Site symmetry and host sensitization-dependence of Eu$^{3+}$ real-time luminescence in tin dioxide nanoparticles

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ABSTRACT

A detailed investigation of the dependence of the real time luminescence of Eu$^{3+}$-doped tin dioxide nanopowders on rare earth site symmetry and host defects is given. Ultrafast spectroscopy shows that host-rare earth energy transfer occurs at a transfer rate of about $1.5 \times 10^6$ s$^{-1}$, whereas the intrinsic broad band SnO$_2$ emission has a very short build up time, of the order of 60 ps, and a lifetime of hundreds of picoseconds. These results validate the hypothesis that both host and matrix-excited RE emissions are decoupled due to the different origins of the involved physical mechanisms.

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 (SnO$_2$) 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.

In a previous study [5] the optical properties of Nd$^{3+}$ and Er$^{3+}$-doped tin oxide nanocrystals were investigated. Our study pointed out the important role of the 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. However, neither the precise nature of the luminescence induced by direct RE-pumping nor the one obtained by host-RE transfer are well understood due to the imprecise knowledge about the site symmetry and/or position of the RE in the host lattice and/or the different possibilities for charge compensation if any.

The present work focuses on these difficulties and provides a thorough study of the optical properties of multilevel Eu$^{3+}$-doped tin dioxide. We have chosen this trivalent RE ion because it is a well known structural probe used to investigate the crystal field symmetry and/or coordination type displayed at the cation site.
This study faces a triple challenge. First of all, the particular case of Eu$^{3+}$-doped SnO$_2$ is a paradigmatic example of the fundamental role played by the use of adequate experimental techniques to obtain reliable spectral information. On the other side, it provides a structural model explaining the role of the main host defects, oxygen vacancies (OVs), on the behaviour 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 of reaching the RE excited states by direct host excitation and subsequent energy transfer and, last but not least, shows the spectro-temporal dynamics of the host and the RE emissions obtained by multiphoton pumping of the band gap by using ultrafast IR femtosecond pulses. The multiphoton excitation of the host allows to synchronously measure the second harmonic generated by the nanocrystals (NCs) as well as the host broadband emission, and therefore, to estimate the absolute build up time of the host emission as well as the host-RE energy transfer rate.

The spectroscopic results show that a variety of optically non-equivalent sites exist for the europium ion in the tin dioxide structure associated to different allowed positions of the OVs which gives rise to slightly different crystal field symmetries which have been resolved by using site-selective fluorescence line-narrowing spectroscopy [6]. Moreover, electron paramagnetic resonance (EPR) measurements show the tight relationship between RE doping and the OVs related to the Eu$^{3+}$ emission. For the first time, the decoupling between the OVs responsible for the VIS-NIR emission of the tin dioxide matrix and those originated by the RE doping involved in the matrix-RE energy transfer has been demonstrated.

2. EXPERIMENTAL SECTION

Samples of SnO$_2$ doped with 0.5% Eu$^{3+}$ 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. Stoichiometric amounts of SnCl$_2$$\cdot$2H$_2$O (Merck, 98% purity) and Eu$_2$O$_3$ (Strem Chemicals, 99.99%-Eu purity) were used. Eu$_2$O$_3$ was firstly dissolved under heating with stirring in a dilute HNO$_3$ solution (10 ml distilled water and 5 ml 69 wt % HNO$_3$). After complete evaporation, this product and SnCl$_2$$\cdot$2H$_2$O were dissolved in ethanol (absolute ethanol, Emplura Merck) at room temperature with magnetic stirring, and the gel formation was achieved by dropwise addition of dilute NH$_4$OH to the above acidic solution, adjusting the pH value to 10. The gel was transferred to a Teflon-lined pressure reactor, which was heated during 24 h to 185ºC. The resultant product was collected by centrifugation and washed with ethanol several times, and then overnight dried at 120 ºC. This solvothermal material was subjected to further annealing at temperatures ranging between 600 ºC and 900 ºC to remove defects typically associated to wet low-temperature synthesis methods and to promote its better crystallization, allowing us to test the associated possible improvement of the Eu$^{3+}$ emission efficiency.

