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

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Abstract: The present work gives a detailed investigation of the dependence of the real time luminescence of Eu^{3+} -doped tin dioxide nanopowder on rare earth (RE) site symmetry and host defects. Ultrafast time-resolved analysis of both RE-doped and undoped nanocrystal powder emissions, together with electronic paramagnetic resonance studies, show that host-excited RE emission is associated with RE-induced oxygen vacancies produced by the non-isoelectronic RE-tin site substitution that are decoupled from those producing the bandgap excited emission of the SnO_2 matrix. A lower limit for the host-RE energy transfer rate and a model for the excitation mechanism are given.

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1. Introduction

The wide band gap of metal-oxide semiconductors allows not only the possibility of wide spectral range emissions but also of being functionalized by cation-doping for optoelectronic and biomedical applications. Moreover, when they are synthesized as nanostructured particles they can easily be incorporated in thin films and/or other convenient structures to conform the

desired device [1,2]. High temperature magnetism in dilute magnetic oxide thin films based on cation-doped and/or undoped oxides has been reported as potentially applicable to the next generation of spintronic devices [3,4]. Multifunctional compact RE-doped metal oxide layers have been used to enhance the photoelectric conversion efficiency of solar cell devices [5] and RE-doped oxide nanopowders are also used for luminescence thermometry at the micro-nanoscale with good spatial resolution [6–8].

Rare earth dopants deserve special attention because their luminescence can be efficiently sensitized by energy transfer from the host matrix allowing to overcome the low absorption of Laporte-forbidden f-f transitions; however, in spite of the huge amount of RE-doped oxides studied, 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. Moreover, when dealing with non-isoelectronic cation substitutions, besides the own characteristic host defects, charge compensation has a determinant influence on the resulting final defects as well as on the spectroscopic behavior and efficiency of the RE emitter (quenching, wavelength, tuning range of the emission, etc.).

The present work focuses on these difficulties and provides answers to most of them by means of a thorough study of the optical properties of multilevel Eu^{3+} -doped tin dioxide.

The reason to choose SnO_2 as a host for the RE ions is twofold; on one hand, there are relative little investigations, if compared with other wide gap semiconductor oxides [9], about the light emission potentialities of this RE-doped wide band gap semiconductor for optoelectronic applications. As has been recently pointed out [10], the main problem could be related to the forbidden band-edge UV absorption transitions of the bulk un-doped SnO_2 due to the even parity of both states at the minimum and maximum of the respective conduction and valence bands (at the Γ point), and to the odd parity character of the bulk electric-dipole operator. However, in semiconductor nanocrystals (NCs), the size effects introduced by large surface-to-volume ratio may induce small lattice distortions which may be enough to affect their band structure and to relax the dipole-forbidden rule. The second reason, as already mentioned above, is to investigate the relation and dependence of the europium emission on the particular defect structure of the host matrix. 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, and at the same time, referring to potential applications, it is one of the most important RE VIS emitters for lighting, biochemical and biomedical sensing and/or imaging applications [11].

In spite of the huge amount of studies using europium as a probe and/or as a luminophore, a rigorous interpretation of the europium spectra could be sometimes a difficult task for newcomers in the field of spectroscopy. To avoid pitfalls in the interpretation of the europium spectra a complete set of high resolution spectro-temporal experimental data (absorption, emission, excitation spectra, lifetimes,...), as well as a correct theoretical interpretation is always needed [11]. With a few exceptions [12, 13], most of the results found in the literature by direct pumping of Eu^{3+} ion levels in SnO_2 were obtained by pumping high excited RE levels with standard spectrophotometers and/or low resolved photoluminescence detection [14] whereas those obtained by host sensitization made little effort to investigate the nature of the host-RE energy transfer process and mechanisms involved [15].

This study faces a double challenge. First of all, it provides a structural model explaining the role of the main host defects, oxygen vacancies (OVs), 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 of reaching the RE excited states by direct host excitation and subsequent energy transfer. On the other side, shows the real time spectro-temporal dynamics of the host and the RE emissions obtained by multiphoton pumping of the band gap by using ultrafast spectroscopy.

The obtained 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 [16]. Moreover, electron paramagnetic resonance (EPR) measurements show the tight relationship between RE doping and the OVs related with the Eu^{3+} emission.

