Optical and Transport Properties of Rare-earth Trivalent Ions
Located at Different Sites in Sol-gel SnO$_2$

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Abstract. Photoluminescence and photo-excited conductivity data as well as structural analysis are presented for sol-gel SnO$_2$ thin films doped with rare earth ions Eu$^{3+}$ and Er$^{3+}$, deposited by sol-gel-dip-coating technique. Photoluminescence spectra are obtained under excitation with various types of monochromatic light sources, such as Kr$^+$, Ar$^+$ and Nd:YAG lasers, besides a Xe lamp plus a selective monochromator with UV grating. The luminescence fine structure is rather different depending on the location of the rare-earth doping, at lattice symmetric sites or segregated at the asymmetric grain boundary layer sites. The decay of photo-excited conductivity also shows different trapping rate depending on the rare-earth concentration. For Er-doped films, above the saturation limit, the evaluated capture energy is higher than for films with concentration below the limit, in good agreement with the different behaviour obtained from luminescence data. For Eu-doped films, the difference in the capture energy is not so evident in these materials with nanosccopical crystallites, even though the luminescence spectra are rather distinct. It seems that grain boundary scattering plays a major role in Eu-doped SnO$_2$ films. Structural evaluation helps to interpret the electro-optical data.

1. Introduction

Tin dioxide (SnO$_2$) is a wide bandgap material (about 3.6eV), [1,2] which presents high transparency in the visible (90%) and high reflectivity in the infrared range [3]. In the undoped form, this compound exhibits n-type conductivity, due to oxygen vacancies and interstitial tin atoms, generated during sample processing, which acts as donors in the matrix. The wide bandgap makes SnO$_2$ an attractive oxide for electrically activated emission [4], since wide bandgap semiconductors have higher excitonic ionization energy. Besides, the wide gap decreases the luminescence quenching effects [5]. One of the most promising electroluminescent display technologies is the thin films electroluminescence (TFEL). Among the TFEL devices, luminescent properties are related to intra 4f rare-earth transition [6], mainly the ions Eu$^{3+}$ and Er$^{3+}$, because their transitions take place on a wide energy range, with emissions from the visible to the infrared, allowing application in several optical communication devices.

We have investigated optical properties and optically induced transport properties of Eu and Er doped SnO$_2$ thin films, through measurements of photoluminescence and decay of photo-induced

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conductivity. The acceptor nature of ions Er$^{3+}$ and Eu$^{3+}$ [7,8] creates a high charge compensation degree in the material, which is naturally of n-type, leading to a high resistivity compensated semiconductor. When produced by the sol-gel process, SnO$_2$ thin film presents nanoscopic crystallites (about 5-20nm). This nanostructured material exhibits a high concentration of grain interfaces by unit area, which favors the impact ionization of luminescent centers, because hot carriers are promoted by the interface active layer/dielectric in a TFEL device layout [9]. Then, the electrical properties are strongly influenced by grain boundary scattering. It is also important to mention that optical and transport properties of rare-earth doped SnO$_2$ is strongly influenced by the location of the doping ion, at lattice site, substitutional to Sn$^{4+}$ or at grain boundary [8,10].

In this work, the luminescence spectra, under separated excitation with various distinct light sources, such as Kr$^+$, Ar$^+$ and Nd:YAG lasers, have been measured. Emission from these rare-earth ions confirms the different shapes of luminescence spectra whether the dominant luminescent center presents high symmetry, at lattice sites, substitutional to Sn$^{4+}$, or is located at asymmetric sites, segregated at boundary layer. Transport properties are also influenced by rare-earth ion location, because thin films excitation with the fourth harmonic of an Nd:YAG laser (4.65eV) at low temperature, yields distinct types of conductivity decay when the illumination is removed, which is related with the capture by rare-earth related defects located at different sites. Based on the model of trapping defects with thermally activated cross section [8,11], $E_{cap}$ (capture energy) is evaluated for the trapping centers substitutional at Sn$^{4+}$ lattice sites and located at grain boundary interface.

It is important to evoke that the thin film matrix presents a very useful shape for technological application, since it allows optical integration and the application of electric fields to operate electroluminescent devices.