The purity of the tetragonal cassiterite SnO$_2$ phase was verified by 300 K powder X ray diffraction (XRD) performed in a Bruker AXS D-8 Advance diffractometer, using K$_\alpha$ radiation. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images as well as energy dispersive X ray spectroscopy analysis were obtained by using a JEOL JEM3000F microscope operating at 300 Kv. XRD patterns collected for 0.5%Eu-SnO$_2$ samples reproduce the scheme of Bragg reflections of the tetragonal $P4_2/mmm$ (136) cassiterite phase of SnO$_2$, so, the described preparations have yielded the pure expected crystal phase. However, the full width at half maximum (FWHM) of the observed Bragg peaks strongly depends on the subsequent thermal treatment applied to the solvothermal samples. Conventional excitation and emission spectra were performed with a FS5 spectrofluorometer (Edimburg Instruments). Resonant time-resolved line-narrowed spectra were performed by exciting the samples with a pulsed frequency doubled Nd:YAG pumped tunable dye laser of 9 ns pulse width and 0.08 cm$^{-1}$ linewidth and detected by an EGG-PAR optical multichannel analyzer. For ultrafast time-resolved anti-Stokes spectroscopy, multiphoton excitation at 800 nm (of 0.5 mJ) with 100 fs pulses were used as well as a 2 ps resolution Streak camera.

X-band EPR measurements were carried out on a Bruker ELEXSYS E500 spectrometer equipped with a super-high-Q resonator ER-4123-SHQ and standard Oxford Instruments low temperature devices. Samples were placed in quartz tubes and spectra were recorded at different temperatures between 5 and 300 K using a modulation amplitude of 0.05 mT at a frequency of 100 kHz. The magnetic field was calibrated by a NMR probe and the frequency inside the cavity (~9.4 GHz) was determined with an integrated MW-frequency counter.
3. STRUCTURAL CHARACTERIZATION OF Eu$^{3+}$-DOPED SnO$_2$ SAMPLES

Figure 1 (a-c) show the comparison of XRD scans for raw solvothermal non-annealed 0.5% Eu$^{3+}$-SnO$_2$, after annealing at 600 °C for 1 h, and then after consecutive thermal treatments at 800 °C and 900 °C during 1 h in each step. The FWHM of Bragg reflections of the above annealed sample 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 by Scherrer’s equation, namely from $D_{\text{XRD}} = 2.6$ nm for the solvothermal non-annealed sample to 40 nm when annealed up to 900 °C.

Crystallographic structure of SnO$_2$. Tin dioxide SnO$_2$ crystallizes in the rutile-type structure, tetragonal space group $P4_{2}/mmn$ (number 136), with unit-cell parameters $a = 4.73735(9)$ Å and $c = 3.18640(7)$ Å, and oxygen positional parameter $x = 0.30562(9)$ [7]. The Sn atoms at $2a$ sites with local $m.mn$ ($D_{2d}$) symmetry are surrounded by six O atoms at $4f$ sites in an octahedral arrangement. These SnO$_6$ octahedra show an apically compressed geometry, with apical and equatorial Sn-O distances 2.047(1) Å and 2.058(2) Å, respectively. The structure can be described as formed by chains of edge-sharing SnO$_6$ octahedra along the $c$ direction, being the chains cross-linked by shared corners so that each chain is connected to four neighboring chains; see the general view in Figure 2a. For next discussion purposes the second cationic coordination sphere around a Sn atom must be also considered. This coordination sphere around the central Sn atom contains two Sn atoms at 3.186 Å, which correspond to closest up and down octahedra along the $c$ direction, and eight Sn atoms at 3.709 Å, from octahedra in neighboring crossed chains, see Figure 2b. It should be noted that apical O atoms only connect Sn atoms at 3.709 Å distance, while equatorial O atoms connect Sn atoms at 3.709 Å and at 3.186 Å distances.

