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Rare-earth-doped wide-bandgap tin-oxide nanocrystals: pumping mechanisms and spectroscopy

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ABSTRACT

The present work displays a thorough study of the optical spectroscopy of multilevel RE-doped tin oxide nanocrystals. Our study provides the structural grounds about the behavior of the RE emission under site-selective excitation as well as the capability of the host to hold the RE ions at the nanocrystal lattice sites and, as a consequence, the possibility to reach the RE excited states by direct host excitation.

Keywords: Rare earth, wide band-gap semiconductors, site-selective laser spectroscopy, energy transfer.

1. INTRODUCTION

Metal-oxide semiconductors attract much attention due to their wide transparency in the UV-VIS and near IR regions, and to the possibility of being functionalized by rare-earth (RE) doping for optoelectronic and biomedical applications. Moreover, most of them can be easily nanostructured which opens new channels for both applied and fundamental research. Tin oxide (SnO₂) is a well-known wide band gap n-type semiconductor with potential applications as gas sensors, dye based solar cells, catalytic supports, and optoelectronic devices [1-4]. The light emission from the RE generally arises from intrashell transitions of 4f electrons which are, in first order, electric dipole forbidden. Hence, a resonant excitation of the RE leads to a weak luminescence efficiency. However, the possibility to obtain efficient host sensitization by energy transfer from the excited host to the RE ions is a convenient way to overcome the low absorption of Laporte f-f transitions.

The present work displays a thorough study of the optical properties of Nd³⁺ and Er³⁺ doped tin oxide nanocrystals. We have chosen two paradigmatic trivalent RE ions: neodymium and erbium. Both display a quite complicate energy level scheme, interesting enough from the fundamental point of view and at the same time, referring to potential applications, are two of the most important RE ions. Nd³⁺, as an emblematic source for stimulated emission as well as efficient near IR-VIS emitter for biomedical sensing and imaging, and Er³⁺ as a multi-colour UV-VIS-IR source of both linear and nonlinear emissions for telecommunications and biomedical uses in the domain of sensors (nano thermometers) and phototherapy. Our study provides a structural model explaining the role of the main host defects on the behavior of the RE emission as well as the capability of the host to hold the RE ions at the nanocrystal lattice and, as a consequence, the possibility to reach the RE excited states by direct host excitation and subsequent energy transfer.

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2. EXPERIMENTAL SECTION

Sets of nanocrystals of SnO_2 doped with Er^{3+} (0.2, 0.3, 0.5, 0.7, 1, 2, 5 mol %) or Nd^{3+} (0.2, 0.3, 0.5, 0.7, 1, 2 mol %) and co-doped with Er^{3+} (0.3, 0.5, 0.7 mol %) and Nd^{3+} (fixed to 1 mol %) have been prepared through a synthesis process involving firstly a sol-gel step, in which a colloidal suspension is formed, followed by the solvothermal treatment of the gel. The required stoichiometric amounts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, 98 % purity), $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or/and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Strem Chemicals, 99.9 % purity) were dissolved in ethanol (absolute ethanol, Emplura Merck) at room temperature with magnetic stirring, and the gel formation was achieved by dropwise addition of dilute NH_4OH to the above acidic solution, adjusting the pH value to 10. The gel was dried at 120 °C for 3 h, and then dispersed in absolute ethanol and transferred to a Teflon-lined pressure reactor, which was heated during 24 h to 185 °C. In each case the product resultant was collected by centrifugation and washed with ethanol several times, and then overnight dried at 120 °C. These solvothermal materials were subjected to further annealing at temperatures ranging between 400 °C and 1000 °C to remove defects typically associated to wet low-temperature synthesis methods, as oxygen vacancies and local lattice defects, and to promote their better crystallization [5], allowing us to test the associated possible improvement of the Er^{3+} and Nd^{3+} emission efficiency. The purity of the tetragonal cassiterite SnO_2 phase was verified in each case by 300 K powder X ray diffraction (XRD) performed in a Bruker AXS D-8 Advance diffractometer, using K_α radiation.

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images as well as energy dispersive X ray spectroscopy analyses were obtained using a JEOL JEM3000F microscope operating at 300 Kv.

Hydrodynamic particle size distributions by number, volume and intensity were measured by dynamic light scattering using a Vasco 2-Cordouan equipment.

Excitation spectra were recorded by using a FLS900 fluorescence spectrometer (Edinburgh Instruments Ltd, UK) equipped with a 450 W Xenon lamp. The emission was detected by Hamamatsu R928P and liquid nitrogen cooled Hamamatsu R5509-72 photomultipliers in the 470-750 nm and 650-1150 nm ranges respectively.

