Physical properties and up-conversion development of Ho$^{3+}$ ions loaded in nano-composite silica titania thin film

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Abstract
Structural and fluorescence properties were investigated for different concentrations of Ho$^{3+}$ ions doped silica titania nano-composite thin films. These films were deposited on glass substrates at two different annealing temperatures 300 and 500 °C for 3 h. The obtained films were transparent, smooth and adhesive to the substrate glass surface. The crystallite sizes were in the nano-scale phase with values ranged from 15 to 20 nm. The average thin film thickness was found to be equal to about 1.7 μm. Blue, red and green up-conversion emissions are detected using 808 nm laser diode. The highest emission bands were observed in the doped film with 0.4 mol% of Ho$^{3+}$ ions. The prepared thin films could be considered promising candidates for higher efficiency up-down shifting solar cell, photonic, photo-catalytic and optical sensor applications.

1. Introduction
Silica–titania thin films have been gained great interest due to their role in solar cell, catalyst and photonic applications [1]. The most flexible method for the preparation of the silica–titania thin films is the sol–gel method which is suitable to adapt the uniform thickness of the prepared materials in addition to substrates variation [2, 3]. Silica has attracted high interest due to its physicochemical properties such as higher thermal stability, high surface area, low refractive index, good transparency, adsorption capacity and solubility of rare earth ions [4–6]. In general the refractive index improvement of the optical thin films has been used in many optical applications, such as photonic crystals, optical fibers, bio-sensing technology and wave guides. On the other hand, TiO$_2$ was often selected to dope with different materials due to their excellent chemical resistance, a high refractive index and high transparency to visible light [7, 8]. In addition TiO$_2$ has attracted interest due to their wide optical properties, photovoltaic cells, gas sensors and photo-catalytic applications. However it has some serious drawbacks, due to decreasing surface area and thermal instability [9]. When Titania composites are used instead of pure titania, the surface area has further more increased [10] and Titania addition outcomes in the refractive index increase [11].

In fact, Rare earths (RE) loaded in different hosts have gained much potential curiosity in consequence of their smart optical and physical properties. Luminescence of RE can be divided according to down conversion or up conversion; where the latter one corresponding to be able to emit shorter wavelength light as a result of long wavelength excitation. This phenomenon has applications in optical devices such as optical amplifiers, optical data storage, color display, under-sea optical communications, biomedical diagnostics and sensors, etc [12]. The up conversion photoluminescence (UPL) of many lanthanide ions doped different glass materials have been fascinating among the rare earth ions. The Ho$^{3+}$ ion is one of the most important active ions, due to its favorable energy level structure [13, 14]. It shows strong luminescence at various wavelengths including the visible region [13] and has been widely studied due to laser action at visible and infrared regions.

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In this work, we have prepared Silica–Titania (ST) thin film as host materials and doped with different Ho$^{3+}$ ion concentrations. Thin films were prepared by modified sol-gel technique using home-made spin-coating equipment. The optical, structural and morphological studies were evaluated by means of x-ray diffraction XRD, field emission scanning electron microscope (FESEM), and energy dispersive x-ray (EDX) analysis, and photoluminescence measurements. The obtained data indicate that the prepared thin film samples are suitable for optical sensor, photonic, and higher efficiency up-down shifting solar cell applications.

2. Experimental

2.1. Material

The chemical reagents used for the Silica–titania oxides ST preparation and ST co-doped with Ho$^{3+}$ ions at different contents (0.4, 1, and 1.4 mol% Ho$^{3+}$ ions) are listed in Table 1. Tetraethylorthosilicate (TEOS) (C$_4$H$_9$O)$_4$Si, Titanium(IV) n-butoxide Ti(OCH$_2$CH$_3$)$_4$, and Holmium nitrate hydrate Ho(NO$_3$)$_3$.H$_2$O were the precursors used for obtaining SiO$_2$, TiO$_2$, and Ho$^{3+}$ ions respectively. Table 1 shows the compound, chemical form, molecular weight and purity of the used materials. Silica–titania oxides (SiO$_2$–TiO$_2$) were refereed as ST and ST co-doped with Ho$^{3+}$ ions thin films at different concentrations (0.4, 1, and 1.4 mol% Ho$^{3+}$ ions) were refereed as; [ST0.4HT, ST1HT and ST1.4HT], respectively.