2. Experimental

Colloidal suspensions of SnO$_2$ undoped and doped with Er$^{3+}$ or Eu$^{3+}$ have been prepared through the sol-gel route. Firstly, it has been prepared an aqueous solution of SnCl$_2$.5H$_2$O (0.5 M). The incorporation of Eu has been provided by dissolution of Eu$_2$O$_3$ in HCl, being the desired amount added to the starting solution. In the case of Er doping, the reagent used was ErCl$_3$.6H$_2$O. Under stirring with a magnetic bar, NH$_4$OH was then added until the pH reaches 11, leading to hydrolysis and condensation reactions. The remaining precipitated was submitted to dialysis against distilled water for about 10 days, in order to eliminate Cl$^-$/NH$_4^+$ ions. This procedure leads to a stable suspensions (sol) of SnO$_2$:Eu and SnO$_2$:Er. Xerogels (powders) were obtained by drying the suspension at room conditions and treated at 1000°C during 6 hours. For photoluminescence (PL) measurements at low temperature, the xerogel (powder) was treated at 1000°C during 6 hours and compressed down with a load of $5\times10^3$ kgf/cm$^2$ to the shape of a pellet. Sample cooling was done in a He closed-cycle cryostat from Janis.

X-ray diffraction data of films were obtained with a a RIGAKU diffractometer, model D/MAX-2100/PC, with a scanning rate of 1°/min in range of 20–80 degrees. For luminescence data presented here a few experimental setups were used: 1) for low temperature measurements, an Ar$^+$ laser from Spectra Physics model 2017 for sample excitation and signal recorded by a germanium detector from Edinburgh Instruments. 2) a xenon lamp of 450W, a fluorimeter SPEX F212I and a germanium detector North Coast Scient. Corporation model EO-8171. 3) excitation with a Kr$^+$ laser, tuned on an ultraviolet multi-line mode (3.67eV, 3.53eV and 3.47eV), 4) excitation with a Kr$^+$ laser, tuned on 2.57eV. A photomultiplier tube (PMT) R446 from Hamamatsu was used for signal measuring and recording in the experimental setup 3 and 4. 5) The fourth harmonic of a Nd:YAG laser, 4.65eV. The signal was detected by a CCD detector coupled with a Jobin Yvon monochromator, model T64000.

For the decay of photo-excited conductivity, it was used the fourth harmonic of a pulsed Nd:YAG laser (4.65eV), with 15Hz of frequency, and a Keithley 6517A for recording electrical characteristics. The AFM micrograph were obtained using a Nanoscope III-a from Digital Instruments and samples of imaging areas as large as 1 µm$^2$ were taken.
3. Results and discussion

X-ray diffraction data are shown in figure 1 for undoped SnO$_2$ and doped with some concentrations of Er$^{3+}$ or Eu$^{3+}$. Generally speaking, the definition of the obtained peaks is lower when compared to xerogels with the same composition [12]. It may be related to the influence of substrate, which decreases the signal magnitude obtained when the measurement is done under a shallow angle, 1.5°. Besides the thermal annealing temperature (550°C) does not allow a large crystallite growth, leading to broaden peaks in the X-ray pattern, typical of nanocrystalline domain. Comparing these results with rutile structure cassiterita phase (JCPDF, 41-1445) [13], there is good agreement as indicated by the main crystal directions shown in figure 1. The crystallite size, evaluate through the Scherrer equation [14], decreases for the increasing of rare-earth doping. For instance, taking into account the (101) direction, the crystallite size is 7.4, 5.2 and 3.5nm, for samples doped with 0.0, 0.1 and 4.0at% of Er respectively, whereas for Eu-doped SnO$_2$ films the evaluated value is about 7 nm for all the concentrations. The increase of rare-earth concentration inhibits the crystallite growth, which is similar to what happens in xerogels, because the excess of doping impurities segregates to the particles surface. Rietveld refinement data for rare-earth doped SnO$_2$ xerogels [12] allows evaluating the distortions for the rutile structure, caused by Er$^{3+}$ and Eu$^{3+}$ incorporation, as well as the distortion generated by the oxygen vacancies formation during its processing [15]. Comparing the undoped powder with Eu-doped samples, it is noticed that the structural disorder decreases with the introduction of up to 0.5% of Eu, and the increase of concentration to 1% Eu increases the disorder degree to a value close to the undoped xerogel. Then, the low doping leads to stabilization of cassiterite structure of SnO$_2$. Concerning the Er doping, there is an increase in the disorder for the sample doped with 0.1% of Er compared to the undoped sample. The disorder also increases when the doping level reaches 4%, similar to the observed behavior of samples highly doped with Eu. The excess of doping decreases the material crystallinity, because it generates clusters of a secondary phase, involving the SnO$_2$ matrix and inhibits the crystallite growth during the crystallization process. A secondary phase Eu$_2$Sn$_2$O$_7$ has been reported for Eu-doped SnO$_2$ with concentrations higher than 0.1at% of Eu [16], but this phase was not found in the present work.

