

Supporting Information

Multiple Intersystem Crossing Processes in Ge-doped Silica Glass: Emission Mechanism of Twofold Coordinated Ge atoms

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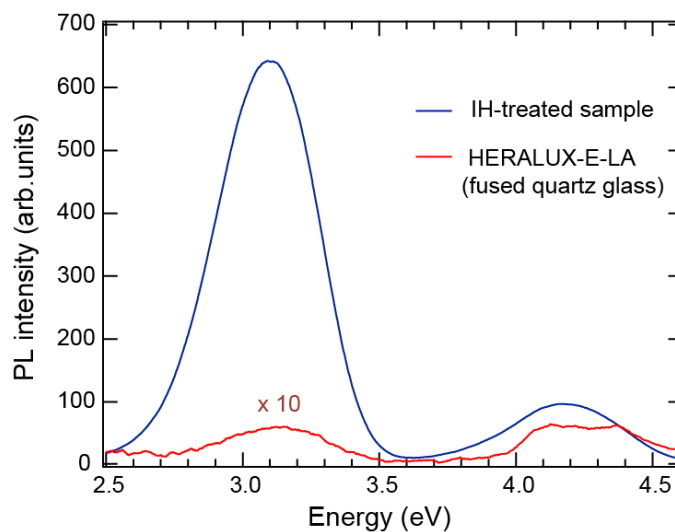


Figure S1. Room-temperature PL spectra of a Ge-doped silica sample prepared by IH method and a commercial fused quartz sample (HERALUX-E-LA) measured under $S_0 \rightarrow S_1$ excitation at 5 eV.

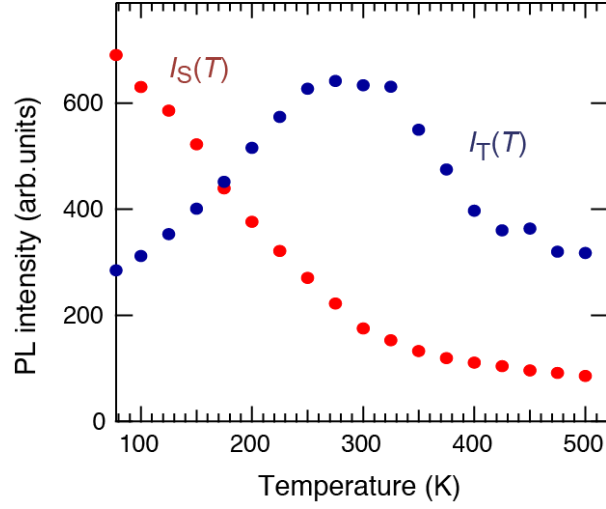


Figure S2. Temperature dependence of the PL signals of a commercial fused quartz sample measured under 5-eV excitation. PL intensities of the $S_1 \rightarrow S_0$ ($I_S(T)$) and the $T_1 \rightarrow S_0$ ($I_T(T)$) emission bands peaking at ~ 4.2 and ~ 3.1 eV, respectively, are shown as a function of temperature T .

Detailed derivation of Eqs. (5)-(8)

According to the emission scheme shown in Fig. 1(a), the kinetic equations for the respective energy levels can be written as follows:

$$\frac{dN_0}{dt} = -\alpha N_0 + k_S^R N_1 + (k_T^R + k_T^{NR}) N_2 \quad (S1)$$

$$\frac{dN_1}{dt} = \alpha N_0 - (k_S^R + k_{ISC}) N_1 \quad (S2)$$

$$\frac{dN_2}{dt} = k_{ISC} N_1 - (k_T^R + k_T^{NR}) N_2 \quad (S3)$$

where N_0 , N_1 , and N_2 are the population of the S_0 , S_1 and T_n states, respectively,

When we treat the above equations under the steady state approximation $dN_0/dt=dN_1/dt=dN_2/dt=0$, the quantum efficiency η of the $S_1 \rightarrow S_0$ (η_S) and $T_n \rightarrow S_0$ (η_T) emission can be represented by

$$\eta_S = \frac{k_S^R N_1}{\alpha N_0} = \frac{k_S^R}{k_S^R + k_{ISC}} \quad (S4)$$

$$\eta_T = \frac{k_1 N_2}{\alpha N_0} = \frac{k_T^R k_{ISC}}{(k_T^R + k_T^{NR})(k_S^R + k_{ISC})} \quad (S5)$$