On the other hand, multiphoton excitation of the host, with IR femtosecond pulses, allows to synchronously measure the second harmonic generated by the NC's as well as the host broadband emission, and therefore, to estimate the absolute build up time of the host emission and, as a consequence, the host-RE energy transfer rate. Moreover, from a fundamental point of view, it demonstrates, 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.

2. Experimental section

2.1 Synthesis process

Samples of SnO_2 doped with 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 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, 98% purity) and Eu_2O_3 (Strem Chemicals, 99.99%-Eu purity) were used. Eu_2O_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 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 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_4OH 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 185 °C. The resultant product was collected by centrifugation and washed with ethanol several times, and then overnight dried at 120 °C. This solvothermal material was subjected to further annealing at temperatures ranging between 600 °C and 900 °C to remove defects typically associated to wet low-temperature synthesis methods, as oxygen vacancies and local lattice defects, and to promote its better crystallization, allowing us to test the associated possible improvement of the Eu^{3+} emission efficiency.

2.2 Characterizations

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_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 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 $P4_2/mnm$ (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.

2.3 Optical spectroscopies

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 a 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.

2.4 EPR measurements

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. Result and discussion

3.1 Site selective spectroscopy of Eu^{3+} in SnO_2

The optical properties of RE^{3+} centers in any solid state structure strongly depend on their precise local atomic environment, in particular, whether interstitial or substitutional sites are available. Moreover, in the case of nanostructures, where the surface to volume ratio changes as a function of the nanoparticle size, the lattice distortions near the surface may produce distinct RE environments even if RE ions are on substitutional sites and, as a consequence, different crystal field sites and/or glassy-like disorder could be detected in the RE emission spectrum. In the case of Eu^{3+} doped SnO_2 nanoparticles the main luminescence emission is currently attributed to the RE occupying a tin substitutional site with a near D_{2h} point symmetry [17]. Only a few works discuss the presence of some glassy-like spectral disorder when exciting at a direct RE level [12, 13].

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 center 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 [18] of the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions by using tunable resonant excitation into the inhomogeneously broadened $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition, and different time delays after the laser pulse. Figure 1(a) shows a selection of the low temperature (10K) TRFLN spectra corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions of a tin dioxide nanopowder (thermally quenched, average grain size 40 nm) doped with 0.5 mol % of Eu_2O_3 obtained with a time delay of 10 μs after the pump pulse ($\sim 0.08 \text{ cm}^{-1}$ 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 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions, their relative intensity, and the magnitude of the observed crystal-field splitting for each $^7\text{F}_J$ state. Indeed, the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ 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 [19, 20].

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 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions of Eu^{3+} show some site overlapping and/or broad structures similar to those found in glassy matrices [21]. The presence of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ 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 [15]. Figure 1(b) presents the energy levels for the three A(A*), B, and C sites. On the other hand, the spectrum of site D shows no $^5D_0 \rightarrow ^7F_0$ line and exhibits only three main lines corresponding to the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition and a very weak presence of the $^5D_0 \rightarrow ^7F_2$ 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 .

Fig. 1. (a) Low temperature TRFLN spectra corresponding to the $^5D_0 \rightarrow ^7F_{0-4}$ transitions of a tin dioxide nanopowder (average grain size 40 nm) doped with 0.5 mol % of Eu_2O_3 obtained with a time delay of 10 μs after the pump pulse. (b) Observed energy levels of Eu^{3+} in SnO_2 corresponding to sites A (A*), B, and C.

The estimated lifetimes of A, B, C, and D sites, obtained by analyzing the time-resolved emissions corresponding to the different sites, are 1.06, 1.02, 2.07, and 4.5 ms respectively. To realize the difference between conventional and TRFLN spectroscopies, Fig. 2 shows the room temperature excitation spectrum (a) of the same sample used for TRFLN as well as its emission spectra obtained by direct excitation of the 5D_2 level of Eu^{3+} at 465 nm (b) and by exciting above the band gap at 300 nm (c). It is worth noticing that when pumping at 300 nm, the observed spectrum shows mainly the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition contribution of site D with minor contributions from the $^5D_0 \rightarrow ^7F_{0,2,3,4}$ electric dipole transitions, whereas when directly pumping the 5D_2 level, the observed weak Eu^{3+} emission is mostly of an electric dipole nature. This result agrees with the fact that all four Eu^{3+} sites can be excited by energy transfer from the excited host. However, due to the different population densities of the different sites, site D dominates the whole emission, as we shall further discuss.

