Concentration Dependence of Afterglow Suppression in CsI:Tl,Sm

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Abstract. Combined radioluminescence, afterglow and thermoluminescence experiments on single-crystal samples of co-doped CsI:Tl,Sm suggest that deeper samarium electron traps scavenge electrons from shallower thallium traps and that electrons subsequently released by samarium recombine non-radiatively with holes trapped as $V_{KA}(Tl^+)$ centers, thus providing a mechanism for suppression of trapped-charge accumulation in repetitive applications. In the present investigation, experiments performed on two single-crystal samples of CsI:Tl,Sm with nominal concentrations of 0.11% Tl$^+$ and of 0.2% and 0.05% Sm$^{2+}$, respectively, support the inference that electrons tunnel freely between samarium ions and are trapped preferentially near $V_{KA}(Tl^+)$ centers where non-radiative recombination is the rate-limiting step.

1. Introduction
The feasibility of substantially diminishing afterglow in CsI:Tl scintillator material by co-doping with Sm$^{2+}$ has been demonstrated. [1] Rate equations informed by experiment predict that deeper samarium electron traps, involving diffuse 6s orbitals of Sm$^+$, scavenge electrons from shallower thallium traps, and combined radioluminescence, afterglow and thermoluminescence experiments on single-crystal samples of CsI:Tl,Sm suggest that most electrons released by Sm$^+$ recombine non-radiatively with holes trapped as $V_{KA}(Tl^+)$ centers, thus providing a mechanism for suppression of trapped-charge accumulation in repetitive applications. [2] A linear-coupling model in the harmonic approximation, based on quantum-chemistry calculations with selective lattice relaxation, suggests further that non-radiative charge transfer is enabled by low-energy excited states of Sm$^{2+}$ within the ground configuration and is mediated by spin-orbit interaction, as illustrated in Figure 1. Although recombination is primarily non-radiative, tracking of the process with increased sensitivity of the optical detection system is enabled both by radiative recombination following thermal ionization and by a small radiative component of the charge-transfer recombination associated with magnetic-dipole transitions from low-energy excited states of Sm$^{2+}$. In the present investigation, combined scintillation and afterglow experiments were performed on two single-crystal samples of CsI:Tl,Sm with nominal concentrations of 0.11% Tl$^+$ and of 0.2% and 0.05% Sm$^{2+}$, respectively, in order to determine the concentration dependence of the rate of non-radiative charge transfer and thus to construct a more nuanced model of the non-radiative process.
2. Experiment
An electron Van de Graaff accelerator operated at a beam voltage of 1.0 MeV was employed as the primary radiation source with the 1.0 µA electron beam stopped by a thin copper target that served as a point source of 0.5 MeV gamma rays. The sample was mounted on a heated pedestal and cooled by flowing nitrogen gas, the sample temperature was monitored by a thermocouple and luminescence was conducted to a photomultiplier by a shielded optical fiber. Immediately following four-minute irradiations at each of several temperatures, the gain was increased by three orders of magnitude to monitor the decay of the afterglow at constant temperature. Light output data were recorded at four-second intervals. The afterglow, normalized to the scintillation light output, is plotted as a function of time after irradiation in Figures 2 and 3 for the samples with 0.2% and 0.05% Sm$^{2+}$ concentration, respectively.

3. Rate Equations
Complete rate equations for each phase of the process were presented in [2]. Rate equations for the irradiation phase in terms of the normalized trapped-hole concentration $\tilde{n}_h$ and normalized light output $\tilde{I}$ are

$$\frac{d\tilde{n}_h}{dt} = \tilde{f}_r (1 - \tilde{n}_h) - \tilde{n}_h p_c^{(Sm)} - \alpha \tilde{n}_h^2,$$

(1)

$$\tilde{I} = \tilde{f}_c + \tilde{f}_r - \left( \frac{d\tilde{n}_h}{dt} + (1 - r)\alpha \tilde{n}_h^2 \right),$$

(2)

$$\alpha \equiv s_A \exp\left( -E_A / k_B T \right),$$

(3)

$$p_c^{(Sm)} \equiv s^{(Sm)} \exp\left( -E^{(Sm)} / k_B T \right),$$

(4)
where $\tilde{f}_x$ and $\tilde{f}_r$ are, respectively, the normalized rates of production of excitons and of electron-hole pairs during irradiation. The parameters $\alpha$ and $r$ respectively determine the rate of charge-transfer recombination and its radiative fraction, and the parameter $p_e^{(Sm)}$ determines the rate of thermal ionization. It is assumed that $\text{Tl}^+$ is too shallow to be an effective electron trap in the temperature range of interest. With the added assumption that $\text{Sm}^{2+}$ does not trap electrons in the afterglow phase, thus reducing the kinetics to first order, rate equations for the afterglow phase are

$$\frac{d\tilde{n}_h}{dt} \equiv -p_e^{(Sm)}\tilde{n}_h - \alpha\tilde{n}_h^2,$$

$$\tilde{I} \equiv -\frac{d\tilde{n}_h}{dt} - (1-r)\alpha\tilde{n}_h^2 = r\alpha\tilde{n}_h^2 + p_e^{(Sm)}\tilde{n}_h,$$

with explicit solution as a function of afterglow time $t$:

$$\tilde{n}_h = \frac{\tilde{n}_{ho} \exp[-p_e^{(Sm)}t]}{1 + [\alpha\tilde{n}_{ho} / p_e^{(Sm)}] [1 - \exp[-p_e^{(Sm)}t]]}.$$  \hspace{1cm} (7)

Subscript 0 refers to initial values immediately following irradiation.