![Figure 1. X-ray diffraction patterns of solvothermal 0.5% Eu-doped SnO$_2$ samples: a) raw non-annealed sample; b) after annealing at 600 °C for 1 h; c) after annealing at 600 °C, 800 °C and 900 °C for 1 h at each temperature. For comparison, the XRD pattern scheme of tetragonal $P4_{2}/mmn$ (136) phase of SnO$_2$ (JCPDS File 88-0287) has been also included at the bottom.](image-url)
Figure 2. (a) The structure of SnO$_2$ viewed along the $c$ axis, and (b) a steroview showing bonding distances of the first coordination polyhedron of oxygens (red spheres) and of the closest cationic sphere around a central Sn atom (small blue spheres).

4. **TIME-RESOLVED FLUORESCENCE LINE-NARROWING OF $^5D_0\rightarrow^7F_{0-J}$ TRANSITIONS**

The knowledge about the existence of well defined and/or disordered sites for the RE in a wide band gap semiconductor is of paramount importance because the RE$^{3+}$ ion can be optically excited either directly or indirectly. In the second case, by using photons with energy above the band gap of the host matrix, electron-hole pairs generated near the RE centre may transfer nonradiatively their energy to the RE$^{3+}$ ion. To investigate the existence of different crystal field sites for Eu$^{3+}$-doped tin dioxide, we have performed low temperature time-resolved fluorescence line-narrowing (TRFLN) spectroscopy [8] of the $^5D_0\rightarrow^7F_0$ transitions by using tunable resonant excitation into the inhomogeneously broadened $^7F_0\rightarrow^5D_0$ transition, and different time delays after the laser pulse.

Figure 3 shows a selection of the low temperature (10K) TRFLN spectra corresponding to the $^5D_0\rightarrow^7F_{0,4}$ transitions of a tin oxide nanopowder doped with 0.5 mol % of Eu$_2$O$_3$ obtained with a time delay of 10 $\mu$s after the pump pulse (~0.08 cm$^{-1}$ spectral width) at five different pumping wavelengths. As can be seen, depending on the excitation wavelength the emission spectra present different characteristics, regarding the number of observed $^5D_0\rightarrow^7F_J$ transitions, their relative intensity, and the magnitude of the observed crystal-field splitting for each $^7F_J$ state. Indeed, the $^5D_0\rightarrow^7F_{0,4}$ spectra obtained by selectively exciting at 579.1 nm (A), 579.65 nm (B), 582.2 nm (C), 583.95 nm (A$^*$) and 587.9 nm (D) respectively, show the presence of at least four isolated Eu$^{3+}$ sites. It is important to notice that site A$^*$ is spectrally
identical to site A and seems to correspond to an anti-Stokes energy transfer feeding of site A assisted by one phonon of about 140 cm\(^{-1}\) associated with a Raman-active \(B_{1g}\) vibration mode in SnO\(_2\).

![Figure 3. Low temperature TRFLN spectra corresponding to the \(^{5}D_0 \rightarrow ^{7}F_j\) transitions of a tin oxide nanopowder (average grain size 40 nm) doped with 0.5 mol % of Eu\(_2\)O\(_3\) obtained with a time delay of 10 \(\mu\)s after the pump pulse.]

It is worth noticing that exception made of site D the TRFLN spectra of sites A, B, and C show some disordered background that can be related to contributions of europium ions occupying a broad distribution of glassy-like crystal field sites near the nanoparticle surface and/or crystallite interfaces where the crystalline order breaks. In fact, outside the mentioned excitation wavelengths the \(^{5}D_0 \rightarrow ^{7}F_j\) transitions of Eu\(^{3+}\) show some site overlapping and/or broad structures similar to those found in glassy matrices [9].