Fig. 2. Excitation spectrum of the 0.5 mol% Eu^{3+} -doped SnO_2 powder obtained by collecting the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission at 612 nm (a). Emissions of the mentioned sample resulting from direct excitation at the $^5\text{D}_2$ level (b). Emissions obtained by pumping this powder sample above the band gap at 300nm (c).

3.2 On the relation between different Eu^{3+} crystal field sites and OV defects in tin dioxide

It is well known that nanocrystalline materials can be considered as polycrystals consisting of two main components: a crystalline component and an interfacial component. The crystalline component has the same structure as the bulk crystal whereas the interfacial component due to random orientation of adjacent crystallites and the interface itself shows a disordered

character [22]. As a consequence, the measured physical properties of defects and/or dopants introduced in a nanocrystal may suffer the influence of different atomic species and surrounding symmetries. In general, we would expect at least two 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. In the case of europium-doped tin dioxide 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 neighbors induced by OV 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 D_{2h} point symmetry lattice sites. 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.

3.2.1 SnO_2 native oxygen vacancies and electronic properties

Although the stoichiometric SnO_2 behaves as an insulator, it is commonly accepted that its conductance depends on the amount of OVs acting as shallow donors which would convert the oxygen deficient form in an n-type semiconductor with a band gap of 3.6 eV. Experimental investigation of the electric conductance of SnO_2 as a function of oxygen partial pressure at elevated temperatures showed that the native defect in tin dioxide is a double ionized OV forming shallow donor levels with energies ~ 0.03 and 0.15 eV below the bottom of the conduction band [23]. However, among the known computational results (mainly based on density functional theory studies within different approximations) there is no complete agreement concerning either the type of OV (doubly occupied V_O^0 , single ionized V_O^+ , or double ionized V_O^{++}) or whether they appear combined or accompanied by other defects such as interstitial Sn_i , tin vacancies V_Sn with different ionizations states (Sn^{4+} to Sn^{2+} as charge compensation mechanism), or forming defect clusters. Moreover, there are also discrepancies about the defect formation energies as well as about the role played by the defects on the electronic and optical properties [24–26].

3.2.2 SnO_2 native oxygen vacancies and broad band VIS-NIR optical properties

The origin of the band gap excited broad band VIS-NIR photoluminescence (400–800 nm) observed in undoped SnO_2 nanoparticles and different geometrical configurations (nanobelts, nanowires) [27–29], is not compatible with radiative transitions involving only the above mentioned shallow levels of the bulk electronic structure of tin dioxide. First-principles and experimental studies carried out by different authors [30, 31] 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 [31] 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.

3.2.3 RE induced oxygen vacancies in RE-doped SnO_2 nanocrystals

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 [32] predicted for trivalent dopants to form substitutional solutions with OV compensation. In particular, for Eu_2O_3 the lowest solution energy corresponds to a substitutional Eu^{3+} with OV compensation. Following this study, Bush et al. [33] calculated the energy of a variety of cluster of impurities and compensating defects in SnO_2 ; in particular, for a solution of trivalent Ga_2O_3

oxide they showed that clustering of two nearest neighbor substitutional Ga^{3+} ions compensated by an OV (V_O^{++}) gave the lowest solution energy.

3.2.4 Configuration and charge of the induced oxygen vacancies around the RE and crystal field symmetries

We show in Section 3.1 that when pumping above the host band gap, the emission spectrum of Eu^{3+} exhibits mostly 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 neighbor octahedral coordination oxygens; otherwise, the symmetry would break down to a lower point symmetry [34] (C_s , C_2 or C_1 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 (with V_O^{++} vacancy-type) due to the increased lattice distortion. On the contrary, as shown by A. Dieguez and associates by studying the vibrational properties of SnO_2 nanoparticles [35], 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 favorable 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. It is worth noticing that this could explain the low total contribution of these sites to the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions in the spectrum shown in Fig. 2(c) if compared with the main $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission of the bulk site D, as well as the disordered spectral background found in the TRFLN spectra obtained by direct pumping of the Eu^{3+} levels.