Site-selective steady-state emission and excitation spectra were recorded by exciting the samples with a continuous wave (cw) Ti:sapphire ring laser (0.4 cm^{-1} linewidth) in the 770–920 nm spectral range. The fluorescence was analyzed with a 0.25 m monochromator, and the signal was detected by an extended IR Hamamatsu H10330A-75 photomultiplier and finally amplified by a standard lock-in technique.

3. STRUCTURAL, COMPOSITIONAL AND MORPHOLOGICAL CHARACTERIZATION OF $\text{Er}^{3+}/\text{Nd}^{3+}$ -DOPED SnO_2 SAMPLES

XRD patterns collected for Er-SnO_2 , Nd-SnO_2 and Er,Nd-SnO_2 samples reproduce in all cases the scheme of Bragg reflections of the tetragonal $P4_2/mnm$ (136) cassiterite phase of SnO_2 , [6] that is, the described preparations have yielded the pure expected crystal phase. However, the full width at half maximum (FWHM) of observed Bragg peaks strongly depends on the subsequent thermal treatment applied to solvothermal samples. Figures 1(a-d) show the comparison of XRD scans for raw solvothermal non annealed 5% Er^{3+} - SnO_2 and for the three codoped $x \text{ Er}^{3+}$, 1% Nd^{3+} - SnO_2 ($x = 0.3 \text{ \%, } 0.5\%, 0.7\%$) samples after a same annealing process consisting in consecutive thermal treatments at 600, 800 and 875 °C during 1 h in each step. The FWHM of Bragg reflections of the above annealed samples experiences a clear narrowing with regards to that of the non annealed sample, which corresponds to an increase of the mean particle size value calculated using Scherrer's equation, namely from $D_{\text{XRD}} = 6 \text{ nm}$ for the solvothermal non annealed sample to 15-18 nm for the annealed samples. For the raw solvothermal sample the calculated D_{XRD} totally agree with D_{XRD} reported for previous hydrothermally prepared non annealed SnO_2 samples, whether from both reaction time and temperature similar to these in the current solvothermal synthesis [7], or from different reaction conditions [8]. Moreover, no difference in D_{XRD} associated to the composition can be appreciated among the three $x \text{ Er}^{3+}$, 1% Nd^{3+} - SnO_2 samples. On the other hand the increase of time up to 5 h in the thermal treatment at 600°C produces an additional reduction of FWHM, i.e., an enlargement on the particle size up to around 30 nm, but extended (up to 15 h) 600 °C isothermal annealings as well as successive thermal treatments at higher temperatures do not produce any additional FWHM reduction, that is, the size of the nanocrystal does not experiences further growth above 30 nm. In all early indicated D_{XRD} calculated sizes would

correspond to individual crystalline domains or ‘primary crystalline nanoparticles (NPs)’, also named crystallites, present in the prepared material. From these DRX results it seems that upon indicated performed annealings up to 875 °C the transformation of the microstructure of the initial solvothermal SnO₂ xerogel would have consisted on extensive dehydroxylation and decrease of the surface defects at the interface of agglomerated NPs, along with some particle size growth, and more importantly, with considerable improvement of the crystallinity of individual NPs [9,10]. However the larger growth, well above 50 nm, usually reported as the final state of high temperature annealed SnO₂ NPs [10], has not been currently reached.

Fig. 1. X ray diffraction patterns of solvothermal Ln-doped SnO₂ samples: a) The raw non annealed 5% Er- SnO₂ sample; samples annealed at 600 °C, 800 °C and 875 °C for 1 h in each step: b) Codoped 0.3% Er, 1% Nd- SnO₂; c) Codoped 0.5% Er, 1% Nd- SnO₂; d) Codoped 0.7% Er, 1% Nd- SnO₂; for comparison, the XRD pattern scheme of tetragonal *P42/mnm* (136) phase of SnO₂ (JCPDS File 88-0287) has been also included in e).

TEM images of all annealed Er³⁺,Nd³⁺-SnO₂ samples show NPs with similar pseudo-polygonal shapes, and sizes of around 20 nm for samples after short thermal treatments at up to 875 °C, Figure 2 (a,b), while those in samples with prolonged thermal treatments are typically larger, ≈40 nm, Figure 2c, all of them appearing agglomerated in some degree. HRTEM micrographs provide more precise insight into the morphology of these NPs, see Figures 3(a-d). HRTEM images reveal that Er³⁺/Nd³⁺-doped and Er³⁺,Nd³⁺-codoped SnO₂ NPs are very well crystallized, with observed prominent lattice fringes corresponding to distances of 0.334 nm and 0.264 nm, consistent with *d*-spacings for (110) and (101) planes of tetragonal SnO₂, respectively [6]. The achieved crystallinity improvement, while maintaining the nanosize of SnO₂ particles in these annealed samples, has been considered the better suitable approach for preparing SnO₂ particles with adequate luminescence efficiency. Measured energy dispersive X-ray spectra over individual NPs indicate Sn and O contents very close to the expected in SnO₂ and the presence of Nd and Er.