![Figure1. X-ray diffractograms of thin films a) undoped SnO$_2$ and doped with 0.1 and 4at% of Er, b) SnO$_2$ doped with com 0.1, 0.5 and 1at% of Eu.](image-url)
Figure 2 (a) shows temperature dependence of photoluminescence (PL) spectra measured at temperatures 50 K and 280 K for a 2at% Er doped SnO$_2$ xerogel sample. Sample was excited with an Ar$^+$ laser, operating with 2.53eV of excitation energy, according to setup 1. The Er$^{3+}$ transition $^4I_{13/2}$→$^4I_{5/2}$ around 0.8eV is clearly evidenced by the presence of several peaks. The excitation energy (2.53eV) corresponds to the transition from ground state to $^4F_{7/2}$. The inset of Figure 2(a) shows PL spectra for tin dioxide xerogel codoped with 2at% of Er and Yb, excited by a Xenon lamp plus a monochromator (setup 2). It can be noticed in figure 2 that the cooling down leads to PL intensity increase, since the it decreases the lattice vibration of SnO$_2$, and then phonon assisted nonradiative processes, which enhance light emission from Er$^{3+}$ core transition. It allows the observation of spectra details at low temperature, not observed at higher temperatures. In the measurement carried out at 50 K, it is clearly seen the presence of others peaks not observed at 280 K. This vanishing is probably related to lattice vibration. All the observed peaks are related to the decay of excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$. The presence of several peaks can be attributed to the splitting of $^4I_{13/2}$ and $^4I_{5/2}$ levels due to the matrix crystalline field [17]. The Er$^{3+}$ $^4I_{13/2}$ manifold has upper states of the excited degenerate $^4I_{13/2}$ level populated due to local laser heating [17], as evidenced by the fact that such a line splitting does not take place when the sample is irradiated with monochromatic light coming from a xenon lamp (inset of fig. 2(a)). In the inset of figure 2(a), the two different excitation energies were used: 3.77eV and 2.35eV, according to the experimental setup 2. The codoping with Yb$^{3+}$ allows verifying the energy transfer process, by exciting with 1.26eV, corresponding to transition $^2F_{5/2}$→$^2F_{5/2}$ of Yb$^{3+}$ and an energy transfer to transition $^2F_{5/2}$→$^4I_{11/2}$ of Er$^{3+}$. However the verification of this energy transfer process is not the scope of this paper, and has been done elsewhere [18]. As can be seen in the inset of figure 2(a), the spectra present rather distinct shape depending on the energy excitation. They are related to two families of Er sites: substitutional to Sn$^{4+}$ and segregated at boundary layer. The second family is related to the solubility limit of rare-earth (RE) ions in tin dioxide, which is about 0.05at%, and the doping excess become located at boundary layer [19]. For the high doping concentration (2%) of the samples reported here, it is expected very many Er complexes segregated at boundary layer. The inset of figure 2(a) shows the emission of Er$^{3+}$ at room temperature, excited directly. The spectra observed by excitation by 2.35eV, is similar to the observed by excitation with 1.26eV [18], which is effective only for Er$^{3+}$ complexes located at particles surface. On the other hand, the rare-earth ions located at Sn$^{4+}$ sites are not substantially excited by this procedure. Substitutional sites located Er$^{3+}$ ions are excited via band-to-band excitation of SnO$_2$ [18] and the spectra is as shown in the inset of figure 2(a) by 3.77eV excitation.

