

## Photoluminescence dynamics in strontium titanate

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(Dated: October 19, 2009)

The recombination dynamics of electron-hole pairs of pure and  $n$ -doped strontium titanate (STO) bulk samples after an intense UV laser-pulse excitation has been investigated by collecting and analysing the frequency- and time-resolved photoluminescence (PL) signal, as a function of the sample temperature. The observed PL decay is in the nanosecond time-scale and it shows a peculiar mixed kinetics. In particular, two decay channels are clearly singled-out: the faster one has a decay-time that is markedly dependent on the photo-excited carrier density and it is well described as a bimolecular recombination process, while the second slower channel shows an excitation-independent rate and follows an unimolecular law. The PL spectra show a considerable variation with temperature, with a previously unreported, pronounced difference between pure and doped samples emerging at high temperatures. A first discussion of the possible underlying mechanisms is attempted.

PACS numbers: 78.55.-m, 71.35.Ee, 73.50.Gr, 78.47.+p

### I. INTRODUCTION

Strontium titanate, SrTiO<sub>3</sub> (STO), plays a crucial role in the research on transition metal oxides for a number of reasons. First, it can be considered as a “prototype material” in the class of functional oxides having a perovskite or perovskite-like structure, and, thus, a deeper knowledge of its properties is thought to be a first step for reaching a better understanding about many related compounds, such as high- $T_c$  superconductors and ferromagnetic, ferroelectric or multiferroic materials. A second reason is its wide use as a substrate for the epitaxial growth of many of the above cited oxides. A third reason is that STO, in spite of its simple structure, shows a number of interesting and still poorly understood features, ranging from quantum paraelectricity to strain-induced ferroelectricity<sup>1,2</sup>. Intrinsic STO is a band insulator, characterized by a record-high low temperature static dielectric constant which mainly results from the soft elastic coupling of the small Ti<sup>4+</sup> ion with the surrounding octahedral O<sup>2-</sup> cage. The empty and rather flat conduction band is made up mainly of Ti 3d  $t_{2g}$  states, while the valence band largely comes from O 2p states, the edge being located quite far from the  $\Gamma$  point of the Brillouin Zone<sup>3</sup>. Therefore, STO has an indirect gap of about 3.2 eV, while the direct (optical) transition edge is at about 3.4 eV, both values having a non negligible sample and temperature dependence<sup>4</sup>. Its transport and optical properties are very changeable too: a slight  $n$ -doping turns the material from an indirect-gap transparent insulator into an opaque conductor with a large low-temperature mobility<sup>5,6</sup>. In this regime, it is well accepted that the charge carriers behave as large polarons, whose mass increases with temperature<sup>7</sup>.  $n$ -doped samples show superconductive transport properties too<sup>8</sup>, while  $p$ -type doping is still a challenge, although some interesting progresses have been recently made<sup>9</sup>.

A recent paper<sup>10</sup> has focused the researchers atten-

tion on an interesting photoluminescent band, emitted by  $n$ -doped STO under exposure to UV-light irradiation. According to Kan *et al.*, pure STO samples exhibit a significant blue PL emission at room temperature if previously irradiated with an Ar<sup>+</sup>-ion beam. Since the main effect of ion bombardment is believed to be the creation of oxygen vacancies inside the material, and since a very similar PL emission was found in La<sup>3+</sup> and Nb<sup>4+</sup> doped samples<sup>11</sup>, the blue-band PL has been connected to the presence of electron-donating defects. However, a rather similar blue-band PL emission has been also observed in pure samples under very intense pulsed excitation<sup>12–14</sup>. This points to a more complex underlying scenario, possibly associated with intrinsic properties of STO, yet to be clarified.

In this paper, after briefly reviewing our recent results on the PL of STO for pure and  $n$ -doped STO under high excitation intensities, we report new results on the behavior of the PL spectra and decay dynamics as a function of temperature, ranging from room temperature to about 900 K. The reported results add another piece of experimental evidence to the widely studied, ill understood phenomenology of photo-generated electron-hole pairs recombining and radiating in STO.

