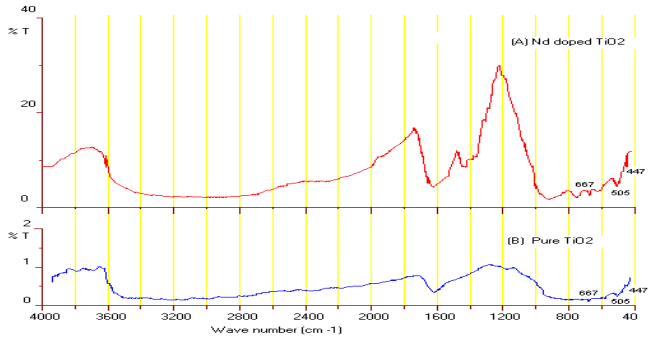

Figure 2: FTIR spectrums for doped and undoped samples.

(A) Nd doped TiO_2.
(B) Pure TiO_2.

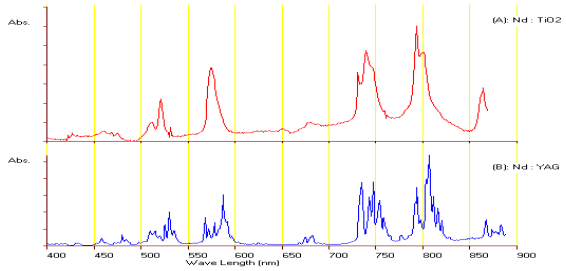

Figure 3: Absorption spectrums for:

(A) Nd:TiO_2.
(B) Nd:YAG Crystal.

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 [25]:

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

where J is the total angular momentum of the initial ground manifold, found from the $^{2S+1}L_J$ designation. $\sigma(\lambda)$ is the absorption cross section as a function of wavelength λ. The absorption bands were chosen to determine the phenomenological Judd-Ofelt parameters [25-27]. The J-O parameters for Nd:YAG crystals and Nd:TiO_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 [25]:

$$S_J^2 = \sum_{i=1}^{3} M_{ij} \Omega_i \quad ----(2)$$

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 [28-29].
The radiative transition probabilities $A(J;J')$, are given in Eq. (3) [25], were obtained with the line strength for the excited $^4F3/2$ to $^4I_{J'}$ manifold for Nd^{3+}

$$A(J;J') = \frac{64\pi^4}{3h(2J+1)\lambda^3}\left[\frac{n(n^2+2)^2}{9}\right] S_{ed} \quad ---(3)$$

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 [30]:

$$\sigma_{em} = \frac{\lambda_p^4}{8\pi c \Delta\lambda_{eff}} \frac{A(J;J')}{(n(\lambda_p))^2} \quad -----(4)$$

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 TiO_2.

	Nd : YAG		**Nd : TiO_2**	
Transitions from $^4I_{9/2}$	$\bar{\lambda}$ (nm)	S_{m*10}^{-20} (cm^{-1})	$\bar{\lambda}$ (nm)	S_{m*10}^{-20} (cm^{-1})
$^2K_{15/2} + {}^2G_{9/2} + {}^4G_{11/2}$	481	0.233	460	0.1683
$^2K_{13/2} + {}^4G_{7/2} + {}^4G_{9/2}$	531	1.330	518	0.3844
$^2G_{7/2} + {}^4G_{5/2}$	588	2.335	575	0.8722
$^4F_{9/2}$	684	0.218	678	0.0671

$^4F_{7/2} + {}^4S_{3/2}$	748	3.072	739	1.1826
$^4F_{5/2} + {}^2H_{9/2}$	808	3.439	799	1.4031
$^4F_{3/2}$	882	0.345	866	0.3355
	Ω_2=0.72, Ω_4=2.208 and Ω_6=4.929		Ω_2=0.024, Ω_4=1.207 and Ω_6=1.858	

According to **Table (1) and (2)**, it can noted that λ for the absorption and fluorescence peaks of titania dopant sample are mismatching with the same peaks of Nd:YAG. That's main the titania medium effect on the energy level of Nd^{3+} and forced it to split into sublevel difference from the known sublevel of Nd:YAG. It's clearly seen that the absorption and fluorescence peaks band width of ND:TiO_2 are widely while ND:YAG have a narrow peaks. That's because of amorphous structure of prepared TiO_2 sample. The optical properties of Nd:YAG have a good agreements with other results[23-24], which gives a good indication about the accuracy of measured parameters to doped titania.
From **Table (1) and (2)**, it could note that spectroscopic properties of Nd:TiO_2 are close to spectroscopic properties of Nd:YAG crystal. This suggests that Nd^{3+} doped titanium dioxide material may be more favorable as laser material.

Table 2. Spectroscopic properties of Nd:YAG and Nd:TiO_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
	$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1063	11	1236	7.601
		1109	19	1070	4.617
Nd:TiO_2	$^4F_{3/2}\rightarrow{}^4I_{9/2}$	908	31	1735	2.035
	$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1011	15	1260	4.681
		1069	18	484	1.869

4. CONCLUSION

Nd^{3+} doped Nanotitania is successfully prepared by wet chemical synthesis method, and seems to be transparent and unbroken which due to the suitable sol-gel parameters used. The optical properties of doped samples are close similar to optical properties of Nd:YAG crystal. The Nd^{3+} doped Titania network have a high peak emission cross-section σ_p. This suggests that it could be use Sol-Gel technique to prepare of Nd:TiO_2 as solid state Laser active medium.

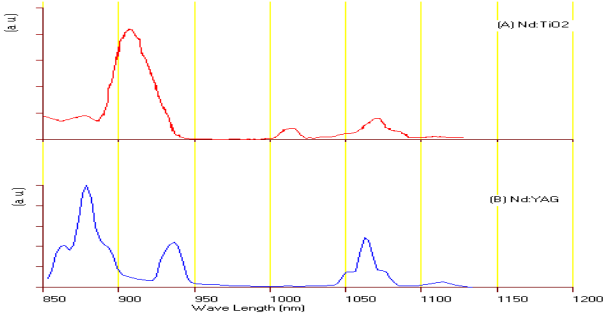

Figure 4: fluorescence spectrums for:

(A) Nd:TiO_2.
(B) Nd:YAG Crystal.

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