The presence of the \(^{5}D_0 \rightarrow ^{7}F_0\) line in each spectrum (except for site D) indicates a site of \(C_{nv}\), \(C_n\) or \(C_s\) symmetry for the Eu\(^{3+}\) ion. These symmetries allow the transition as an electric dipole process, according to the group theory selection rules [10]. On the other hand, the spectrum of site D shows no \(^{5}D_0 \rightarrow ^{7}F_0\) line and exhibits only three main lines corresponding to the \(^{5}D_0 \rightarrow ^{7}F_1\) magnetic dipole transition and a very week presence of the \(^{5}D_0 \rightarrow ^{7}F_2\) emission. This crystal field splitting agrees with the \(D_{2h}\) point symmetry of a Eu\(^{3+}\) ion occupying a regular cation lattice site in SnO\(_2\).

### 4.1 Oxygen vacancies around Eu\(^{3+}\) and crystal field symmetries

The complexity of the FLN spectra of europium ion shows the existence of a variety of crystal field sites which may be assigned either to different RE lattice localizations and/or to the change of nearest neighbours induced by OVs and/or other defects. However, it is also clear that by pumping above the host band gap there is an efficient host-RE energy transfer mainly involving Eu\(^{3+}\) ions substituting Sn\(^{4+}\) ones at regular lattice sites (site D). In order to understand the mechanisms involved in this process we need to know why the emission of this high symmetry site is the predominant one if compared to those of the other crystal field sites and how these sites depend on the OVs aiding to stabilize the
non-isoelectronic substitution of tin by europium; in particular, the nature and number of different crystal field site possibilities for different vacancy configurations.

Besides the Eu$^{3+}$ emission, bandgap excited samples, including undoped ones, also exhibit a weak broad band VIS-NIR photoluminescence (400-800 nm) also reported by other authors. First-principles and experimental studies carried out by different authors [11,12] strongly suggest the existence of deep localized OV states associated with the energy dispersion of surface OVs bands as responsible for the observed photoluminescence. The conclusion proposed by the authors in [12] is that electronic transport in SnO$_2$ is associated with shallow bulk-like OVs whereas the surface OV states are responsible for the observed optical properties.

Besides the bulk or surface nature of the OVs and the position of their electronic energies in the SnO$_2$ band gap, another relevant issue, regarding the necessary charge compensation for the substitution of tin by trivalent RE, is the structure of the defect. Extensive computer modeling studies of defect and dopant states in SnO$_2$ by Freeman and Catlow [13] predicted for trivalent dopants to form substitutional solutions with OV compensation. In particular, for Eu$_2$O$_3$ the lowest solution energy corresponds to a substitutional Eu$^{3+}$ with OV compensation. Following this study, Bush et al. [14] calculated the energy of a variety of cluster of impurities and compensating defects in SnO$_2$; in particular, for a solution of trivalent Ga$_2$O$_3$ oxide they showed that clustering of two nearest neighbour substitutional Ga$^{3+}$ ions compensated by an OV (V$_{O^{-}}$) gave the lowest solution energy.

Referring to observed point symmetries corresponding to the possible defect sites induced by the RE substitution and the corresponding nearby charge compensation by OVs, we have seen, when pumping above the host band gap, that the emission spectrum of Eu$^{3+}$ exhibits a crystal field splitting which agrees with the $D_{2h}$ point symmetry of a Eu$^{3+}$ ion occupying a regular cation lattice site (site D). This result suggests that when substituting Eu$^{3+}$ by Sn$^{4+}$, the charge compensation by the OV cannot be situated in any of the nearest neighbour octahedral coordination oxygens; otherwise, the symmetry would break down to a lower point symmetry [15] ($C_4$, $C_2$ or $C_3$ symmetries) as in fact is observed for sites A, A*, B, and C. Moreover, due to the higher size of the trivalent europium ion (98 pm) if compared with tetravalent tin (74 pm), the bulk SnO$_2$ lattice could not accept the above mentioned cluster-type solution due to the increased lattice distortion. On the contrary, as shown by A. Dieguez and co-workers by studying the vibrational properties of SnO$_2$ nanoparticles [16], as we enter the lattice shell close to the nanoparticle surface (~1.1 nm) the stoichiometry may fail promoting the existence of different local atomic arrangements symmetries corresponding to a more energetically favourable defect formation such as the cluster-type mentioned above. As a consequence, in this small shell, occupying about 16% of the total volume of our 40 nm SnO$_2$ nanoparticle, we face enough room to consider lattice symmetry distortions giving rise to the origin of sites A, A*, B, and C.