Fig. 2. TEM images of solvothermal nanocrystalline Er,Nd-SnO_2 samples: a) 0.3% Er, 1% Nd- SnO_2 annealed at 800 °C for 1 h; b) 0.5% Er, 1% Nd- SnO_2 annealed at 600 °C, 800 °C and 875 °C for 1h in each step; c) 0.3% Er, 1% Nd- SnO_2 annealed at 600 °C, 800 °C and 875 °C for 15 h, 10 h and 5 h, respectively.

Fig. 3. HRTEM images of solvothermal nanocrystalline pseudo-polygonal samples: For 0.3% Er, 1% Nd- SnO_2 samples: a) and b) after annealing at 600 °C, 800 °C and 875 °C for 1h in each step; c) 0.5% Er, 1% Nd- SnO_2 after annealing at 600 °C, 800 °C and 875 °C for 1h in each step. d) after annealing at 600 °C, 800 °C and 875 °C for 15 h, 10 h and 5 h, respectively, with a Fast Fourier Transform image in the inset.

3.1 Spectral reflectance

The diffuse reflectance of the samples has been measured by using a Cary 5 spectrometer with an integrating sphere. As an example, Fig. 4 shows the UV-VIS-NIR reflectance spectrum of $\text{SnO}_2\text{:Nd}^{3+}$ powders in the 200-900 nm spectral range for the sample doped with 1 mol% Nd^{3+} treated at 800°C-1h. The spectrum shows a strong absorption in the UV-blue range together with the peaks corresponding to the absorption from the $^4\text{I}_{9/2}$ ground state of Nd^{3+} to the upper excited states. The presence of Nd peaks in the spectrum confirm the incorporation of Nd^{3+} in the host matrix.

Fig. 4. Spectral diffuse reflectance of the sample with 1 mol% of Nd^{3+} .

3.2 $\text{SnO}_2\text{:Nd}^{3+}$: Direct Nd^{3+} excited state pumping

In this section we report the spectroscopic properties of Nd^{3+} ions in tin dioxide nanopowders under direct excitation in the $^4\text{F}_{5/2}$ and $^4\text{F}_{3/2}$ levels. The excitation spectra corresponding to the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2,5/2}$ transitions were obtained by collecting the luminescence at different wavelengths along the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ laser emission. The excitation spectra shows that Nd^{3+} ions can be directly excited. As an example, Fig. 5 shows the room temperature excitation spectra of the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2,5/2}$ transitions measured at 1064 and 1088 nm for a sample doped with 1 mol% treated at 800°C-1h. The spectrum at 1064 nm shows a glass-like behaviour with broad bands, however the spectrum obtained at 1089 nm shows superimposed to the broad bands, two sharp peaks at 826.5 and 902.3 nm which suggest the presence of different environments for Nd^{3+} ions in this matrix.

Fig. 5. Room temperature excitation spectra for a sample doped with 1 mol% treated at 800°C-1h obtained by collecting the luminescence at 1064 nm (black) and 1088 nm (grey).

In order to confirm the existence of different environments for Nd^{3+} ions, site-selective steady-state emission spectra for the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2,13/2}$ transitions were recorded by exciting at 805 nm and 826.5 nm. Figure 6 shows the emission spectra obtained under excitation at 805 nm and 826.5 nm (sharp peak in the excitation spectrum) for the sample doped with 1 mol%. The spectrum obtained under excitation at 805 nm shows broad bands similar to those obtained in glass samples which suggests the presence of neodymium ions occupying a broad distribution of glassy-like crystal field sites. However, the spectrum obtained under 826.5 nm excitation presents sharp peaks which indicates that Nd^{3+} ions are incorporated in a crystalline environment.

Fig. 6. Room temperature emission spectra for a sample doped with 1 mol% treated at 800°C-1h obtained under excitation at 805 nm (a) and 826.5 nm (b).

The excitation wavelength dependence of the emission spectra can be associated to the crystal field variations near the nanoparticle surface and/or crystallite interfaces where the crystalline order breaks. The crystalline component has the same structure as the one of a bulk crystal whereas the interfacial component due to random orientation of adjacent crystallites and the interface itself, shows a disordered character [11]. As a consequence, the dopants introduced in a nanocrystal may suffer the influence of different atomic species and surrounding symmetries. In general, we would expect at least two main kinds of responses, a sharp one related with normal crystalline material and another with a glassy-like character showing the inherent disorder associated to interfaces and surface boundaries.