Under normal excitation conditions, the emission intensity is linearly correlated with η . Accordingly, the resulting emission intensity of the $S_1 \rightarrow S_0$ (I_S) and $T_n \rightarrow S_0$ (I_T) processes are

$$I_S = K_1 \frac{k_S^R}{k_S^R + k_{ISC}} \quad , \quad (S6) \text{ or } (5)$$

$$I_T = K_2 \frac{k_T^R k_{ISC}}{(k_T^R + k_T^{NR})(k_S^R + k_{ISC})} \quad (S7) \text{ or } (6)$$

where K_1 and K_2 are the scaling (temperature independent) constants depending on a given excitation intensity and the instrumental conditions. Using the functional form of k_{ISC} [see Eq. (4) in the text], Eq. (S6) can be modified into the following form:

$$\begin{aligned} I_S(T) &= K_1 \frac{k_S^R}{(k_S^R + k_{ISC}^{(1)} + A_{ISC}^{(2)} \exp(-E_{ISC}^{(2)}/k_B T) + A_{ISC}^{(3)} \exp(-E_{ISC}^{(3)}/k_B T))} \\ &= K_1 \frac{1}{(1 + (k_{ISC}^{(1)}/k_S^R) + (A_{ISC}^{(2)}/k_S^R) \exp(-E_{ISC}^{(2)}/k_B T) + (A_{ISC}^{(3)}/k_S^R) \exp(-E_{ISC}^{(3)}/k_B T))} \end{aligned}$$

$$= \frac{C_1}{1 + C_2 \exp\left(-\frac{E_{\text{ISC}}^{(2)}}{k_B T}\right) + C_3 \exp\left(-\frac{E_{\text{ISC}}^{(3)}}{k_B T}\right)}, \quad (\text{S8) or (7)}$$

where

$$C_1 = \frac{K_1 k_S^R}{k_S^R + k_{\text{ISC}}^{(1)}},$$

$$C_2 = \frac{A_{\text{ISC}}^{(2)}}{k_S^R + k_{\text{ISC}}^{(1)}},$$

$$C_3 = \frac{A_{\text{ISC}}^{(3)}}{k_S^R + k_{\text{ISC}}^{(1)}},$$

Similarly, Eq. (S7) can be modified into the following form using the functional form of k_T^{NR} [see Eq. (3) in the text] and k_{ISC} [see Eq. (4) in the text]:

$$I_T(T) = K_2 \frac{k_T^R(k_{\text{ISC}}^{(1)} + A_{\text{ISC}}^{(2)} \exp(-E_{\text{ISC}}^{(2)}/k_B T) + A_{\text{ISC}}^{(3)} \exp(-E_{\text{ISC}}^{(3)}/k_B T))}{\left(k_T^R + A_T^{\text{NR1}} \exp(-\frac{E_T^{\text{NR1}}}{k_B T}) + A_T^{\text{NR2}} \exp(-E_T^{\text{NR2}}/k_B T)\right) \left(k_S^R + k_{\text{ISC}}^{(1)} + A_{\text{ISC}}^{(2)} \exp(-E_{\text{ISC}}^{(2)}/k_B T) + A_{\text{ISC}}^{(3)} \exp(-E_{\text{ISC}}^{(3)}/k_B T)\right)}$$

$$= \frac{C_4(C_5 + C_2 \exp\left(-\frac{E_{\text{ISC}}^{(2)}}{k_B T}\right) + C_3 \exp\left(-\frac{E_{\text{ISC}}^{(3)}}{k_B T}\right))}{(1 + C_6 \exp\left(-\frac{E_T^{\text{NR1}}}{k_B T}\right) + C_7 \exp\left(-\frac{E_T^{\text{NR2}}}{k_B T}\right))(1 + C_2 \exp\left(-\frac{E_{\text{ISC}}^{(2)}}{k_B T}\right) + C_3 \exp\left(-\frac{E_{\text{ISC}}^{(3)}}{k_B T}\right))}, \quad (\text{S9) or (8)}$$

where

$$C_4 = K_2,$$

$$C_5 = \frac{k_{\text{ISC}}^{(1)}}{k_{\text{S}}^{\text{R}} + k_{\text{ISC}}^{(1)}},$$

$$C_6 = \frac{A_{\text{T}}^{\text{NR1}}}{k_{\text{T}}^{\text{R}}},$$

$$C_7 = \frac{A_{\text{T}}^{\text{NR2}}}{k_{\text{T}}^{\text{R}}}.$$

From the fits of the data shown in Fig. 2(a) to Eqs. (7) and (8), we can obtain the values of activation energies, i.e., $E_{\text{T}}^{\text{NR1}}$, $E_{\text{T}}^{\text{NR2}}$, $E_{\text{ISC}}^{(2)}$, $E_{\text{ISC}}^{(3)}$, along with the parameters related to the frequency factors, i.e., C_i ($i=1-7$). The fitted values are shown in Fig. 2(a). It should be noted, however, that the values of C_i ($i=1-7$) do not represent the absolute values of the frequency factors but are the relative values among these frequency factors.