2.2. Thin films preparation

2.2.1. Preparation of Silica–titania (SiO$_2$–TiO$_2$) nano-composite doped with different concentrations of Ho$^{3+}$ ions

Nanocomposites silica–titania thin films containing (90 mol% SiO$_2$–10 mol% TiO$_2$) were prepared using a modified sol gel technique. First, the tetraethyl orthosilicate (TEOS) was dissolved in ethanol (CH$_3$CH$_2$OH) solution, then hydrolyzing under vigorous stirring after dissolved in distilled water (H$_2$O) and HCl was added whereas a catalyst. In order to have solutions with constant concentration of Si/Ti molar ratios; 90/10, the obtained solution was stirred for 1 h at room temperature. The Ho$^{3+}$ ions were introduced in the process, by dissolving Ho (NO$_3$)$_3$.H$_2$O in the obtained solution with different molar ratios (0.4, 1 and 1.4 mol%), respectively and stirred for another 30 min giving solution (S1). Then the ST was doped with different concentrations of Ho$^{3+}$ ions as follow (0.4, 1 and 1.4 mol% Ho$^{3+}$), Titanium (IV) n-butoxide dissolved separately in acetyl acetone solution and stirred for 30 min solution then was added to the obtained solution giving solution S2. The final solution S2 was left to react under vigorous stirring for 24 h at RT to increase the solubility of the mixture. The final used mixture solution was homogeneous, transparent, clear, and no precipitates appeared.

2.2.2. Preparation of thin film Silica–Titania nano-composite doped with Ho$^{3+}$ ions

The prepared solutions were spun at 3500 rev./min for 30 s on glass substrates by using a home-made spin coater. Two successive coatings were required to provide suitable effective film thickness. The film samples were dried and then heated at 300 and 500 °C, respectively for 3 h. The prepared films are free of cracks, homogeneous, clear, and transparent thin films refereed as [ST0.4HT, ST1HT, and ST1.4HT], respectively.

2.3. Characterization

2.3.1. XRD analysis

X-ray diffraction (XRD) patterns of the prepared samples were recorded with an x-ray diffractometer using monochromatized CuK$_\alpha$ radiation of wavelength $\lambda = 1.54056$ Å. Crystallite sizes G were determined from the Scherer’s equation [15]:

$$G = \frac{K \cdot \lambda}{D \cdot \cos}$$
Where $K$ is the Scherer constant (0.89), $\lambda$ is the wavelength, and $D$ is the full width of the peak at half maximum intensity (FWHM) (in radians) and $\theta$ is the diffracted angle.

2.3.2. FESEM and EDX
Field emission scanning electron microscopy (FESEM) with energy dispersive x-ray (EDX) analysis provided with variable pressure FESEM instrument (FEI, model: Quanta 250 FEG), equipment operating at 35 kV employed in the present work.

2.3.3. Refractive index measurement
The refractive indices of the prepared samples have been measured using PTR 46X refractometer at 589 nm (Sodium Yellow lamp). The monobromonaphthalene were used as the contact layer between the sample and prism of the refractometer. The devise can measure refractive index from 1.32 to 1.68.

2.3.4. The optical measurements
Transmission spectra were measured in the range between (350 and 1650 nm) using JASCO V-570 UV/VIS/NIR spectrophotometer. The instrument specified by resolution 0.1 nm and wavelength accuracy $\pm 0.3$ nm (at a spectral bandwidth of 0.5 nm). The measurements were made on glass, immediately after glass preparation and all spectra were measured at room temperature.

2.3.5. Photoluminescence measurements
Photoluminescence was measured under excitation with 808 nm continuous laser diode. The laser is chopped via chopper at 900 Hz. the emission is collected to monochromator 750 M, the emission were detected using a photomultiplier tube and lock-in amplifier SR510 was used for amplification. All measurements were done at room temperature at the same geometrical conditions.

3. Results and discussion

The XRD patterns of (a) ST, (b) ST0.4HT and (c) ST1HT heated at 500 °C for 3 h were shown in figures 1(a)–(c). As suggested by other authors it was clearly seen that a mixed intensity crystalline phases of anatase (A) and rutile (R) [15] appeared in all samples at $2\theta^\circ$ = (25.2, 36 and 53.9°) (A) and (27.4°) (R) assigned to different preferred orientations at ((101), (103) and (105)) (A) and ((110) (R)), respectively. Planes of tetragonal structure TiO$_2$ is in agreement with [JCPDS 77-0440 and 21-1272] cards. It was observed that there is no obvious phase appeared, referring to Ho$^{3+}$ ions, then these rare earth ions are completely dissolved and embedded in the SiO$_2$–TiO$_2$ crystal lattice host material. The obtained data are compatible with the previously reported by Li. Et. Al., [16] who suggested that the Rutile phase did not appeared before 600 °C.

