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Temperature dependence of luminescence decay in Sn-doped silica

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Abstract

We report an experimental study on the temperature dependence, in the range 18–300 K, of the decay kinetics of the emission at 4.1 eV from the first excited electronic state of oxygen deficient centers in a 2000 ppm Sn-doped sol–gel silica. At low temperature, this luminescence decays exponentially with a lifetime of 8.4 ns, whereas, on increasing the temperature, the time decay decreases and cannot be fitted with an exponential function. These results are expected if there is a competition between the radiative and the thermally activated intersystem-crossing decay channels toward the associated triplet state. The comparison with previous data in pure oxygen-deficient and Ge-doped silica gives new insight on the effect of the host-matrix dynamics on the electronic properties of this type of point defect.

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1. Introduction

In recent years, attention has been given to studies on Sn-doped silica because of its ultraviolet (UV) photosensitivity and its use in the field of optical fibers [1,2, and reference therein]. In this respect, the study of point defects in this material is relevant since they affect its optical properties. Some works have shown that the UV optical absorption (OA) of Sn-doped silica is dominated by a band peaked at 4.9 eV, which excites two photoluminescence (PL) emissions at ~4.1 eV, decaying in few nanonseconds, and at ~3.2 eV, decaying in few microseconds [3–7]. On the basis of the comparison with optical transitions observed in oxygen-deficient and Ge-doped silica, the above reported OA and PL bands were ascribed to a twofold coordinated Sn, $=Sn^{\cdot\cdot}$, where (=) indicates the bonds with two oxygen and (··) indicates two paired electrons, which is isoelectronic to $=Si^{\cdot\cdot}$ and $=Ge^{\cdot\cdot}$. In agreement with an unified picture accounting for the optical properties related to this isoelectronic series [3], the $=Sn^{\cdot\cdot}$-related OA at 4.9 eV originates from the transition between the ground singlet (S_0) and the first excited singlet (S_1) states, the 4.1 eV emission is associated with the radiative decay $S_1 \rightarrow S_0$ while the 3.2 eV is due to the spin-rule forbidden transition from the triplet state $T_1 \rightarrow S_0$ and is excited by an intersystem crossing (ISC) process linking the two excited states. The reliability of this scheme has been till now experienced by looking at the intensity ratio between the two PL bands as a function of temperature, which has evidenced the effectiveness of the ISC process [3,4,6].

In this paper, we report an experimental investigation on the temperature dependence of the kinetics of the 4.1 eV emission aiming to clarify the competition

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between the two active relaxation channels from the excited state S_1, the radiative and the ISC. This study is also relevant on the one hand in view of the comparison between the de-excitation properties of the twofold coordinated Sn and those associated with the isoeletronic Si-, Ge-defects studied in previous woks [8,9] and on the other hand to shed new light on their relationship with the host-matrix dynamics.

2. Experimental methods

Experimental data were obtained on a silica sample, rod shaped with a diameter of 4 mm and thickness of 1.4 mm, prepared by sol–gel method [10] and doped with 2000 ppm of Sn atoms. Sol–gel synthesis from hydrolysis of tetraetoxysilane and dibutyl-tin-diacetate was employed to obtain Sn-doped silica containing tin in substitutional position for silicon atoms, avoiding Sn segregation [10]. The final material was obtained heating the xerogels in O_2 by a thermal ramp (4 °C/h) up to 1050 °C. Inductively-coupled-plasma spectroscopy analysis of the Sn concentration after the thermal treatment revealed no change of tin content above the uncertainty (about 10%) of the nominal value.

The OA spectrum was measured on a double-beam spectrophotometer (JASCO V-570), mounting a deuterium lamp and a 1200 grooves/mm Czerny–Turner grating. A bandwidth of 0.5 nm, a scan speed of 20 nm/min and a time constant value of 1 s were used.