The charge compensation of site D deserves a detailed comment because the electron paramagnetic resonance (EPR) investigations of undoped and doped SnO$_2$ point to the existence of V$_{O^{-}}$ charge compensation centres stabilized by the RE doping. No EPR resonance lines were found in our SnO$_2$ samples prior to europium doping but a complex signal arises when the RE is introduced. Based on these results, it can be assumed that the paramagnetic centres which are responsible for the observed EPR signal are singly ionized OVs. V$_{O^{-}}$ defects are thermodynamically unstable in perfect SnO$_2$ crystals[17], but the presence of other imperfections in the structure can create deep electron traps associated with OVs due to local lattice distortions [18]. In this case, the presence of Eu$^{3+}$ ions in the vicinity of V$_{O^{-}}$ can contribute to the stabilization of the centre and allows its detection by EPR spectroscopy.

4.2 Analysis of local environments around low symmetry Eu$^{3+}$ sites

To interpret the TRFLN luminescence spectra of Eu$^{3+}$-doped SnO$_2$ corresponding to the crystal field symmetry observed at the A, A*, B, and C rare earth sites, the nature of possible sites accommodating Eu$^{3+}$ and their local symmetries should be considered. As commented above, the approach developed to determine the location of Ga$^{3+}$ substituting Sn$^{4+}$ in SnO$_2$, would lead in our case to a preferred (low enthalpy) mechanism with Eu$^{3+}$ predominantly substituting Sn$^{2+}$ ions at lattice sites, and the formation of stable clusters with two nearest-neighbour Eu$^{3+}$ ions compensated, in this case, by one V$_{O^{-}}$ vacancy. Following this hint we have analysed the effect of the local symmetry of envisaged environments around the two Eu$^{3+}$ being part of the considered cluster (hereafter named Eu$^{3+}$(1), always at the centre of the unit cell, and Eu$^{3+}$(2), occupying other Sn$^{4+}$ site in or close to the unit cell), which will be different depending on the location of the involved OV. Figure 4, shows the three main cluster possibilities involving a V$_{O^{-}}$-type vacancy.

Other possible still low-energy locations for the trivalent dopant cation in SnO$_2$, with short-range environments which result from charge compensation involving self-compensation processes i.e., either interstitial Eu$^{3+}$ or Sn$^{2+}$, are considerably less likely to appear, since the large size of Eu$^{3+}$ will produce an important expansion of its oxygen coordination polyhedron, so the sizes of the adjacent interstitial sites would be very much reduced.
In conclusion, as a consequence of the charge compensation process produced by the cluster-type substitution $2\text{Sn} \Rightarrow 2\text{Eu} + \text{VO}^{++}$, there would appear three different crystal field sites for the Eu$^{3+}$ ion with lower symmetry than the tetragonal $D_{2h}$ corresponding to the Sn site (site D). In these three sites, different splitting of the $^7F_1$ level as well as an intensity enhancement of the electric dipole transitions are expected in agreement with the experimental TRFLN spectra results shown in Figure 3 for sites A, B, and C.

4.3 The Eu$^{3+}$ excitation mechanism

The presence of the RE ions in the SnO$_2$ matrix does not affect the weak VIS-NIR broad band matrix emission after band gap excitation. Moreover, it is worth noticing that the weakness of this emission is consistent with the thermal treatment of the sample in air, which partially removes the surface OVs. However, as we have seen above, the RE doping creates additional VO$^{+}$-type bulk OVs near the tin lattice sites occupied by the Eu$^{3+}$ ions and, as a consequence, these defects can play an important role in direct matrix-RE excitation.

In this SnO$_2$ matrix, and possibly in many other oxides with similar characteristics (similar charge compensation as in TiO$_2$, for example) the RE excitation mechanism for the regular substitutional sites (site D) may occur through energy transfer from donor-acceptor-like pairs in which the Eu$^{3+}$ centres themselves would act as acceptors and the VO$^+$ near OVs as donors.