### II. EXPERIMENT

The experimental setup and data analysis procedure were described elsewhere<sup>13</sup>. Here we just summarize the main physical parameters. The UV light source we used for excitation is the third harmonic of the emission of a mode-locked Nd:YAG laser. Its wavelength of 355 nm corresponds to a photon energy of 3.49 eV, well above the STO bandgap of 3.27 eV and slightly above its optical absorption edge (about 3.4 eV)<sup>15,16</sup>. The UV pulses had a duration of 25 ps (full width at half maximum, FWHM) and a repetition rate of 10 Hz. This low repetition rate

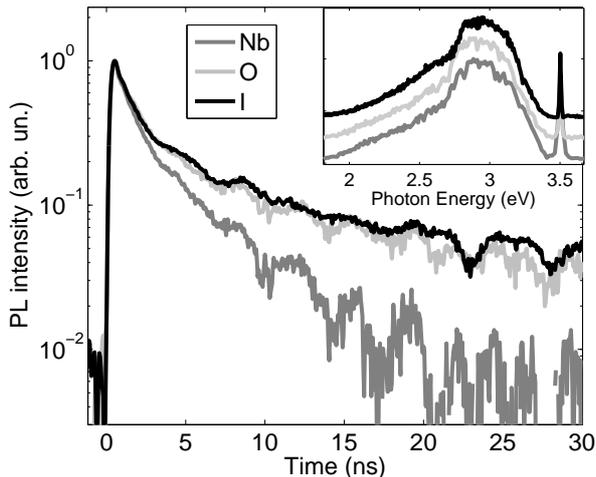


FIG. 1: Room temperature normalized PL decay of I-STO (black), O-STO (pale gray) and Nb-STO (gray) samples under UV irradiation with a pulse energy of 0.5 mJ. Oscillations in the decays are due to the instrumental response function. Inset: room temperature normalized PL spectra of the same samples at the same irradiation energy. The sharp peak at 3.5 eV is ascribed to residual scattered pump light. Spectra are vertically shifted for clarity.

ensures that most cumulative effects are negligible. The maximum excitation energy we have used in the measurements presented here was 1 mJ per pulse, in a gaussian spot with a waist of  $1.2 \pm 0.1$  mm. Assuming an optical penetration length of about a micron<sup>16</sup>, this corresponds to an energy density of about  $300 \text{ J/cm}^3$  and, hence, to a number of photogenerated electron-hole pairs (e-h) of about  $6 \times 10^{20} \text{ cm}^{-3}$ . Because of this high pump intensity, we paid much attention to any possible laser-induced damages on the sample surface, but we have never seen any visible damage and all measurements were found to be fully reproducible.

At our excitation energies the PL emission was clearly visible to the naked eye, although rather weak. The integrated PL emission was found to scale linearly with the pump energy, although somewhat noisy, with signs of saturation appearing only above about 0.7-1 mJ (depending on the sample). This high saturation intensity seems incompatible with impurity-levels filling and it could be connected with the onset of Auger nonradiative recombination. Auger recombination was actually proposed as the main mechanism for nonlinear PL dynamics even at lower excitation energies<sup>17</sup>. However, our “global” (i.e., simultaneous) fits to the full set of decays measured in each sample for a range of excitation energies rule out the possibility of a third-order Auger effect (although a defect-assisted bimolecular Auger process is not ruled out)<sup>13</sup>. A simulation we performed on the data reported in<sup>17</sup> shows that even for these data a third-order Auger process, although it can fit fairly well the single decay, cannot explain the variation of decay rate (and signal

amplitude) with energy.

