Up-conversion luminescence application in Er\(^{3+}\): TiO\(_2\) thin film prepared by dip coating sol-gel route

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Sol-gel derived nano-crystalline titanium dioxide films doped with 1 up to 5% Er\(^{3+}\) ions were prepared by dip coating sol-gel method. The coating sol was obtained by hydrolysis of Ti(OC\(_3\)H\(_7\))\(_4\) in ethanol/HCl solution. The FT-Raman and the X-ray diffraction (XRD) were carried out to determine the crystal structure of the prepared samples. The morphology SEM and the cross-sectional of the film were used to characterize the microstructure and the thickness of the prepared film. It is shown that relative homogeneous, crack-free and transparent film was achieved via dipping process at 500°C. After the excitation with laser diode at wavelength 808 nm, visible (Vis) and infrared (IR) up-conversion emissions were evidenced in the thin film samples under investigation. The up-conversion was found to depend strongly on the Er\(^{3+}\) ion concentrations. The visible emission was found to be at 540, 560, 590 and 640 nm for thin film. They are attributed to intra-4f transition of Er\(^{3+}\) ions and assigned to the \((^4I_{11/2} + ^4S_{3/2})\) and \(^4I_{9/2}\), which are populated through excited state absorption (ESA) for 808 nm excitation.

**Keywords:** Dip coating sol-gel technique, Thin film, Up-conversion, XRD, Anatase, FT-Raman

1 Introduction

Many studies have been reported on the preparation of amorphous and crystalline coatings using sol-gel process\(^{1,2}\). The relationships between physical properties, such as crystal structure, surface morphology, particle size, etc and photocatalytic of TiO\(_2\) have been studied\(^{3-5}\). To prepare porous films the sol-gel method, sputtering technique and spray pyrolysis\(^6\) were used. The sol-gel process is one of the most appropriate technologies for the preparation of thin oxide films. The microstructure of the gels, i.e. the crystallite size, the pore volume, pore size and surface morphology can be controlled by changing the composition of the precursor solutions and the sintering temperature\(^8\).

Visible up-conversion lasing at room temperature has already been achieved in thin film crystals\(^{9,10}\) doped with rare earth ions such as Er\(^{3+}\): TiO\(_2\) and Er\(^{3+}\): SiO\(_2\): TiO\(_2\). Previously, it was reported on the fluorescence around 1.53 \(\mu\)m of Er\(^{3+}\): TiO\(_2\) waveguides\(^7\) and on the first observation of blue, green and red up-conversion fluorescence in Er\(^{3+}\): TiO\(_2\) optical planar waveguides were prepared by a sol-gel process and a dip coating technique. Many Er\(^{5+}\) doped materials have been extensively studied for up-conversion process because of the fact that in the near infrared spectra region Er\(^{3+}\) has a favourable energy level structure with two transitions \((^4I_{15/2} \rightarrow ^4I_{9/2})\) at 810 nm and \((^4I_{15/2} \rightarrow ^4I_{11/2})\) at 980 nm being efficiently pumped with high power semiconductor lasers, yielding to blue, green and red emissions\(^11\).

One of the major advantages of the sol-gel process is the possibility to prepare multi-component systems\(^3,12\). Rare earth ions are used as dopants in glasses mainly for two reasons. In the first one is their well defined and sharp energy levels, which may serve as structural probes for the environment of the dopants, and the other one is the modifications of the energy level structure of the rare earth ions caused by the glassy environment may lead to interesting applications, e.g., solid state lasers\(^13\). The glass compositions are more favourable for high-density memory devices, because the inhomogeneous widths of the transition between the energy levels are much broader than those of crystals. In addition, the high transparency and easy mass production are also particularly promising for practical application in optical device\(^14\).

In the present work, nano-structure TiO\(_2\) thin film pure and doped with 1 up to 5% Er\(^{3+}\) ions using sol-gel technique, were successfully prepared by a simple
dip coating sol-gel method. The effect of increasing the concentration of Er$^{3+}$ ion on the up-conversion of the prepared samples was studied. The data are presented for the structure evolution of pure and doped samples by X-ray diffraction (XRD) and FT-Raman. The morphology of the prepared sample sintered at 500°C was characterized by SEM.