Moreover it appears a peak at $2\theta^\circ$ = 22.5° assigned to (101) attributed to tetragonal structure of alpha cristobalyte phase SiO$_2$ which is in agreement with [JCPDS 82-1557] card.
As introduced by other researchers, in general the rare earth dopants influence the transition to rutile from anatase TiO$_2$ phases as a result of perturbation in the crystal nucleation process for either interstitial or substitutional dopant ions embedded in the different host materials lattice [17, 18]. In fact, the rare earth ion doped in the TiO$_2$ internal structural causes distortions in the lattice site as a result of the large difference in ionic radii between Ho$^{3+}$ (0.9 Å) and Ti$^{4+}$ (0.68 Å). Furthermore, an internal stress in the crystal which associated with coarse and fine grains in the prepared thin film samples, may causes a decrease in the crystallite sizes, giving the following values follows 20, 19 and 15 nm respectively for ST, ST0.4HT, and ST1HT.

3.1. FESEM characterization

Figures 2(a) and (b) shows the FESEM surface morphology (a) and the cross section view (b) of the ST1.4HT as a representative sample annealed at 500 °C for 3 h. From figure 2(a) it is observed that the film is crack free, uniform, homogeneous and dense. Smooth surface properties indicated a good adhesion and regularity among the two layers of the prepared film at 500 °C. While from figure 2(b) it is detected that it exhibited higher thickness with average value equal about 1.69325 μm.

Figure 3 indicates the Si, Ti, Ho and O elements presence in the nano-composite ST1.4HT thin film sample confirming high purity film quality by using dispersive x-ray analysis (EDX) analysis. The EDX spectrum of the ST1.4HT sample shows a high-intensity peaks corresponding to Silica, Oxygen and Titanium elements. A smaller peaks attributed to Ho element can be observed.

Table 2 illustrates the dispersive x-ray analysis (EDAX) spectrum of the ST1.4HT sample and its atomic, weight and oxygen ratios. Higher intensity peak was detected for the Silica host material. The Oxygen and Ti elements possess smaller intensity peaks than silica; however the Ho element shows a very weak intensity in comparison with the other elements. The obtained data confirming that no impurities are present in sample, which is highly suitable for optical, photonic, photocatalytic and sensing applications.

3.2. Refractive index $n$ of nano-composite ST, ST0.4HT, ST1HT and ST1.4HT thin film

The measured refractive indices ($n$) of ST, ST0.4HT, ST1HT and ST1.4HT are shown in table 3. Their values increased at higher Ho$^{3+}$ ions concentrations. The measured values were 1.5181, 1.519, 1.587 and 1.6446 nm for the above mentioned series respectively. The obtained increase in $n$ values by increasing the Ho$^{3+}$ ions concentration are attributed to the materials densification and condensation processes. When the titanium and Ho$^{3+}$ ions are present in the silica- gel Si–O–Si bonds broken appeared and the non-bonding oxygen (NBOs) is present, subsequently increasing the network molar volume structure. However, by increasing the Ho$^{3+}$ ions concentration; ($n$) linearly increased as a result of chemical structure change, densification, re-arrangement and re-crystallization of the nano-composite silica titania.

![Figure 2. FE-SEM micrographs of ST1.4HT annealed at 500 °C in the air for 3 h.](image-url)
3.3. The optical properties

Figure 4 shows the Transmittance (%) for (a) ST0.4HT, (b) ST1HT and (c) ST1.4HT, respectively annealed at 500 °C for 3 h. The observed spectra in figure 4 confirmed good transparency for the prepared films; Films have high transmittance (%) ranging from about 97% up to more than 99% in the wavelength range between 300 and 900 nm for the prepared films annealed at 500 °C. It is observed that the ST0.4HT transmittance is the highest among all the transmittance prepared films equal to or bigger than (99%) at the wavelength equal to 400 nm.

The transmittance decreased as the Ho³⁺ ions concentration increased up to 1.4 mol.%, due to the density increase at the highest Ho³⁺ ions concentration. The obtained results were compatible with the previously reported [19]. The higher transparency percent appeared in figure 4 can be considered as one proof that the prepared films are suitable for the low losses active waveguide and photonic fabrications.

3.4. Factors affecting the photoluminescence spectra (UC)

3.4.1. Effect of temperature on the ST0.4HT (UC) emission

UC Emission intensity is affected by annealing temperatures. Figure 5 shows that, the UC intensity was very weak when the ST0.4HT sample is annealed at 300 °C. While the annealing temperature was increased up to 500 °C, the UC intensity was increased. The obtained data might be due to the increase in heating effect hence the presence of hydroxyl bonds (OH) is decreased [20].
3.4.2. Effect of increasing Ho³⁺ ions concentration on the up-conversion emission (UC)

Figure 6 shows up-conversion emission (UC) spectra of ST0.4HT, ST1HT, and ST1.4HT annealed at 500 °C under 808 nm excitation with power 415 mW at room temperature [14, 21–24]. Blue, green and red up-conversions were observed. The emission band near 442 nm (blue) is assigned to the (5G6 → 5I8) transitions [24], while the red and green bands are observed at (604 & 644) nm for the former and 562 nm for the latter. These emission bands are corresponding to (5F5 → 5I8) and (5F4, 5S2 → 5I8) intra-4 F - transitions respectively [13, 14, 25].