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 centers stabilized by the RE doping. X-band EPR spectra were recorded between 5 and 300 K on powdered samples. 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. It can be seen that resonance occurs over a range of 35 mT, with an intense central line at $g = 2.003$ and several minor peaks symmetrically distributed around it (see Fig. 3(a)).

Based on the above results, it can be assumed that the paramagnetic centers which are responsible for the observed EPR signal are singly ionized OVs. V_O^+ defects are thermodynamically unstable in perfect SnO_2 crystals [25], but the presence of other imperfections in the structure can create deep electron traps associated with OVs due to local lattice distortions [36]. In this case, the presence of Eu^{3+} ions in the vicinity of V_O^+ can contribute to the stabilization of the center and allows its detection by EPR spectroscopy. In fact, the $g = 2.003$ and $A_\text{Sn} = 34$ mT values that can be obtained from the position of the outer lines of the spectrum (317, 351 mT) are in good agreement with the density-functional theory calculations carried out by Özcan *et al.* for an F center in SnO_2 [37]. Moreover, with the same value of g but a considerably lower hyperfine coupling constant, $A_\text{Sn} = 4.2$ mT, one can also fit the multiplet appearing at the center of the resonance (see Fig. 3(b)). For this purpose we have followed the procedure used by Albanese *et al.* with the EPR signals observed in N-doped SnO_2 samples [38]. As a conclusion, Eu^{3+} ions are at least contributing to the stabilization of two different paramagnetic centers, one being more abundant than the other as shown by the relative intensity of their EPR signals.

Fig. 3. (a) X-band (9.39 GHz) EPR spectra recorded on a tin dioxide nanopowder doped with 0.5 mol % of Eu_2O_3 . (b) Best fit obtained for the EPR signal of the most abundant V_O^{++} center detected on this nanopowder.

3.2.5 Configuration of local environments around low symmetry Eu^{3+} sites

To interpret the observed TRFLN luminescence spectra of Eu^{3+} -doped SnO_2 , the nature of the possible defect geometries that give rise to the lowering of local symmetry observed in A, A^* , B, and C crystal field sites accommodating Eu^{3+} should be considered.

As commented above, the approach developed to determine the location of Ga^{3+} substituting Sn^{4+} in SnO_2 [33], would lead in our case to a preferred (low enthalpy) mechanism with Eu^{3+} predominantly substituting Sn^{4+} ions at lattice sites (in the distorted lattice shell close to the nanoparticle surface), and the formation of stable clusters with two nearest-neighbor Eu^{3+} ions compensated, in this case, by one V_O^{++} vacancy. Following this hint we analyzed, in Fig. 4, the effect of the local symmetry of envisaged environments around the two Eu^{3+} being part of the considered cluster (hereafter named $\text{Eu}^{3+}(1)$, always at the center of the unit cell, and $\text{Eu}^{3+}(2)$, occupying other Sn^{2+} 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:

Cluster i: In this case, the $V_{O^{++}}$ vacancy is over an equatorial oxygen connecting the europium pair, being the distance from $V_{O^{++}}$ to each Eu^{3+} ion the same, 2.058 Å. The two nearest Eu^{3+} are at a 3.186 Å distance. In this scheme, the only remaining symmetry element is a mirror plane containing both europium ions and the OV. Thus, the symmetry is lowered to C_s . This [$Eu^{3+}(1)-V_{O^{++}}-Eu^{3+}(2)$] cluster will be described as $i(C_s)$ from now on (see Fig. 4(a)). By symmetry considerations, if the OV vacancy were over any of the other three equatorial oxygens the cluster would be equivalent to the one described. Consequently, the “multiplicity” of cluster $i(C_s)$ is four.