2 Experimental Details

2.1 Thin film preparation

Pure TiO$_2$ thin films doped with 1 up to 5 mol% Er$^{3+}$ ions were prepared by a modified sol-gel method using titanium butoxide (Ti(C$_2$H$_4$O)$_4$), acetic acid (AcOH) and isopropanol (PrOH). At first, the titanium butoxide was mixed with acetic acid, which acts as a modifier. This mixture has a lower hydrolysis / condensation rate which enhances the possibility of obtaining stable and clear sol for dip coating process. Reaction was allowed to continue for 1 h under vigorous stirring. In the second step, we add the isopropanol (PrOH) which reacts with acetic acid to generate water in-situ by homogeneous estrifrication reaction:

PrOH + AcOH → PrOAc + H$_2$O

In this case, each molecule of the modified alkoxide is coordinated with uniform distribution of reactant water molecules, thus enabling uniform hydrolysis to take place. The mixture was stirred for 1 h before use, the solution obtained is clear. Er$^{3+}$ ions were introduced by adding ErO$_3$ in molar ratio TiO$_2$:x ErO$_3$ (x = 1 up to 5 mol%). The erbium was introduced in the initial stage of the process by dissolving 1 up to 5 mol% of erbium oxide in nitric acid, resulting in a clear and light pink solution. The obtained solution was heated at 200°C till dryness. The solid left was dissolved in solution I prepared before to produce (solution II). The solution II obtained was filtered on a filter paper and remains stable for four days which is long enough for a multiple dip coating process. All these operations were performed at room temperature.

The Er$^{3+}$: TiO$_2$ were synthesized in thin films on silica substrates. Indeed, the silica substrates were carefully cleaned, then immersed into the mixture and withdrawn from the bath at a rate of 60 mm/min. The films obtained are first dried at 100°C for 15 min. At least 7 successive coatings were required to provide suitable effective film thickness. Then, the films were annealed in air in conventional oven at sintering heat treatment temperature 500°C for one hour.

The X-ray diffraction (XRD) patterns of the prepared samples were recorded with Philips X-ray diffractometer PW/1710; with Ni filter, with monochromatised CuK$_a$ radiation of wavelength 1.5418 Å at 40 kV and 30 mA. Crystallite sizes G were determined from the Scherrer’s equation ($G=\lambda/D\cos\Theta$), where $\lambda$ is the diffraction for a particular Bragg diffraction peak and $D$ is the (corrected) full width (in radians) of the peak at half - maximum (FWHM) intensity. The correction to the measured FWHM $D$s for a sample peak was made to accommodate systemic instrumental broadening and utilized peak widths $Dq$ measured from a diffraction scan, taken under identical conditions, from a strain-free powdered quartz sample, with crystallite size ranging between 5 and 10 µm. The corrected sample peak widths were calculated as $D = (Ds ^2 -Dq)^{1/2}$ Micro-strain and crystallite size contributions to $D$ were separated using the Win-Fit program, using standard samples for estimation of instrumental broadening. The final sample crystallite sizes $G$ were obtained by Fourier analysis, using the corrected profile. The diffraction peak used was the most intense diffraction peak of, assigned to the (101) reflection from the anatase phase, appears at $\Theta = 25^\circ$. FT-Raman spectrometer of the type BRUKER IFS 6/s with Nd–Yag laser wavelength 1064 nm as light source, was used in this investigation.

For PL measurement, the sample excited by the chopped laser diode at 810 nm ( mW) and the emission was analyzed by Spex 750 M monochromator (Gratting 1200) and detected with a photomultiplier tube. Incident beam power was 100 mW. The PL emission obtained using lock-in amplifier (SR 510-Stanford) technique and recorded by computer. The measurements were performed at room temperature.