When the system is excited above the band gap, the photocarriers (electron and holes) created by the pump pulse are efficiently captured, simultaneously or sequentially, on the donor-acceptor trap pair producing bound excitons which may then relax through radiative or non-radiative processes. Due to the proximity of the OVs to the RE centre, the non-radiative transfer of the excitation energy to the 4f shell of the Eu$^{3+}$ ion is thus a preferred channel.

Similar excitation processes could also occur in the case of substitutional europium pairs linked by VO$^{++}$ type OVs, giving rise to the low symmetry sites.

5. ULTRAFAST SPECTROSCOPY

In order to deepen our knowledge about the origin of Eu$^{3+}$-doped tin dioxide emissions, and to demonstrate the decoupling between the processes generating the VIS-NIR host luminescence and the RE emission, we investigated their temporal behaviour by performing time-resolved ultrafast photoluminescence by using femtosecond multiphoton IR (800 nm) excitation to pump above the SnO$_2$ band gap and a Streak camera detector with 2 ps resolution time.

Figure 5a shows the normalized integrated emission spectra of Eu$^{3+}$ in the region between 550 and 750 nm obtained by pumping above the bandgap at 800 nm and collecting the fluorescence with a CVI spectrometer. As can be seen, this spectrum shows that all the Eu$^{3+}$ sites are simultaneously excited by the energy transfer mechanism from the host matrix. The characterization of the multiphoton pumping order was obtained by measuring the Eu$^{3+}$ emission as a function of the IR pump pulse energy. Figure 5b shows the power dependence of the VIS Eu$^{3+}$ integrated emission intensity on a log-log scale.
scale. The straight line represents the linear fit to the logarithmic data. Within experimental accuracy, the Eu$^{3+}$ VIS emission shows a slope of 2.5 up to a 0.5 mJ excitation energy, which indicates a three-photon excitation process.

![Figure 5](image.png)

Figure 5. a) Normalized emission spectrum of the 0.5 mol% Eu$^{3+}$-doped SnO$_2$ powder pumped at 800 nm. b) Excitation power dependence of the Eu$^{3+}$ VIS luminescence for the SnO$_2$: 0.5 mol % Eu$^{3+}$-powder sample after excitation at 800 nm with a fs laser in a double logarithmic representation showing the linear fit.

**SnO$_2$ emission:** The emission of both undoped and Eu$^{3+}$-doped nanopowders in the spectral region 420-520 nm (around the maximum of the matrix emission) is shown in Figure 6a with a time window of 1 ns. The samples were excited by 100 fs laser pulses of 0.5 mJ at 800 nm. Figure 6a shows that no appreciable differences exist between both emissions. The decay curves of the luminescence extracted over the mentioned spectral range in the undoped and 0.5 mol % Eu$^{3+}$ doped SnO$_2$ powder samples are shown in Figure 6b. The lines correspond to the fitting to two-exponential decay components. The short-lived component of both decays is in the range of a few tens of picoseconds, 47 and 43 ps, for the Eu$^{3+}$-doped and undoped samples respectively. The slow component amounts to a few hundreds of picoseconds, 323 and 226, for the doped and undoped samples, respectively. The huge contribution (99.9%) of the fast component can be attributed to the strong influence of room temperature nonradiative processes in the exciton recombination dynamics whereas the slow one, with much lower contribution (0.1%), could be originated from free-carrier recombination with much lower oscillator strength.

The similar behaviour of both doped and undoped samples suggests that the host-RE pumping mechanism is independent of the one involved in the host emissions. Because of the small time scales involved in the broad band host emission and in order to investigate if both RE and host emissions are or not decoupled we establish an absolute time origin reference for the arriving pulse on the sample, and therefore for all the subsequent events, based on the second harmonic generated by the symmetry breaking at the nanoparticle surface. For this purpose, we have simultaneously measured the second harmonic generation (two photon absorption) as well as the bandgap excited photoluminescence (three photon absorption) induced in the tin oxide nanoparticles in the same spectro-temporal window of the Streak camera.

