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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 nanoseconds, 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^{••}, where (=) indicates the bonds with two oxygen and (••) indicates two paired electrons, which is isoelectronic to =Si^{••} and =Ge^{••}. In agreement with an unified picture accounting for the optical properties related to this isoelectronic series [3], the =Sn^{••}-related OA at 4.9 eV originates from the transition between the ground singlet (S₀) and the first excited singlet (S₁) states, the 4.1 eV emission is associated with the radiative decay S₁ → S₀ while the 3.2 eV is due to the spin-rule forbidden transition from the triplet state T₁ → S₀ 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 isoelectronic Si-, Ge-defects studied in previous works [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 tetraethoxysilane 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-

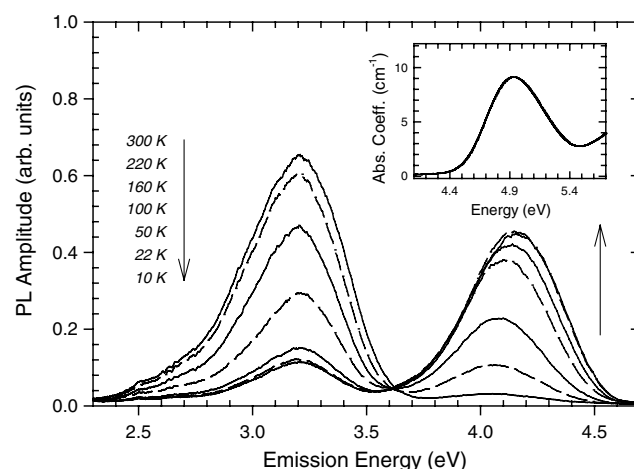


Fig. 1. Photoluminescence spectra detected at various temperatures in the Sn-doped silica sample under excitation at 5.0 eV. Arrows indicate the changes induced on decreasing the temperature. In the inset is also reported the absorption band measured at room temperature.

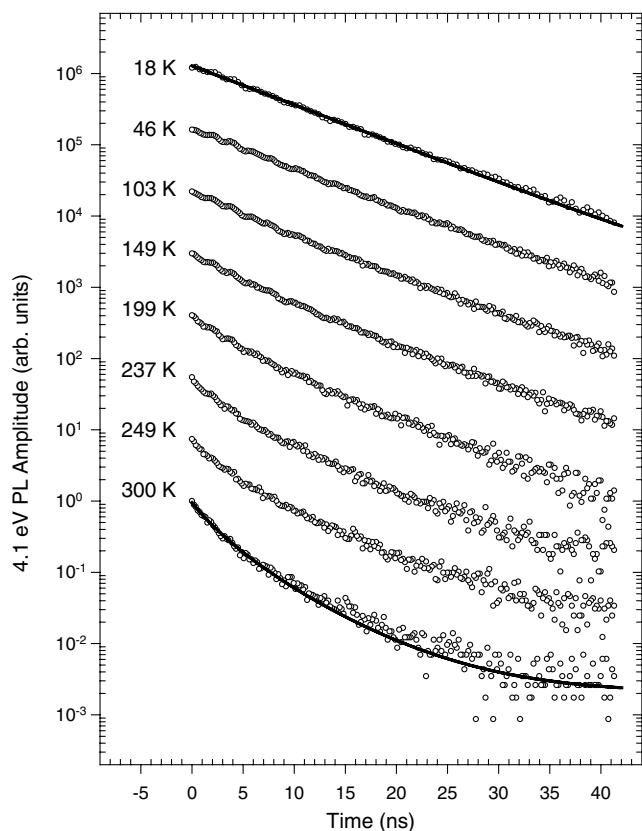


Fig. 2. Decay kinetics of the 4.1 eV emission, detected under pulsed excitation at 5.0 eV, at various temperatures from 18 to 300 K. For viewing purposes, the curves are vertically scaled. Solid lines plot the fitting to the data at 18 and 300 K, according to Eq. (1).

tive analysis of the data reported in Fig. 2 is made by fitting the decay curves with a stretched exponential function:

$$I \propto \exp[-(t/\tau)^\gamma], \quad (1)$$

where τ is a characteristic decay time and γ is a stretching parameter that measures the deviation from a single exponential law.

In Fig. 3, the τ and γ obtained by this fitting procedure are plotted as a function of temperature. As shown in Fig. 3(a), τ decreases monotonically from 8.4 ± 0.3 ns at $T = 18$ K to 1.0 ± 0.5 ns at $T = 300$ K. The parameter γ , reported in Fig. 3(b), also decreases with temperature: from 1.0 measured at low temperature when the decay curve is well fitted by a single exponential law to 0.6 at room temperature.

4. Discussion

The temperature dependence of the two emissions at 4.1 and 3.2 eV reported in Fig. 1 can be explained assuming the presence of two relaxation rates from the S_1 state: the pure radiative one, k_S , temperature indepen-