The samples we studied are of three kinds: I-STO (for “intrinsic”), O-STO (for “oxygen vacancy”) and Nb-STO (for “niobium”-doped) samples. I-STO samples were pure, as-received,  $5 \times 5 \times 0.5 \text{ mm}^3$  slabs of (100) oriented STO single crystals, with a nominal impurity level below 150 ppm; O-STO samples were obtained from I-STO samples by annealing for 1 h at  $950^\circ\text{C}$  in a  $10^{-9}$  mbar vacuum; Nb-STO samples were commercial STO single crystals with a 0.2% mol Nb concentration. During PL measurements, the samples were mounted in a thermostat for temperature control in the range 300-900 K, with a stability of  $\pm 0.1$  K. For each sample and temperature, the PL spectra was measured for relatively low ( $50 \mu\text{J}$  and high ( $500 \mu\text{J}$ ) excitation energies. Moreover, for each sample and temperature a set of decays was measured at varying pump energies. It is worth noting that I-STO and Nb-STO samples did not show any aging or hysteretic behavior due to oxygen exchange with atmosphere, as we checked by repeated measurements. O-STO samples were, on the contrary, found to be rapidly oxidized above a critical temperature (about 500 K), so that we could not investigate the high temperature behavior.

### III. EXPERIMENTAL RESULTS

In the inset of Fig. 1, the typical PL spectrum of I-STO, O-STO, and Nb-STO samples at room temperature is shown. No significant difference is seen among different kinds of samples. All spectra peak at about 425 nm (2.9 eV, Stokes shift of 0.35 eV) and present a long tail up to 650 nm (1.9 eV). The PL yield was found to be of the same order of magnitude in all samples; a typical factor two of yield reduction was seen in Nb-STO samples as compared with I-STO and O-STO, although this variation falls within the sample-to-sample variations occurring within the same kind of samples. Typical PL temporal decay curves of each kind of samples are shown in the main panel of Fig. 1, in a semilogarithmic (vertical) scale: the overall dynamic features are also found to be very similar for all observed samples, although Nb-STO samples again show a systematically faster decay.

The most interesting feature of the PL decay is its behavior when increasing the excitation energy. The initial decay rate, in particular, changes significantly: the higher the pumping, the faster the decay. Besides this fast initial decay, in the PL decay a slower “tail” is clearly visible, which changes its amplitude with the excitation energy, but not its decay rate. We have shown<sup>13</sup> that this behavior can be explained by a model assuming two separate e-h populations with two different decay channels, one following a simple unimolecular (UD) decay, and the other a bimolecular (BD) one. The predicted overall PL intensity  $I$  at any time  $t$  is then found to be

$$I(t) = C_1 \exp[-t/\tau_{UD}] + C_2/(1 + t/\tau_{BD})^2 \quad (1)$$

where,  $U$  being the excitation energy density,  $\tau_{UD}$  and

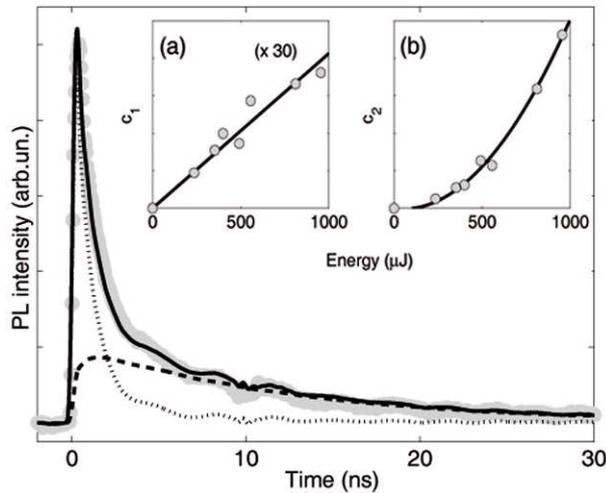


FIG. 2: An example of a PL decay best fit (on a I-STO sample) as resulting from our BD-UD model. Pale gray dots are data, the dotted line is the faster BD term, the dashed line is the slower UD term and the solid line is the total best fit. Inset: the UD (a) and BD (b) coefficients as a function of the excitation energy. Solid black lines are the corresponding linear and quadratic best fits, respectively. The scale of the (a) panel is multiplied by a factor 30 for clarity.