3 Results and Discussion

Fig 1 shows XRD patterns of the 1 up to 5% Er$^{3+}$: TiO$_2$ thin films prepared samples, were heat treated at 500°C sintering temperature for one hour. Three weak peaks attributed to the main peak of the anatase phase appeared at 2 $\Theta = 25$, 37.5 and 49° of (101), (004) and (200) orientations, respectively in the prepared sample doped with 1% of Er$^{3+}$ ions. These results are in agreement with the results previously studied. The intensity of the mentioned peaks increases by increasing the Er$^{3+}$ ion concentrations up to 5%. No phase other than
anatase, such as rutil or crystalline SiO$_2$ (silica substrate) was found in the XRD patterns examined. This indicates that at 500°C the constituent crystallites of the film samples were anatase. The average crystallite size calculated from the broadening of the (101) XRD peak of TiO$_2$ doped with 5 wt% Er$^{3+}$ ions sintered at 500°C, using Scherrer's formula was about 5 nm.

Fig. 1—XRD patterns of TiO$_2$: 1 - 5% Er$^{3+}$ thin films, sintered at constant heat treatment temperature 500°C for one hour, (a) 1%, (b) 2%, (c) 3%, (d) 4% and (e) 5%, all prepared by dip coating sol-gel technique

Fig. 2 shows the FT-Raman spectra of the TiO$_2$ thin film doped with 1-5 wt% of Er$^{3+}$ ions, heat treated at constant sintering temperature 500°C. The peak at 50 cm$^{-1}$ is the boson peak, characteristic of the disordered glassy structure. The characteristic peaks of the titanium dioxide network are observed at the intense band 145 cm$^{-1}$ and two less intense bands at 518 and 637 cm$^{-1}$, characteristic for the anatase form$^{15, 16}$. It is observed that by increasing the doping ions concentration the intensity of the FT-Raman spectra of the doped samples increases. We expect that the atoms coalesce by increasing the dopant concentrations due to the increase in the density of the prepared films giving rise to increasing the scattering FT-Raman. Two anti-stokes bands were observed; a sharp one shifting to higher wave number with increasing Er$^{3+}$ ions concentration at 500 cm$^{-1}$, and a broader one at about 150 cm$^{-1}$. The intensity of both bands increases by increasing the Er$^{3+}$ ions concentration. They are presumed to be attributable to the host material.

Fig. 3 shows the excited state absorption (ESA) corresponding to the visible emissions of Er$^{3+}$ embedded in TiO$_2$ thin films upon excitation at 808 nm. The absorption in the intensity range 750 - 825 nm ($^4$I$_{15/2}$$\rightarrow$$^4$I$_{9/2}$) indicates that the laser diodes operating at 808 nm are the efficient pump sources for the green up-conversion emission.

When laser diode is tuned to a strong absorption, ($^4$I$_{15/2}$$\rightarrow$$^4$I$_{9/2}$) of Er$^{3+}$ ions ($\lambda$ = 808 nm), green and red photoluminescence from (2$^3$H$_{11/2}$ + $^4$S$_{3/2}$) and $^4$F$_{9/2}$ levels, respectively are observed at 540, 560, 590 and 640 nm as shown in Fig. 4. The peak intensities of the up-conversion emissions increase by increasing the concentration of the erbium ion embedded in the host material. The up-conversion was found to depend strongly on the Er$^{3+}$ ions and its peak intensities increase by increasing its concentration as a result of increasing the density at higher concentrations. It has been well addressed that the green emissions at 540, 560, 590 nm have been attributed to the transitions of Er$^{3+}$ ions and were assigned to the ($^4$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$) (560 and 590 nm) and ($^2$H$_{11/2}$$\rightarrow$$^4$I$_{15/2}$) (540 nm) respectively, and the red emission is attributed to a transition of Er$^{3+}$ ions assigned to ($^4$F$_{9/2}$$\rightarrow$$^4$I$_{15/2}$) (640 nm).