The red and green bands emissions are comparatively weak compared to the blue bands. It is observed that the intensity of blue transition is the highest among all the transitions in all the prepared samples. Then one can conclude that the optimum concentration is ST0.4HT for up-conversion [22]. The factors that influence the up-conversion are mainly both the concentration and hydroxyl quenching phenomena. When the critical distances of rare earth ions are broken, a cascade effect will happen. The energy is transferred from one center to another [22], moreover the emission is weaken. That is the reason why the fluorescence intensity of ST1HT and ST1.4HT are lower than that of ST0.4HT. Furthermore, it is reported previously that the vibration of OH groups (2450-3700 cm⁻¹) matches with the maximum phonon energy of silicate (∼1067 cm⁻¹), covers the energy gap inducing non-radiative transitions result in weak emission [22, 26, 27].

Figure 7 shows the relationship between PL intensity and power of pumping laser of (a) ST0.4HT, (b) ST1HT and (c) ST1.4HT, the PL intensity is increased as the laser power is increasing for all the investigated samples.
Figure 6. UC emission of nano-composite thin film annealed at 500 °C (a) ST0.4HT, (b) ST1HT and (c) ST1.4HT excitation under 808 nm laser diode at 415 mW.

Figure 7. The UC emission intensity variation as a function of input powers of (a) ST0.4HT, (b) ST1HT and (c) ST1.4HT, while (d) is the emission intensities 442, 564 and 604 nm as a function of Ho$^{3+}$ ions concentration, annealed at 500 °C for 3 h.
Figure 7(d) shows up-conversion emission intensity as a function of increasing the Ho$^{3+}$ ions concentrations for ST0.4HT annealed at 500 °C for 3 h at the three 442, 564 and 604 nm. According to emissions spectra, the UC intensities of doped ST films were decreased slightly with increasing the Ho$^{3+}$ ions concentrations from 0.4% to 1.4%. The decrease in UC intensity because of filling the quenching sites [28].

Figure 8 Shows the schematic energy level diagram of up conversion processes in ST(0.4, 1&1.4) HT nano-composites. The obtained up conversion is due to the excited state absorption ESA processes of visible and red emissions of Ho$^{3+}$ ions upon excitation at 808 nm. The Ho$^{3+}$ ions are excited from $^5I_8$ ground state to $^5I_5$, by absorbing photons of 808 nm. Then the Ho$^{3+}$ ions in the $^5I_5$ state relaxes to the ground state non-radiatively and transfers its energy to another neighboring on the same state $^5I_5$, rising the latter to excited state $^5G_5$, from which $^5G_6$, $^5S_2$, $^5F_4$ and $^5F_3$ were populated through non-radiative relaxation. The ions radiatively relax from $^5G_6$ to the ground state giving rises to the blue emission band. The green emission is obtained through radiative transition from $^5F_4$, $^5S_2 \rightarrow ^5I_8$ level. The red emission near (604–644) nm is obtained through the following radiative transitions at $^5F_5 \rightarrow ^5I_8$.

4. Conclusions

The sol gel derived Silica-Titania (ST) doped Ho$^{3+}$ ions in the form of thin film were prepared by spin coating sol-gel method. The experimental details demonstrate that for consecutive spin coating depositions each layer should be annealed at 300 °C–500 °C to release residual stresses. The films are transparent, smooth and adhesive to the glass surface. The refractive indices were increased for SiO$_2$-TiO$_2$ nano-composite from 1.5 up to 1.64 while the crystallite size was decreased from 20 up to 15 nm as a result of increasing the holmium ions content. The average mean thickness of ST doped 1.4 mol.% of Ho$^{3+}$ ions is about 1.7 μm. The UC intensity of SiO$_2$-TiO$_2$ doped with Ho$^{3+}$ ions can be controlled or tailored by varying concentrations and annealing temperatures. The optimum concentration was 0.4 mol% of Ho$^{3+}$ while the best annealing temperature was 500 °C. In addition the ST0.4HT was the most transparent film among all the prepared samples. The photoluminescence measurements indicate that the SiO$_2$–TiO$_2$ films doped with Ho$^{3+}$ ions are promising materials for photonic and waveguide applications.

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