Figure 2(b) shows the green emission from an Er doped (4%) SnO$_2$ thin film, excited according to the experimental setup 3, and a SnO$_2$:2%Er pellet, excited by the experimental setup 4. The energy range in both curves of figure 2(b) are in good agreement and assures that the observed wide emission, with a peak about 2.33eV, includes the $^4H_{15/2}$→$^4I_{15/2}$ radiative transition of Er$^{3+}$ ion. The broad shape is probably related to random neighborhood of Er$^{3+}$ in the SnO$_2$ lattice, which could be surrounded by a varying number of oxygen vacancies, interstitial tin atoms and doping ions (the doping concentration is rather high). Besides, it also could be affected by the distance form the grain boundary, since we are dealing with nanoscopic particles, in the range 5-20nm. Besides, the excess of Er is located at grain boundary, as discussed for figure 2(a), which are low symmetry sites and could contribute to the broad band. Luminescence from the matrix of SnO$_2$ itself has been reported recently [20], with very similar shape to the curves of figure 2(b), but shifted to UV-violet, presenting a peak about 3.10eV, which was attributed to oxygen vacancies. On the other hand, the observed broad green emission centered about 2.33eV could be associated to the transition from the excited state $^2H_{11/2}$ to the $^4I_{15/2}$ ground state, as already mentioned. In the spectrum of figure 2(b), film is excited with the multlines UV from a Kr$^+$ laser (most intense line at 3.53eV). Figure 2(b) also shows photoluminescence (PL) emission from a pellet (powder compressed) of SnO$_2$:2%Er, with excitation with 2.57eV, which is coincident with $^4I_{15/2}$→$^4F_{7/2}$ transition. Although the laser line at 2.57eV is not enough to excite the green transition in the SnO$_2$:4at%Er film, it is accountable for the excitation of observed transition in SnO$_2$:2%Er pellet. It means that to obtain efficiently the transition, the number of exciting centers in
the beam light path becomes very relevant. This path is rather long for the pellets but much shorter for the film. However our results in the visible range make sure that luminescence is possible also for the film, which justifies a deeper investigation of film emission in the infrared. Crystallite nanoscopic dimensions could play a relevant role in the emission spectra, due to the possibility of quantum confinement effects [21,22].

Figure 2. (a) Photoluminescence (PL) spectra for 2at% Er doped SnO$_2$ xerogel at 50 K and 280K. Sample was excited with an Ar$^+$ laser, operating with 2.53eV of excitation energy. Inset - PL of SnO$_2$:Er,Yb (2% at.) under excitation at: 3.77eV and 2.35eV (c). PL spectra of SnO$_2$:4% thin film, excited with the multi-lines ultraviolet (3.53eV) of a Kr$^+$ laser, and of SnO$_2$:2%Er pellet, excited with 2.57eV (482nm) from the same Kr$^+$ laser.

Figure 3 shows PL spectra obtained under excitation with 4.65eV (266nm) laser line (experimental setup 5) for Eu-doped SnO$_2$ xerogels with 1.0 and 0.5 at% Eu concentrations. The inset of Figure 3 shows PL spectra of 0.5% Eu doped SnO$_2$ xerogel, under excitation with 4.65eV and 2.53eV (488nm). The energy of 4.65eV is related to matrix band-to-band excitation, followed by energy transfer to Eu$^{3+}$ ions. It is important to point out the nature of the transitions $^5D_0\rightarrow^7F_2$ (2.02eV) and $^5D_0\rightarrow^7F_1$ (2.10eV), labeled in figure 3. The latter one is a magnetic dipole transition and its intensity is not affected by structural changes of the nearest neighborhood, whereas the transition $^5D_0\rightarrow^7F_2$ is ruled by electric dipoles, being hypersensitive to the local crystalline field [23]. The ratio between the areas of these emission lines, i.e., $(^5D_0\rightarrow^7F_2) / (^5D_0\rightarrow^7F_1)$ is called asymmetry ratio. An increase of asymmetry ratio from 0.01 to 5.2 is evaluated for samples with 0.5 to 1at% Eu, respectively, which means that for increasing Eu$^{3+}$ concentration, energy transfer is more efficient to ions located far from the symmetry center, for example, ions located close to the particles surface. For SnO$_2$:0.5%Eu$^{3+}$ samples the PL line shape suggests an asymmetric ratio very close to zero, indicating that the dominant Eu$^{3+}$ ion is actually located at lattice sites, substituional to Sn$^{4+}$. The xerogel SnO$_2$:1at%Eu presents PL spectra with the electric dipole $^5D_0\rightarrow^7F_2$ transition as dominant, suggesting that the Eu$^{3+}$ ion is located close to the particles surface, with low symmetry. The excess of doping must cause the energy transfer to the Eu$^{3+}$ sites belonging to the SnO$_2$ lattice to be less effective, when compared to luminescence from other centers with lesser symmetry. This behavior may be also related with decrease of particle size with increasing of Eu concentration. There is a decrease of the particle size as the Eu concentration increases. Excitation with 4.65eV leads to a very well defined PL spectra,
with peaks centered at 2.11, 2.09 and 2.07 eV, corresponding to the three components of $^5D_0 \rightarrow ^7F_1$, as clearly observed in figure 3. In this case, the observed emission at 2.02 eV presents low intensity. Then the asymmetric ratio is very close to zero, indicating that Eu$^{3+}$ is actually located at lattice sites, substitutional to Sn$^{4+}$ in the SnO$_2$ matrix [24]. On the other hand, directly excitation of Eu$^{3+}$ ion with 2.53 eV leads to an increase of the asymmetric ratio, as can be seen in the inset of figure 3, for SnO$_2$:0.5at%Eu. The solubility limit of Eu in SnO$_2$ is about 0.05 to 0.06 at% [16]. Then the excess of Eu segregates to particle surface, giving rise to a non-homogeneous impurity distribution. The observed broadening in the PL emission may be related to Eu$^{3+}$ ions segregated at particle surface with random distribution of first neighbors. Then, we may conclude that the emission of Eu$^{3+}$ substitutional in the SnO$_2$ lattice is more evident under excitation at 4.65 eV, suggesting a high energy transfer from the matrix due to band-to-band excitation. It is also possible to verify that the emission from Eu$^{3+}$ ions located close to particles surface is more clearly observed by direct excitation of $^7F_2 \rightarrow ^5D_2$ transition with the 2.53 eV laser line.