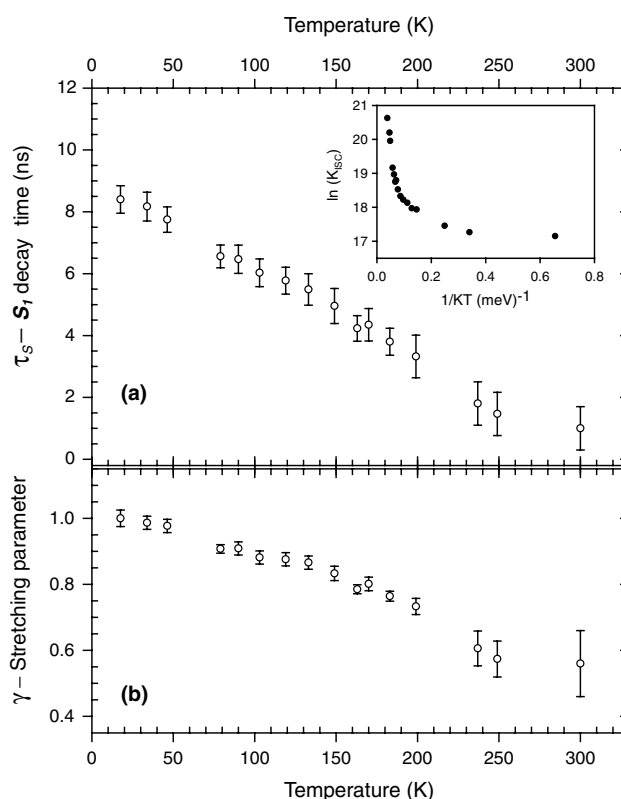


Fig. 3. Temperature dependence of the decay parameters τ (a) and γ (b), as determined by fitting the decay kinetics of the 4.1 eV emission under pulsed excitation at 5.0 eV using Eq. (1). Reported in the inset of panel (a) is the Arrhenius plot of $K_{ISC} = (\tau^{-1} - k_S)$.

dent, and the thermally activated non-radiative, K_{ISC} , toward T_1 , in agreement with previous works [3,4,6]. Then, the temperature dependence of the relative amplitudes of the emissions band is proportional to the strength of the ISC process. Indeed, the ratio between the two emission bands is a quantitative measurement of the K_{ISC} with respect to k_S , as a function of temperature [12,13]:

$$\frac{K_{ISC}(T)}{k_S} = \frac{I_T(T)}{I_S(T)}, \quad (2)$$

where I_T and I_S are the integrated intensities of emissions originating from the triplet (3.2 eV) and singlet (4.1 eV) excited states, respectively. We note that we can assume the validity of Eq. (2) since, apart from K_{ISC} , the other non-radiative relaxation processes from S_1 and T_1 can be neglected in accordance with the observation that the total PL intensity $I_T + I_S$ is constant with temperature.

The thermal dependence of S_1 lifetime, τ , is due to the competition between the radiative channel k_S and the thermally activated K_{ISC} in agreement with

$$\tau = (k_S + K_{ISC})^{-1}. \quad (3)$$

In this respect, the observed reduction of τ with increasing temperature is the counterpart of the K_{ISC} increasing, as discussed about the emission profiles reported in Fig. 1. In particular, our results show that the lifetime shortens more and more at $T \geq 50$ K, so indicating that in this temperature range K_{ISC} is larger than k_{S} .

The comparison between lifetime measurements and PL spectra together with the combination of Eqs. (2) and (3) allows us to single out the different contributions of the rates k_{S} and K_{ISC} . At low temperature ($T = 18$ K) the 4.1 eV emission decays exponentially with rate $\tau^{-1} = k_{\text{S}} \cdot (1 + K_{\text{ISC}}/k_{\text{S}}) = (1.19 \pm 0.03) \times 10^8 \text{ s}^{-1}$; hence, substituting $K_{\text{ISC}}/k_{\text{S}}$ measured from the ratio $I_{\text{T}}/I_{\text{S}} = 0.23 \pm 0.08$, we get $k_{\text{S}} = (0.9 \pm 0.1) \times 10^8 \text{ s}^{-1}$ to which corresponds $\tau_{\text{S}} = k_{\text{S}}^{-1} = 11 \pm 1$ ns. Based on this estimation the temperature dependence of K_{ISC} can be isolated by investigating the values of $(\tau^{-1} - k_{\text{S}})$. As shown in the inset of Fig. 3, K_{ISC} features a non-Arrhenius temperature dependence, suggesting a distribution of activation energies of the ISC process. As an estimate, by the slope in the temperature range 300–200 K we found that this distribution has values up to a maximum of ~ 100 meV. An inhomogeneous distribution of K_{ISC} agrees with previous results for oxygen deficient centers of Si and Ge [6,14–16].

A second point emerging from lifetime data regards the deviations from the single exponential law observed in our experiments and described by Eq. (1) with the introduction of the γ stretching parameter, whose temperature dependence is reported in Fig. 3(b). We note that similar results were found by measuring the time decay of the 4.2 eV PL associated with Ge related defects [9,14].

As a final remark, we comment on the comparison of results reported here with those reported in recent papers [8,9,14] to point out how the time decay parameters, τ and γ , are affected by the substitution of a twofold coordinated Si with Ge and Sn. In fact, in the temperature range 10–300 K, the 4.4 eV PL (Si-related) decays exponentially ($\gamma = 1$) with a lifetime τ poorly dependent on temperature; for the PL at 4.2 eV (Ge-related) τ and γ decrease above ~ 100 K; finally, for the PL at 4.1 eV (Sn-related) τ and γ start to decrease at lower temperature. In agreement with Eq. (3), these features are explained by the K_{ISC} rate, whose effectiveness is larger and larger for the Si-, Ge-, Sn-related defects sequence [3,17]. We note the analogy of this effect with the increase of the radiative decay from the excited triplet state of these defects; so, we corroborate that K_{ISC} is sensitive to the spin–orbit coupling energy, which increases with the atomic number (heavy atom effect) [3].

5. Conclusions

The reported data proves that the ISC process determines the temperature dependence of the time decay of the luminescence arising from the first excited singlet state of the twofold coordinated Sn in silica. The observed kinetics are a consequence of the inhomogeneous distribution of the ISC rates induced by the matrix disorder. These data complete the study of the S_1 de-excitation in the Si-, Ge- and Sn-isoelectronic series and agree with the increased ISC efficiency with increasing atomic number.

Acknowledgments

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