PL measurements were carried out on a spectrofluorometer (JASCO FP-770) equipped with a 150 W Xenon lamp. Emission spectra, in the wavelength range 248–550 nm (5.00–2.25 eV), were detected under excitation at 248 nm (5.00 eV). Both excitation and emission bandwidths were chosen to be 3 nm, and a scan speed of 100 nm/min and a time constant of 1 s were used. PL profiles were corrected for spectral response of the detection system by placing a magnesium oxide scatterer in the sample compartment and performing a synchronous scan of excitation and emission monochromators; the spectral efficiency of the exciting light was determined by using a Rhodamine B sample in glycerol.

For optical measurements as a function of temperature, in the range 3.0–330 K, we used a continuous-flow liquid helium cryostat (Oxford-Optistat^{CF}), equipped with four optical windows. Temperature was controlled by an instrument (Oxford-ITC503). At each temperature, the spectra were recorded after 20 min for thermal equilibrium.

Lifetime measurements, in the temperature range 18–300 K, were carried out by pulsed excitation at 5.0 eV using the synchrotron radiation light with a pulse width of 130 ps at the SUPERLUMI station on the I-beam line of HASYLAB at DESY (Hamburg) [11]. The wavelength of the emitted light was selected by a 0.5 m monochromator Czerny–Turner mounting and detected by a photomultiplier (Hamamatsu R2059). The dead time of the overall detection system was evaluated as 2.3 ns, so that only data for times longer than 2.3 ns were considered for the time decay analysis. For each measurement, the transient decay was acquired by using 1024 channels for scanning a time interval of 192 ns between adjacent pulses.

3. Results

Fig. 1 shows the optical transitions in the Sn-doped silica. The UV absorption at room temperature is dominated by a band peaked at 4.93 ± 0.01 eV, full width at half maximum (FWHM) of 0.51 ± 0.03 eV, amplitude of 8.6 ± 0.1 cm^{-1}. Excitation within this OA induces two emissions peaked around 3.2 and 4.1 eV whose temperature dependence is opposite: on increasing the temperature from 10 K up to 300 K, the 3.2 eV PL increases whereas the 4.1 eV decreases. We note that the total area measured under these two PL bands remains constant with temperature. This thermal dependence is consistent with the occurrence of the phonon assisted ISC process linking the two excited states, depopulating the S_1 state and populating the T_1 state with negligible contribution from other non-radiative channels.

To determine the relation between the ISC and the radiative decay, we investigated the temperature dependence of the time relaxation of the 4.1 eV emission under excitation at 5.0 eV. In Fig. 2 are reported the decay curves at various temperatures from 18 to 300 K. The emission decay occurs in the ns scale and, on increasing the temperature, the decay time decreases and the kinetics deviate from a single exponential law. The quantita-

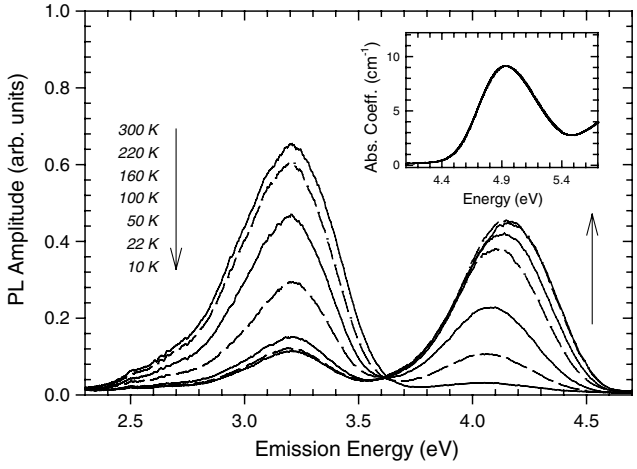

Fig. 1. Photoluminescence spectra detected at various temperatures in the Sn-doped silica sample under excitation at 5.0 eV. Arrows indicate the changes induced on decreasing the temperature. In the inset is also reported the absorption band measured at room temperature.