$\tau_{BD} \propto 1/U$  are the UD and the BD characteristic times respectively and  $C_1 \propto U$ ,  $C_2 \propto U^2$  are the UD and BD coefficients. An example of the decay curve decomposition is given in Fig. 2, where the BD and the UD contributions are drawn separately. In the inset of the same figure is also possible to see the behavior of the UD and BD coefficients  $C_{1,2}$  as a function of the excitation energy. Qualitatively the same dynamics was observed in all kinds of samples and at all investigated temperatures. In Fig. 3, the UD and BD characteristic times  $\tau_{UD}$  and  $\tau_{BD}$  are shown as a function of temperature for I-STO and Nb-STO samples. The BD lifetimes (referred to a pump energy of 1 mJ) of both kinds of sample decrease with almost the same slope, at least above 400K, while the UD lifetimes show a marked difference. In particular, the UD lifetime in Nb-STO samples does not decrease significantly with increasing temperatures up to almost 700 K. Excluding the case of the Nb-STO UD lifetime, the activation energies associated with the lifetimes temperature behavior are in the range of 10-100 meV, with a significant sample-to-sample variation.

High temperature PL measurements allow to highlight a previously undisclosed, remarkable difference in the physical response of our pure and doped samples. In Fig. 4, several spectra obtained at different temperatures and different pump-energies are shown. A progressive depletion of the overall PL generation efficiency is seen. The luminescence yield with temperature follows an Arrhenius law, with a sample-dependent characteristic energy in the 50–100 meV range. It is interesting to notice that under ordinary low-intensity continuous irradiation luminescence is vanishing at temperatures above 500 K<sup>18</sup>.

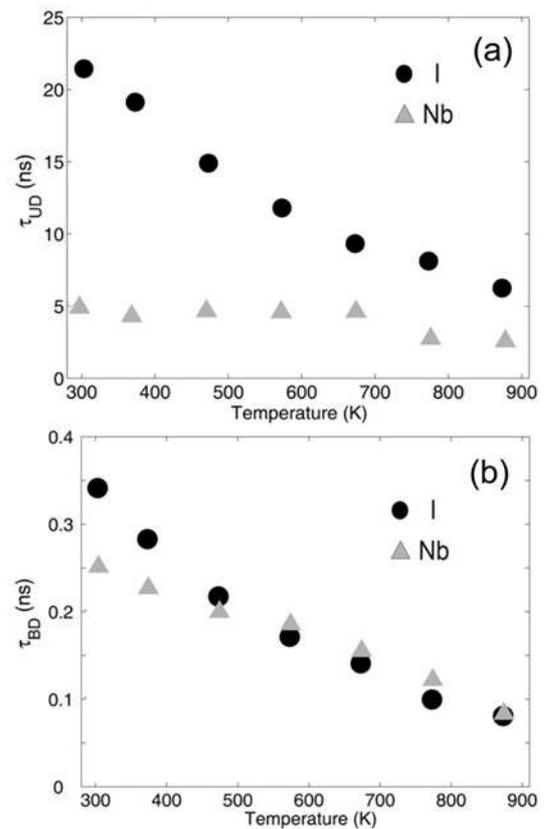


FIG. 3: UD (a) and BD (b) lifetimes of I-STO (black dots) and Nb-STO (grey triangles) samples as a function of temperature. The BD lifetimes are evaluated using a reference pump-energy of 1 mJ.