![Figure 6](image.png)

Figure 6. a) Emission spectral profiles extracted over the whole temporal range in the undoped (blue line) and 0.5 mol % Eu$^{3+}$ doped (red line) SnO$_2$ powder samples under excitation at 800 nm with 100 fs laser pulses (E$_{exc}$ = 0.5 mJ) by setting the time window of the Streak camera at 1 ns. b) Temporal profiles extracted over the 420-520 nm spectral range in the undoped (blue points) and 0.5 mol %
Eu\textsuperscript{3+}-doped (red points) Sn\textsubscript{2}O\textsubscript{2} powder samples under excitation at 800 nm with 100 fs laser pulses (\(E_{\text{exc}} = 0.5\) mJ) by setting the time window of the Streak camera at 1 ns. The continuous red and blue lines are the best fits to two-exponential functions.

Figure 7 compares the normalized time-resolved emissions produced by the 0.5 mol % Eu\textsuperscript{3+}-doped Sn\textsubscript{2}O\textsubscript{2} sample in the 395-417 nm spectral interval (second harmonic generation) with the one observed in the 417-484 nm interval (band gap excited photoluminescence). Account taken of the fact that the second harmonic generation signal can be considered as an quasi-instantaneous process, the difference between the risetimes of both signals, \(\sim 8\) ps, could be taken as an estimation of the electron capture time of the VO\textsuperscript{2+} vacancies for giving the host luminescence.

As we have seen above, the measured lifetimes of both undoped and doped samples (obtained by a double exponential fit) are similar, which suggests that no energy transfer processes from isolated vacancy centres are feeding the Eu\textsuperscript{3+} excited state. It is worth noticing that within the experimental resolution both signals have similar risetimes (\(\sim 60\) ps) suggesting that the beginning of the matrix photoluminescence associated to the excitation of a broad distribution of surface OVs is a very fast process which follows the exciting pulse.

Eu\textsuperscript{3+} emission: Although a direct experimental evidence of the existence of bound excitons as the excitation mechanism of the RE luminescence is impossible at room temperature, it is easy to understand that the observed efficient luminescence of the Eu\textsuperscript{3+} ion could only be related to a sufficiently long-lived bound exciton. Moreover, the trapping time of the exciton should be much less than the transfer time which can be estimated by the risetime of the Eu\textsuperscript{3+} emission.

In order to gain further insight on the energy transfer process which leads to the Eu\textsuperscript{3+} emission under Sn\textsubscript{2}O\textsubscript{2} excitation at 800 nm, we investigated the time dependent behaviour of the emission of this RE ion in the doped Sn\textsubscript{2}O\textsubscript{2} powder by using two different time windows of the Streak camera; one of 100 \(\mu\)s and the other one having the largest available time window, \(i.e.\) 1 ms. Figure 8 shows in red the spectral and temporal profiles in the 570-660 nm spectral range, which mainly correspond to the three \(^5D_0 \rightarrow ^7F_1\) transitions of Eu\textsuperscript{3+}. As can be observed, the temporal profiles show an initial fast decay associated with the Sn\textsubscript{2}O\textsubscript{2} emission, and a much longer decay due to the Eu\textsuperscript{3+} emission. The spectral and temporal profiles of the undoped sample are also plotted with blue lines in Figure 8. Note that both temporal profiles have their maximum at almost the same time position, so account taken of the comparable intensity of the matrix emission in the doped and undoped samples (see Figure 6a), it is possible to remove the short time Sn\textsubscript{2}O\textsubscript{2} contribution from the doped sample decay by subtracting both profiles. The maximum of the obtained differential temporal profile (green line in Figure 8) occurs at slightly longer times which is a fingerprint of the energy transfer process with populates the Eu\textsuperscript{3+} emitting centres. In addition, the shape of the differential profiles shown in Figure 8 suggests a fast feeding of the Eu\textsuperscript{3+} excited state by energy transfer from the Sn\textsubscript{2}O\textsubscript{2} matrix under 800 nm excitation. The Eu\textsuperscript{3+} lifetime value obtained by fitting the longer decay of the differential temporal profile corresponding to the longest 1 ms temporal window with a single-exponential function is 216 \(\mu\)s. However, the lifetime measured with a conventional spectrophotometer, by
pumping above band gap (at 300 nm), exhibits a much longer decay which can be fitted to two exponential components with lifetime values of 3.3 and 11.7 ms respectively.