![Figure 3](image-url)

**Figure 3.** PL spectra for SnO$_2$:0.5at%Eu and SnO$_2$:1.0at%Eu xerogels at 295 K, under excitation with the fourth harmonic of a Nd:YAG laser (4.65 eV). Inset - PL for SnO$_2$:0.5at%Eu under excitation with the same 4.65 eV laser line and with 2.53 eV line of an Ar$^+$ laser.

Figures 4(a) brings results of decay of photo-excited conductivity at several temperatures, for thin films of SnO$_2$ doped with 0.1 at% and 1 at% of Eu$^{3+}$, respectively. In this measurement, films were irradiated with the fourth harmonic of a Nd:YAG laser (4.65 eV), promoting electron-hole pair excitation, increasing the number of charge carriers and thus, the material conductivity. After 10 min of light irradiation, time enough to the excitation promotes a carrier saturation, laser illumination was removed and the decay of current was measured as function of time. Fig. 4(b) shows resistivity as function of temperature for SnO$_2$ thin films doped with 0.1%Er and 0.1%Eu, measured in the dark and also measured a long time after being submitted to the laser irradiation, corresponding to the measured decay presented in figure 4(a). As can be seen in figure 4(b), the Eu$^{3+}$ doped sample presents a higher resistivity when compared to Er$^{3+}$ doped films, which is probably related to the larger size of Eu$^{3+}$ (0.947 Å) compared to Er$^{3+}$ (0.890 Å) [25]. Besides the figure 4(b) also allows verifying the long lasting persistent photoconductivity phenomena in rare-earth doped SnO$_2$ films [26]. As the Er-doped sample remains a longer time under low pressure, its resistivity becomes higher than the Eu-doped
film, due to slow oxygen adsorption. Figure 4 allows verifying that there is a concentration dependent decay of photoexcited current as well as a temperature dependency. Increasing the temperature and Eu concentration, the capture rate also increases, leading to a faster decay. According with the electron capture model presented previously [8,11], the slope of this curve allows evaluating the quantity \((E_{\text{cap}} - \phi)\), where \(E_{\text{cap}}\) is the trapping energy barrier, related to a relaxation process and \(\phi\) is the grain boundary potential barrier. In this model, we consider the electron scattering at grain boundary as the dominant mechanism for the conductivity [8]. Average values were obtained for these films, fig. 4(a), leading to 113meV and 116meV, for 0.1% and 1at% doped films, respectively.

![Figure 4](image-url)

**Figure 4.** (a) Decay of photoexcited conductivity at several temperatures for SnO\(_2\)0.1at%Eu and SnO\(_2\)1at%Eu. (b) Resistivity as function of temperature for SnO\(_2\)0.1at%Eu and SnO\(_2\)0.1at%Er in the dark and long times after submission to the fourth harmonic of a Nd:YAG laser (4.65eV).