Cluster ii: In this situation $Eu^{3+}(2)$ is at a vertex of the unit cell, at 3.709 Å distance from central $Eu^{3+}(1)$ with the $V_{O^{++}}$ vacancy over any of the two apical oxygens at 2.047 Å from the central $Eu^{3+}(1)$ and 2.058 Å from $Eu^{3+}(2)$ [Fig. 4(b)]. In this cluster the only surviving symmetry element is again a plane containing both Eu^{3+} ions and the OV. This [$Eu^{3+}(1)-V_{O^{++}}-Eu^{3+}(2)$] cluster will be described as $ii(C_s)$. Considering the OV at the apical oxygens and changing the $Eu^{3+}(2)$ to the other three vertexes of the unit cell the cluster ii will be the same, thus, its multiplicity is also four. Though the symmetry is similar to the previous case it is worth noticing the different distances between both Eu^{3+} ions as well as their different distances to the OV.

Cluster iii: In this case the $V_{O^{++}}$ vacancy is over any of the two apical oxygens at 2.047 Å from the central $Eu^{3+}(1)$. $Eu^{3+}(2)$ is at one vertex of the unit cell, at 3.709 Å from $Eu^{3+}(1)$, but $V_{O^{++}}$ does not connect $Eu^{3+}(1)$ and $Eu^{3+}(2)$. In this cluster if the two europium ions and the OV are in plane we have a mirror plane element and therefore a C_s point symmetry; if not, as is the case displayed in Fig. 4(c), the symmetry drops to C_1 . This cluster [$Eu^{3+}(1)-V_{O^{++}}-Eu^{3+}(2)$] is described by $iii(C_1-C_s)$. The important issue in this last case is that only one of the Eu^{3+} ions of the pair, ($Eu^{3+}(1)$), loses the octahedral oxygen coordination and as a consequence we expect some spectroscopic similarities with site D discussed previously.

Fig. 4. Variety of possible two nearest neighbor substitutional Eu^{3+} ions clusters $i(C_s)$, $ii(C_s)$ and $iii(C_1-C_s)$ compensated by an oxygen vacancy ($V_{O^{++}}$, in white). Blue, red, yellow, and white spheres represent Sn, O, Eu, and O vacancies, respectively.

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^{4+} , 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 $2\text{Sn} \Rightarrow 2\text{Eu} + \text{V}_{\text{O}}^{++}$, 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 splittings of the ${}^7\text{F}_1$ level as well as an intensity enhancement of the electric dipole transitions are expected in agreement with the experimental TRFLN spectra results shown in Fig. 1 for sites A, B, and C.

3.3 RE excitation mechanism

As we have seen above, the RE doping creates additional V_{O}^{++} -type bulk OV's 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+} centers themselves would act as acceptors and the V_{O}^{++} near OV's 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 OV's to the RE center, the non-radiative transfer of the excitation energy to the 4f shell of the Eu^{3+} ion is thus a preferred channel. Figure 5 shows a sketch of the proposed mechanism. From a formal point of view we can consider the triply ionized RE ions to form “negatively charged” acceptor levels which may trap the hole generated by the UV excitation in one of the orbitals of the neighboring oxygens. As the holes occupy essentially valence band-like states, the recombination energy of the hole with a conduction band electron can be nonradiatively transferred to a nearby 4f-RE level close to the valence band maximum; thus 4f-4f transitions can be efficiently excited at energies close to or above the band gap.

Fig. 5. (a) Donor-acceptor pair and UV pumping photon. (b) Excitation process of the donor-acceptor pair. Under bandgap excitation a hole is trapped by the RE center (RC^-) acting as acceptor and an electron is trapped by the V_{O}^{++} vacancy acting as donor. (c) The nonradiative recombination of the bound exciton produces the Eu^{3+} excited state. (d) The radiative relaxation of the RE center leads to the Eu^{3+} emission.

Similar excitation processes could also occur in the case of substitutional europium pairs linked by V_{O}^{++} type OV's, giving rise to the low symmetry sites.

3.4 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 behavior by performing time-resolved ultrafast photoluminescence by using femtosecond multiphoton IR (800 nm) excitation to pump above the SnO_2 band gap. Figure 6 shows the normalized integrated emission spectrum of Eu^{3+} in the region between 550 and 750 nm obtained by 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 (see figure inset). The results indicate a three-photon excitation process.

Fig. 6. Normalized emission spectrum of the 0.5 mol% Eu^{3+} -doped SnO_2 powder pumped at 800 nm. The inset shows the power dependence of the VIS Eu^{3+} integrated emission intensity on a log-log 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.