![Figure 8. Spectral (a, c) and temporal (b, d) profiles of the 0.5% mol Eu³⁺ doped SnO₂ powder in the 570-660 nm spectral range (red lines), which mainly corresponds to the ⁵D₀→⁷F₁ emission of Eu³⁺. The spectral (a, c) and temporal emission profiles (b, d) of the pure SnO₂ powder are shown in blue. The green profiles of Figure 8 (b) and (d) correspond to the subtraction of the pure and doped sample temporal profiles. Figure 8 (a) and (b) were obtained by using the 1 ms time window whereas (c) and (d) were obtained with the 100 µs time window.

For time windows shorter than 100 µs only the matrix emission can be detected, so we could set a lower limit for the SnO₂→Eu³⁺ nonradiative energy transfer rate based on the build-up time measured with a time window of 100 µs. Note that by using this time window the obtained risetime of the Eu³⁺ temporal emission profile is 650 ns. Therefore, we can conclude that the Eu³⁺ emission via energy transfer from the SnO₂ matrix, starts at around 650 ns after pumping which corresponds to a transfer rate of about 1.5×10⁶ s⁻¹ whereas, as already seen, the intrinsic broad band SnO₂ emission has a very short build up time, of the order of tens of picoseconds (60 ps), and a lifetime of the order of hundreds of picoseconds. Therefore, these results validate the hypothesis that both host and matrix-excited RE emissions are decoupled due to the different origins of the involved physical mechanisms.

6. CONCLUSIONS

This investigation demonstrates the existence of at least four different crystal field sites of Eu³⁺ ion in tin dioxide nanoparticles. The physical nature and spectroscopic properties of these sites are revealed showing why site D emission is prominent when pumped indirectly by energy transfer from the excited host. A plausible model which takes into account the influence of structural defects related to OVs produced during the nanocrystal synthesis, RE doping and/or thermal treatments, is presented to ground the existence of a variety of non-equivalent crystallographic sites, with different densities, for the RE.

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 Eu³⁺ has been demonstrated in SnO₂ nanoparticles. The TRFLN spectroscopy 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 Eu$^{3+}$ sites near the nanoparticle surface.

Under one or three photon bandgap pumping, the Eu$^{3+}$ emissions have, as expected, a preferentially crystalline-like behavior corresponding to well defined substitutional Sn$^{4+}$ sites. It is worth noticing the prominence of the regular high symmetry ($D_{2h}$) crystal lattice site D which carries out most of the RE emission (~84%).

Ultrafast time resolved analysis of the weak bandgap excited VIS-NIR luminescence of the undoped and rare earth doped SnO$_2$ samples, shows that the bandgap excited emission of SnO$_2$ is not coupled to the Eu$^{3+}$ excitation mechanisms.

A model for the RE excitation mechanism has been presented. Time-resolved spectroscopy of Eu$^{3+}$ ion obtained by multiphoton photon bandgap pumping supports the model proposed. We can conclude that the Eu$^{3+}$ emission via energy transfer from the SnO$_2$ matrix, starts at around 650 ns after pumping which corresponds to a transfer rate of about $1.5\times10^6$ s$^{-1}$, whereas the intrinsic broad band SnO$_2$ emission has a very short build up time, of the order of tens of picoseconds (60 ps), and a lifetime of the order of hundreds of picoseconds. Therefore, these results validate the hypothesis that both host and matrix-excited RE emissions are decoupled due to the different origins of the involved physical mechanisms.

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