Recently, we have found the existence of different centers in thin films of SnO\(_2\):Er, through measurements of decay of photoexcited conductivity [8,11]. The electron trapping energy by defects are related to oxygen vacancies as well as rare earth centers. Both types of defects are active in the capture process, but they present distinct capture cross section and trapping times. There is a strong indication that the trapping by Er\(^{3}\+\) centers is dominant for short times, and for longer times the capture by oxygen vacancies becomes a competitive process. A larger variation in the quantity \((E_{\text{cap}} - \phi)\) was found for Er\(^{3}\+\)-doped SnO\(_2\) thin films [8,11], when the doping concentration is greatly varied, being found energies of 78, 70 and 118meV for 0.05, 0.1 and 4at% de Er\(^{3}\+\), respectively. Increasing the concentration from 0.05at% to 0.1at%, we observed a lower capture barrier, which is consistent with a faster decay detected in these measurements. On the other hand, when the Er\(^{3}\+\) concentration increases to a high value (4at%), the value of \((E_{\text{cap}} - \phi)\) increases, which has been interpreted as due to a distinct location of Er\(^{3}\+\)-related trap, located in the particles surface, in opposition to the lower
doping case, where the dominant trapping center is located in the lattice, substitutional to Sn⁴⁺. The increase in the value of (E_{cap} - φ) may be related to the presence of oxygen vacancies at grain boundary, which is reinforced by EXAFS measurements at K edge of Sb⁵⁺ in Sb-doped SnO₂ thin films [15], where it was verified that an increase in the doping concentration decreases the barrier height between grains. Then, if φ decreases, (E_{cap} - φ) may increase. Comparing (E_{cap} - φ) for SnO₂: 0.1at% Er³⁺ and SnO₂: 0.1at% Eu³⁺, assuming that the intergrain potential barrier (φ) has the same height for both samples, the capture barrier (E_{cap}) is higher for Eu doping, which is consistent with a higher disorder obtained by the calculation of structural refinement of these samples [12]. Figure 5 shows atomic force microscopy data for undoped SnO₂ and 4%Er-doped. As can be seen, the undoped sample presents metallurgical grains of about 20-50nm, whereas the doped sample has its granular surface structure destroyed. Instead of grains, some spikes are observed. This figure may help the interpretation that in doped samples the crystallite are indeed the lowest structure, what does not happen in well formed films, where crystallites become part of a larger domain, composed of metallurgical grains. The spikes observed for the 4% doped sample may actually be related to the evaluated crystallite size, which is under investigation.

![AFM images](image.png)

**Fig 5 – AFM of a) undoped SnO₂, b) 4at% Er³⁺-doped SnO₂**

### 4. Conclusions

Temperature dependent excitation of 2at%Er in SnO₂ with 2.53eV promoted the excitation of ions Er³⁺ to its ⁴F₇/₂ level and the probable decay to nonradiative level ⁴I₁₃/₂, with subsequent emission to the ground state ⁴I₉/₂, which means emission in the technologically interesting value of 0.8eV. Broad visible emission from Er-doped thin film has been observed with peak about 2.33eV (green). It corresponds to ⁵H₁₁/₂ → ⁴I₉/₂ radiative transition of Er³⁺ ion. The broad band profile may be related to the random distribution of oxygen vacancies, interstitial tin atoms and doping in the neighborhood of the Er³⁺ lattice sites, substitutional to Sn⁴⁺ or segregated at grain boundary, which are low symmetry sites.

Eu-doped SnO₂ xerogels emission using 4.65eV and 2.53eV laser lines as excitation sources, allows distinguishing two Eu³⁺ families in SnO₂: one located in the lattice sites, substitutional to Sn⁴⁺, and another one, where rare-earth impurity gets preferentially at particles surface due to segregation.
caused by excess of doping. Excitation with 4.65 eV promotes matrix band-to-band excitation and an efficient energy transfer to Eu$^{3+}$ substitutional to Sn$^{4+}$. Above the doping saturation limit, energy transfer is no longer efficient to Eu$^{3+}$ at lattice sites and the energy transfer to ions located close to the particles surface, with lower symmetry, becomes operative.

The difference of capture barrier by the defects and intergrain potential barrier can be evaluated by a trapping model of photo-induced carriers as published elsewhere [8]. Its application for the thin films studied here, leads to higher capture energy for samples doped with Eu$^{3+}$ compared to Er$^{3+}$, which may be an indication that the lattice relaxation is higher for the Eu-centers, even though the lattice relaxation mechanism in these films is still unknown.

The results shown in this paper are very promising under a technological point-of-view, since it reveals the possibility of controlling the emission from Er and Eu-doped SnO$_2$ concerning luminescence spectra structure through rare earth concentration and excitation procedure. Besides, we report emission from thin film, which is a very useful layout for this material, since allows the integration in optical systems and makes the electroluminescence phenomena in this material a reality in a very short time.

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