3.3 $\text{SnO}_2\text{:Nd}^{3+}$: Indirect Nd^{3+} pumping

The NIR emission spectrum of Nd^{3+} has also been obtained in the 1000-1500 nm spectral range under UV excitation above the bandgap of SnO_2 at 266 nm. As can be seen in Fig. 7, the spectrum shows the bands corresponding to the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2,13/2}$ transitions which means that exciting the matrix UV photons are converted into NIR photons due to the energy transfer from the SnO_2 matrix. The spectrum shows the both contributions observed under selective excitation, broad bands with a glassy-like character and superimposed to these bands, the sharp peaks corresponding to the crystalline environment for Nd^{3+} ions.

Fig. 7. Room temperature emission spectrum for a sample doped with 1 mol% Er^{3+} treated at 800°C -1h obtained under excitation at 266 nm.

3.4 $\text{SnO}_2:\text{Er}^{3+}$

Figure 8(a) shows the room temperature emission spectrum of Er^{3+} ions upon band gap excitation at 300 nm for the sample doped with 0.7 mol% annealed at 800°C -1h. The spectrum shows the characteristic $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ emission of Er^{3+} . Sharp peaks are observed being the most intense located at 1550 nm. The presence of sharp and well resolved peaks indicates a crystalline environment for Er^{3+} ions in the host. The spectrum is similar to the one reported in ref. 12 in SnO_2 nanocrystals. The spectral features suggest that Er^{3+} ions are incorporated in the lattice of SnO_2 nanocrystals. Moreover, the excitation spectrum obtained by collecting the luminescence at 1550 nm (see Fig. 8(b)) shows a strong UV band attributed to the absorption of SnO_2 nanocrystals. The presence of Er^{3+} emission after 300 nm excitation clearly indicates that there is an energy transfer from the host to Er^{3+} ions.

Fig. 8. (a) Room temperature emission spectrum of $\text{SnO}_2:\text{Er}^{3+}$ (0.7%) obtained under excitation at 300 nm. (b) Room temperature excitation spectrum of $\text{SnO}_2:\text{Er}^{3+}$ obtained by collecting the luminescence at 1550 nm.

It is noteworthy to mention the absence of excitation bands corresponding to the electric dipole transitions from the $^4\text{I}_{15/2}$ ground state to the excited multiplets of Er^{3+} ions in the excitation spectrum which suggests that Er^{3+} ions are incorporated in the centrosymmetric D_{2h} lattice site of Sn^{4+} [12]. Although these results seem to be related with the presence of only one site for Er^{3+} ions in this matrix, direct site-selective excitation of Er^{3+} ions around 800 nm demonstrates the presence of Er^{3+} ions occupying a broad distribution of glassy-like crystal field sites that could be related with ions sited near the nanoparticle surface and/or crystallite interfaces where the crystalline order breaks.

Figure 9(a) presents the excitation spectrum corresponding to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition of Er^{3+} obtained by collecting the luminescence at 1530 nm for the sample doped with 0.7 mol% annealed at 800°C -1h. The spectrum shows a broad band with some structure which suggests the presence of different sites for Er^{3+} ions. To confirm if these features

correspond to different environments for Er^{3+} ions, we have performed site-selective emission spectra by exciting the sample at different wavelengths along the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition. As an example, Fig. 9(b) shows the normalized emission spectra corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition obtained by exciting at 782.5 and 800.5 nm. The spectrum obtained under 782.5 nm excitation presents narrow bands corresponding to the Stark transitions between $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ levels whereas the one obtained under 800.5 nm excitation is broader and less resolved which indicates a glassy-like environment for Er^{3+} ions at this excitation wavelength.

These results confirm that Er^{3+} direct selective excitation displays a higher complexity of the spectral response if compared with bandgap excitation. Besides well defined narrow band crystalline-like emission, corresponding to substitutional sites, broader band emission is also present which suggests the presence of a wide variety of crystal fields at the Er^{3+} sites.

Fig. 9 (a) Room temperature excitation spectrum corresponding to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition of Er^{3+} obtained by collecting the luminescence at 1530 nm for the sample doped with 0.7 mol% annealed at 800 °C-1h. (b) Normalized room temperature emission spectra obtained under excitation at 782.5 nm (dark line) and 800.5 nm (grey line).

4. CONCLUSIONS

In spite of the limitations imposed by Laporte rule on the electric dipole f-f transitions in high symmetry RE sites, direct site-selective excitation of RE has been demonstrated in SnO_2 . The one photon direct RE selective excitation shows the high complexity of the spectral response of the RE. Besides well defined narrow band crystalline-like emission, corresponding to substitutional sites, broader band emission is also present which suggests the presence of a wide variety of crystal fields at the RE sites.

It is worth noticing the influence of the ionic radius of the RE on its spectral behavior. At moderate concentrations (~0.5 mol%) a less crystalline-like behavior corresponds to a higher ionic radius.

Under bandgap pumping RE emissions have, as expected, preferentially crystalline-like behavior corresponding to well defined substitutional Sn^{4+} sites.

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