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Relaxation processes of point defects in vitreous silica to nanoseconds

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Abstract

We studied ultrafast relaxation of localized excited states at Ge-related oxygen deficient centers in silica using femtosecond transient-absorption spectroscopy. The relaxation dynamics exhibits a biexponential decay, which we ascribe to the departure from the Frank–Condon region of the first excited singlet state at 240 fs, followed by cooling in ~10 ps. At later times, a nonexponential relaxation spanning up to 40 ns occurs, which is fitted with an inhomogeneous distribution of nonradiative relaxation rates, following a chi-square distribution with one degree of freedom. This reveals several analogies with phenomena such as neutron reactions, quantum dot blinking, or intramolecular vibrational redistribution. © 2008 American Institute of Physics.

Silica (amorphous SiO2) is a material of paramount importance in solid-state physics and in material science, both because it provides a model for disordered amorphous systems and because of its widespread applications. Many of these applications are related to optically active point defects, their generation (e.g., photosensitivity), and their relaxation dynamics upon excitation of localized excited states (e.g., in case of scintillators). During these processes, an excited defect and an out-of-equilibrium local matrix are created, which thermalize to a new configuration on the timescales of femtoseconds and picoseconds. There is a strong connection among the matrix dynamics on the subpicosecond timescale, photosensitivity, and point defect generation, as corroborated by studies on femtosecond laser-modified optical properties of silica and by recent experimental and computational work.

In this work, we used femtosecond transient absorption (TA) spectroscopy to identify the ultrafast relaxation processes of excited states localized on point defects in silica and their dynamical interaction with the local matrix. Specifically, we focus on Ge-related defects because of their fundamental role in photosensitivity and in optical device technology. In particular the twofold coordinated Germanium (often indicated with =Ge−) has a distinct optical activity (so-called B activity) and a rather simple energy level scheme, which makes it a suitable system for our studies. B activity consists of two broad (full width at half maximum ~0.5 eV) absorption bands at ~5 and at ~7.5 eV due to transitions from the S0 ground state to the first S1 and second S2 excited singlet states, respectively. Emission bands from S1 at ~4.2 eV and from the first excited triplet state T1 at ~3.1 eV have been observed, with typical room-temperature lifetimes of 2–4 ns and 110 μs, respectively.

The only nonradiative relaxation channel from S1 is a phonon-assisted intersystem crossing (ISC) to the T1 state, which occurs at (ns)−1 rates at room temperature. Here, we follow in real time the conformational relaxation dynamics, upon excitation to the S1 state. The silica sample was doped with Ge atoms at 10−2M³, resulting in a final amount of ~Ge− of ~1018/cm³. As a reference, we have used an undoped, Ge-free, commercial sample. Both samples have optically polished surfaces and a nominal thickness of 1 mm.

TA measurements were performed in a pump-probe scheme. Femtosecond pump and probe pulses at 266 nm (4.7 eV) and 400 nm (3.1 eV), respectively, were obtained from the amplified output of a 1 kHz Ti:Sapphire laser (nominally, 100 fs, 0.8 mJ, at 800 nm). Subsequently the two pulses were focused onto the sample with a spot size of ~70 μm for the pump and ~30 μm for the probe, orthogonally polarized with respect to each other. The cross correlation between the pump and probe pulses is 140 fs at the sample site. After verifying the linearity of the TA signal as a function of pump and probe intensities, these were set to 9 × 1012 and 3 × 1011 mW/cm2 pulse, respectively. Under these conditions, we observe no significant bleaching of the optical B activity over several hours, as monitored by the intensity of the two emission bands induced by the pump pulse. Since the probe depletion ΔI was a small fraction of the transmitted probe intensity I0, we calculated the TA signal as log10(e)ΔI/I0 as a function of time delay with respect to the pump pulse.

The TA kinetics of Ge-doped and undoped samples are shown in Fig. 1. The absence of any signal from the undoped specimen and the linear dependence of the probe depletion on the pump and probe intensity proves that the depletion signal is due to the B activity only, specifically to the S1 →S2 transition (see the aforesaid B-activity energy level scheme). Under our experimental conditions (linear regime and ΔI/I0 ≤ 1), the signal is proportional to the product of the S1 population n1 and the S1 →S2 absorption coefficient α, where in general both factors are time dependent. The

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change of $\alpha$ is expected due to conformational rearrangement and cooling processes toward the $S_1$ energy minimum whereas $n_1$ is affected by the population loss from $S_1$ to $S_0$ and $T_1$. In Fig. 2, the TA kinetics of Fig. 1 is complemented with time resolved $S_1\rightarrow S_0$ luminescence measurements from 2 up to 40 ns upon excitation at 4.7 eV previously reported (see Ref. 7). To merge them, we scaled the two data to match the expected $S_1\rightarrow S_0$ emission quantum yield of 0.33. Overall, we identify three main timescales: a fast exponential-like decay ($<1$ ps) followed by a slower one ($\sim$10 ps) and a third, nonexponential and much slower decay ($\sim$ns). We focus first on the early dynamics ($\sim$20 ps). The two fast components are fitted with the sum of two exponential decays sitting on top of the slowest component. All these functions are convoluted with the temporal instrumental response which is assumed Gaussian

$$I(t) = \exp\left[-\frac{1}{2}(t/\sigma)^2\right] \otimes \left[I_0(t) + \sum_{i=1,2} I_i \exp(-t/\tau_i)\right], \quad (1)$$

where $I_0$ and $\tau_i$ are amplitude and lifetime of the exponential decays, respectively, $\sigma$ is the standard deviation of the instrumental response, and $I_0(t)$ accounts for the slowest component and just looks like a step function on this time scale [see Eq. (2) and relative discussion]. The fit and the relative parameters are reported in Fig. 1 and Table I, respectively.