Fig. 5 shows the excited state absorption (ESA) processes of the green emissions of Er$^{3+}$ ions upon
excitations at 808 nm. To compare the green and red up-conversion, we can propose two mechanisms; First one for dominant green luminescence in which, the laser light brings the Er$^{3+}$ ion in to $^4I_{9/2}$ level, which then decays through a non-radiative process into the $^4I_{11/2}$ metastable levels and subsequently into the $^4I_{13/2}$ metastable level. Energy transfer processes bring the Er$^{3+}$ ion into ($^4F_{7/2}$) state from which ($^4S_{3/2}$) is populated through the non-radiative relaxation. The second mechanism is the red luminescence one, which is stronger than the green one in which, the laser beam brings the Er$^{3+}$ ion to the excited state $^4I_{9/2}$ level. One ion non-radiatively decays to the $^4I_{13/2}$ metastable level, and the second decays to the $^4I_{11/2}$ metastable levels. Energy transfer processes bring the Er$^{3+}$ ion to the $^4F_{9/2}$ and a red emission can be observed. The spin-allowed radiative transition from the preceding levels to the ground state gives rise to the visible up-conversion emission. The energy transfer (ET) between two close ions also takes place and plays a significant role in the up-conversion emission.

It is observed that the $^4F_{9/2}$ is predominantly excited in this material, observed for the high intensity of the $^4F_{9/2} \rightarrow ^4I_{15}$ transition. The probable mechanism that takes the high intensity of the red emission is shown in Fig. 6. The absorption 808 nm radiation results in the $^4I_{11/2}$ (Er) level, with population proportional to the

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**Fig. 3**—Excitation spectra of TiO$_2$: 1 - 5% Er$^{3+}$ thin films with 808 nm IR radiation in the range between 750 and 850 nm assigned to ($^4I_{15/2} \rightarrow ^4I_{9/2}$)

**Fig. 4**—Up-conversion emission spectrum from TiO$_2$: 1 - 5% Er$^{3+}$ thin films under 808 nm excitation, sintered at constant heat treatment temperature 500°C for one hour, (a) 1%, (b) 2%, (c) 3%, (d) 4% and (e) 5%, all prepared by dip coating sol-gel technique.
pump power. The de-excitation of the $^4\text{I}_{11/2}$ (Er) level, via no-radiation multiphonon relaxation, takes the population of the $^4\text{I}_{13/2}$ (Er) level. The absorption of the second photon (≈ 808 nm) promotes the excitation if the $^5\text{F}_{9/2}$ (Er) level, resulting in the red emission (≈ 640 nm). The predominance of the red emission in relation to green emission has been observed by Wang$^{17}$ in vitroceramic host. The ESA approach occurs only during excitation, whereas the ET can happen both during and after excitation.

Fig. 7 shows the SEM photograph, cross sectional view (down) and surface (up) appearance of TiO$_2$: 5\% Er$^{3+}$ thin films, sintered at constant heat treatment temperature 500°C for one hour. No cracks and flaking off from the substrate were observed. These results indicated that the heating treatment resulted in formation of dense and crack-free nano-structured TiO$_2$ film. The microstructure has a fine scale at this heat treated temperature. These microstructures might be due to condensation, strengthening and densification of the gel at higher temperature. The film thickness was found to be about ≈ 0.2 µm.

4 Conclusions

A simple home made dip coating sol-gel apparatus was successfully used in preparing TiO$_2$ co-doped with 1 up to 5 wt\% Er$^{3+}$ ions thin films to be applied as up-conversion. XRD study indicated that three weak peaks attributed to the main peak of the anatase phase appeared at 2\(\theta\) = 25, 37.5 and 49° of (101), (004) and (200) orientations, respectively in the prepared sample, their intensities increase with
increasing the Er$^{3+}$ ion concentrations. The FT-Raman analysis confirmed the data obtained from the XRD study. The morphology SEM and the cross-sectional of the film were used to characterize the microstructure and the thickness of the prepared film. It is shown that, relative homogeneous, crack-free and transparent film of (∼0.2 µm in thickness) was achieved via dipping process at 500°C.

The green and red up-conversion emissions were evidenced in the thin film doped with Er$^{3+}$ ions under investigation from ($^2\text{H}_{11/2} + ^4\text{S}_{3/2}$) and $^4\text{F}_{9/2}$ levels, respectively. The radiative decay from these levels to the ground state gives rise to the visible up-conversion emissions. The up-conversion was found to depend strongly on the Er$^{3+}$ ions and its peak intensities increase by increasing its concentration as a result of increasing the density at higher Er$^{3+}$ ion concentrations. We can conclude that the efficient ET can occur when two or more ions are sited closely or form a pair or cluster, resulting in almost immediate interaction between the ions.

References