3.4.1 Time-resolved emission dynamics of undoped and doped tin dioxide samples after multiphoton excitation above bandgap

SnO_2 emission: Taking advantage of the Streak camera facilities we have explored the emission of both undoped and Eu^{3+} -doped nanopowders in the spectral region 420-520 nm (around the maximum of the matrix emission) shown in Fig. 7(a) with a time window of 1 ns. The samples were excited by 100 fs laser pulses of 0.5 mJ at 800 nm. Figure 7(a) demonstrates that 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. On the other hand, 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. 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 Fig. 7(b). 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 ps, 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.

Fig. 7. (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 ($E_{\text{exc}} = 0.5$ 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 these undoped (blue points) and doped (red points) powder samples under the above mentioned excitation conditions and time window. The continuous red and blue lines are the best fits to two-exponential functions. (c) Normalized simultaneous emissions of the 0.5 mol % Eu^{3+} doped SnO_2 powder under three photon excitation at 800 nm extracted over the 417-484 nm spectral range (red line) and the two photon excited second harmonic generation extracted over the 395-417 nm spectral interval (blue line). The inset shows the streak camera image from where these temporal profiles were extracted.

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 dioxide nanoparticles in the same spectro-temporal window of the Streak camera. Figure 7(c) compares the normalized time-resolved emissions produced by the 0.5 mol % Eu^{3+} -doped SnO_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, ~ 8 ps, could be taken as an estimation of the electron capture time of the V_O^{++} vacancies for giving the host luminescence [30,31].

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^{3+} excited state. It is worth noticing that within the experimental resolution both signals have similar risetimes (~ 60 ps) suggesting that the beginning of the matrix photoluminescence associated to the excitation of a broad distribution of surface OV's is a very fast process which follows the exciting pulse.

Eu^{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^{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^{3+} emission.

In order to gain further insight on the energy transfer process which leads to the Eu^{3+} emission under SnO_2 excitation at 800 nm, we investigated the time dependent behavior of the emission of this RE ion in the doped SnO_2 powder by using two different time windows of the Streak camera; one of 100 μs 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 $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission of Eu^{3+} . As can be observed, the temporal profiles, Fig. 8(b,d), show an initial fast decay associated with the SnO_2 emission, and a much longer decay due to the Eu^{3+} emission. The spectral and temporal profiles of the undoped sample are also plotted with blue lines in Fig. 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 Fig. 7(a)), it is possible to remove the short time SnO_2 contribution from the doped sample decay by subtracting both profiles. The maximum of the obtained differential temporal profile (green line in Fig. 8) occurs at slightly longer times which is a fingerprint of the energy transfer process which populates the Eu^{3+} emitting centers. In addition, the shape of the differential profiles shown in Fig. 8 suggests a fast feeding of the Eu^{3+} excited state by energy transfer from the SnO_2 matrix under 800 nm excitation. The Eu^{3+} lifetime value obtained by fitting the longer decay of the differential temporal profile (green line) corresponding to the longest 1 ms temporal window with a single-exponential function is 216 μs . However, as can be seen in Fig. 8(b) the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission decay of Eu^{3+} is far to be completed; in fact 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. These long term values have been obtained also by other authors [15].

For time windows shorter than 100 μs only the matrix emission can be detected, so we could set a lower limit for the $\text{SnO}_2 \rightarrow \text{Eu}^{3+}$ nonradiative energy transfer rate based on the build up time measured with a time window of 100 μs . For this case the obtained risetime of the Eu^{3+} temporal emission profile is 650 ns which corresponds to a transfer rate of about $1.5 \times 10^6 \text{ s}^{-1}$ whereas the intrinsic broad band SnO_2 emission has a 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.

Fig. 8. Spectral (a, c) and temporal (b, d) profiles of the 0.5% mol Eu^{3+} doped SnO_2 powder in the 570–660 nm spectral range (red lines), which mainly corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission of Eu^{3+} . The spectral (a, c) and temporal emission profiles (b, d) of the pure SnO_2 powder are shown in blue. The green profiles of Fig. 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.

4. Conclusions

This investigation demonstrates the existence of at least four different crystal field sites of Eu^{3+} 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 OV's 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 Eu^{3+} has been demonstrated in SnO_2 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 RE 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%).

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 $1.5 \times 10^6 \text{ s}^{-1}$, 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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