The fastest processes occur on timescales typical of vibrations in silica ($10^{-12}$–$10^{-13}$ s), and therefore we ascribe them to structural relaxation. This is in good agreement with recent computational results, with the formation time of self-trapped excitons in bulk silica and with the damping of vibrational modes related to four and three-membered SiO$_2$ ring structures. This suggests that the shortest decay component corresponds to departure from the initial out-of-equilibrium configuration, mainly driven by the matrix dynamics. This result is supported by recent measurements, which have revealed that an isoelectronic substitution of Ge atoms with Sn atoms has a minor effect on the defect-matrix coupling. The subsequent relaxation of the system on the $\sim$10 ps timescale corresponds to vibrational cooling in the $S_1$ state, by dissipation to the matrix phonons.

We now turn to the slower decay kinetics (>20 ps). Based on the above discussion, the $S_0$ state is thermalized, and therefore the observed decay reflects its depopulation. The observed nonexponential decay of the $S_1\rightarrow S_0$ luminescence signal (see data in Fig. 2 at $t>2$ ns and compare them with dashed line in the same figure) has been related to an inhomogeneous dispersion of decay rates [specifically, of the nonradiative rates from $S_1$, since the radiative $S_1\rightarrow S_0$ rate $k_S$ ($1.28 \pm 0.03 \times 10^8$ s$^{-1}$) is not affected by inhomogeneous effects]. The data in the 20 ps–40 ns range of Fig. 2 are well described by the modified power law $I_P(t)$ (see solid line in Fig. 2 and Fig. 1 at time $>20$ ps),

$$I_P(t) = \frac{I_{\text{max}} e^{-kt}}{(1 + k_{\text{ISC}})^{n/2}}, \quad (2)$$

where $k_{\text{ISC}}$ is a typical value for the $S_1\rightarrow T_1$ ISC rate (see Table I for the parameter values). This law corresponds to the sum of individual exponential decays

$$\int_0^\infty e^{-(k_{\text{ISC}}/\bar{k}_{\text{ISC}})^n} \frac{d(k_{\text{ISC}})}{\bar{k}_{\text{ISC}}}.$$

where the ISC rates $k_{\text{ISC}}$ are dispersed according to a chi-square distribution $\chi^2_{n/2}$ with $n$ degrees of freedom and $\bar{k}_{\text{ISC}}$ as average value. Accordingly, $\bar{k}_{\text{ISC}}$ agrees well with the rate which was estimated to $1 \times 10^9$ s$^{-1}$ from steady state luminescence measurements. Remarkably, this distribution has been previously used to describe dynamical processes in many, seemingly unrelated systems, such as neutron reactions, quantum dot blinking, or intramolecular vibrational redistribution (see, e.g., Ref. 15). A RMT description of our system is based on two assumptions on the spin-orbit Hamiltonian $H^{SO}$ coupling the initial state $i$ (a vibrationally relaxed $S_1$ state, $S_0^i$) and $N$ final states $j$ (the hot vibrational states of $T_1$ resonantly coupled to $S_0^j$): (i) each individual defect corresponds to one of the possible realizations of $H^{SO}$, where the off-diagonal matrix elements $H_{ij}$ are well described as independently distributed around zero with Gaussian probability $P(H_{ij}^{SO}) \propto \exp[-(H_{ij}^{SO}/\bar{H}_{SO})^2]$, with $\bar{H}_{SO}$ being the average local coupling strength, (ii) the (inhomogeneous) ensemble of the defects probed corresponds to a large and statistically independent sample of all the possible random realizations of the spin-orbit Hamiltonian.

We recall that the ISC rate for a single defect is proportional to $\sum_j |H_{ij}^{SO}|^2$, hence, if $\bar{H}_{SO}$ is the same for every defect,
the ensemble distribution of \( k_{\text{ISC}} \) is a \( \chi^2 \) distribution with \( N \) degrees of freedom, and we should deduce that \( N \approx 1 \), i.e., that \( S_1^0 \) is coupled only to one vibrational level of \( T_1 \). Yet this is typical for systems small enough that not all parts of the energetically allowed phase space are accessible and it can hardly be true for glassy systems. In this systems, excited states have a direct access to a high density of quantum states hardly be true for glassy systems. In this systems, excited states have a direct access to a high density of quantum states, which is typical for systems small enough that not all parts of the lattice disorder has been observed but a satisfactory rationalization has not been found.

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