The yield decrease does not however take place uniformly: the shape of the spectrum clearly changes, at least in I-STO samples. Even to the naked eye, the color of the PL emitted by I-STO samples changes clearly from blue to green when crossing a temperature of about 600 K. By analyzing the spectra more quantitatively, it is possible to resolve at least two bands: one (“blue band”) peaked at about 430 – 440 nm (2.8 – 2.9 eV) and one (“green band”) at about 490 – 500 nm ( $\sim 2.4$  eV). The overall shape is asymmetrical, and both bands are present and distinguishable at any temperature, in spite of a marked overlap. The overlap is even stronger in doped samples, as the data in Fig. 4c demonstrate. At a closer inspection, one further spectral feature located at about 3.0 eV (400 nm) is also seen. This appears as a shoulder in the lowest temperature measurements, while it is better separated, although strongly depressed, at higher temperatures (Fig. 4a). The spectra are qualitatively consistent with the ones reported in the literature: the observed bands have the same energies of those reported by Mochizuki *et al.* at low temperatures<sup>12</sup>. The spectrum of La<sup>3+</sup>-doped STO reported in<sup>11</sup> closely resembles the one in Fig. 4d at 300 K. However, our data show a comparatively higher spectral weight in the green region.

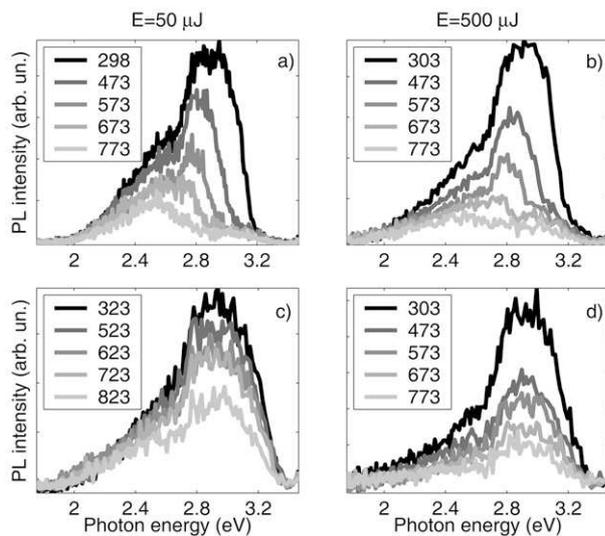


FIG. 4: PL emission spectra at different temperatures (given in the legend boxes, in Kelvin degrees). Data were taken with  $50 \mu\text{J}$  energy per pulse (left column) and  $500 \mu\text{J}$  energy per pulse (right column). Panels (a) and (b) refer to an I-STO sample while panels (c) and (d) to a Nb-STO sample.

The 2.4 eV emission at low temperatures was interpreted in a quantitative way<sup>19</sup> in terms of the annihilation of a self-trapped exciton. In this picture, the broadening of the band is due to the emission of several optical phonons with energy  $\sim 90$  meV. This scenario does not seem to be compatible however with the high-temperature survival of the green band. Moreover, it was found that the UD-

BD kinetics is roughly the same for both blue and green bands of the PL spectrum, so that a simple association of the green band with the UD kinetics and the blue band with the BD kinetics is not possible. Owing to the different temperature quenching and pump-intensity behavior of these two bands, we believe that different recombination centers are involved. Based on our detailed modeling of the luminescence decay (to be published in a forthcoming paper), we believe that the whole luminescence arises from the recombination of the mobile charges with charges that are trapped at some intrinsic defects, yet to be identified. If this interpretation is correct, then the bimolecular dynamics reflects the mainly nonradiative recombination of the mobile charges while the unimolecular dynamics corresponds to the untrapping lifetime of the trapped charges.

#### IV. CONCLUSIONS

In summary, we investigated the spectral and dynamical features of the blue-green photoluminescent emission from both intrinsic and Nb-doped STO crystals, in the so-far unexplored regime of high temperature and high excitation fluence. A peculiar spectral change is seen at high temperature in intrinsic samples, but not in doped ones. The presence of a mixed bimolecular-unimolecular dynamics, previously reported at room temperature, is confirmed in the whole temperature range. This analysis allows to separately address and analyse the temperature dependence of the BD and UD lifetimes.

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