These equations were fitted to afterglow data as shown in Figures 2 and 3. Values $\tilde{f}_r = 0.5\text{min}^{-1}$ and $\tilde{f}_x = 1.2\text{min}^{-1}$ are assumed as in [2] and an additive constant was included to accommodate PM dark current. The parameters $\alpha$ and $p_e^{(Sm)}$ are plotted as functions of temperature in Figure 4 and fitted to Equations (3) and (4) with the optimized parameters listed in Table 1. Optimized values of $r$ are typically ~1%.

**Figure 2.** Recorded ratio of afterglow and scintillation for 0.2% $\text{Sm}^{2+}$ as a function of time following four-minute irradiations at four temperatures (continuous curves), compared with fitted theory from Equations (1)-(7) (dashed curves).
**Figure 3.** Recorded ratio of afterglow and scintillation for 0.05% Sm$^{2+}$ as a function of time following four-minute irradiations at four temperatures (continuous curves), compared with fitted theory from Equations (1)-(7) (dashed curves).

**Figure 4.** Comparison of ln(α) and ln($p_e^{(Sm)}$) as functions of 1/k_BT (continuous curves and solid circles) with Equations (3) and (4) (dashed curves) and the optimized parameters listed in Table 1. Curves in red are for 0.2% Sm$^{2+}$ and curves in black are for 0.05% Sm$^{2+}$.

| %Sm$^{2+}$ | $E_A$ (eV) | ln(s$_A$) | $s_A$ (min$^{-1}$) | $E^{(Sm)}$ (eV) | ln(s$_{Sm}$) | $s_{Sm}$ (min$^{-1}$) |
|------------|------------|------------|------------------|----------------|------------|---------------------|
| 0.2%       | 0.199      | 12.81      | $3.66\times10^5$ | 0.946         | 32.069     | $8.46\times10^{13}$ |
| 0.05%      | 0.180      | 10.87      | $5.26\times10^4$ | 0.925         | 32.072     | $8.48\times10^{13}$ |
4. Promoting-Interaction Model
In the theoretical model of [2], the promoting interaction is proportional to the square of the matrix element of the spin-orbit interaction between initial and final electronic states. Among other factors, it is approximately proportional to the square of the value of the diffuse $6s$ orbital of $\text{Sm}^+$ at the site of the target $V_{K\alpha}(\text{Tl}^\prime)$ center. In application of the theoretical model, we have assumed a fixed value of the promoting interaction for each value of the samarium concentration, implying a fixed separation of the initial and final sites. The model can be elaborated further by adopting a continuum approximation for CsI in which a substitutional $\text{Sm}^{2+}$ ion is represented by a point charge $+e$ embedded in a medium of dielectric constant $\kappa = 6.31$ [3] and effective mass ratio $m^*/m = 1.0$. In this approximation, the diffuse $6s$ orbital centered on the samarium ion at $\vec{r}_0$ is represented by the pseudowavefunction

$$\phi_{6s}(\Delta r) = \frac{\exp(-\Delta r / \kappa a_0)}{\pi^{1/2}(\kappa a_0)^{3/2}}, \quad \Delta r = |\vec{r} - \vec{r}_0|.$$  

(8)

We proceed by assuming that the ratio of separations of initial and final sites in the two crystal samples of CsI:Tl,Sm satisfies

$$\frac{\Delta r_2}{\Delta r_1} = \frac{\rho_1^{1/3}}{\rho_2^{1/3}} = 1.25,$$

(9)

where $\rho_1 = 0.0031$ and $\rho_2 = 0.0016$ are the relative concentrations of dopants, including both $\text{Tl}^+$ and $\text{Sm}^{2+}$. The ratio of promoting interactions is given by

$$\frac{s_{A1}}{s_{A2}} = \left(\frac{\phi_{6s}(\Delta r_1)}{\phi_{6s}(\Delta r_2)}\right)^2 = \exp[2(\Delta r_2 - \Delta r_1) / \kappa a_0].$$

(10)

It follows from Equations (9) and (10) and Table 1 that $\Delta r_1 / a = 2.88$ and $\Delta r_2 / a = 3.59$, where $a = 4.56$ Å is the lattice parameter.

5. Tunneling Model
An earlier tunneling model proposed by Delbecq et al. [4] was based on somewhat different assumptions: A random distribution of trapped charges is accumulated during the radiation phase, and tunneling progresses in the order of increasing separation of initial and final ion sites. These authors derive a simple expression for the light output $I(t)$ in terms of irradiation time $t_0$ and afterglow time $t$:

$$I(t) = \frac{C}{t_0} \ln \left(1 + \frac{t_0}{t}\right),$$

(11)

where $C$ is an adjustable parameter. Unfortunately, Equation (11) provides an egregiously poor fit to the afterglow data for CsI:Tl,Sm, as evidenced by comparison of Figures 2 and 5; the best that can be said for it is that $I(t)$ decreases monotonically. The first assumption of the tunneling model is transparently inappropriate for prolonged, intense radiation that culminates in a dynamic equilibrium between trapping and radiative recombination of electrons and holes. The second assumption of the
The tunneling model differs fundamentally from the premise of the promoting-interaction model, since the rate of tunneling is assumed to depend sensitively on the separation of initial and final sites.

Figure 5. Recorded ratio of afterglow and scintillation for 0.2% Sm\(^{2+}\) as a function of time following four-minute irradiations at four temperatures (continuous curves), compared with fitted theory from Equation (11) (dashed curves).

6. Discussion
The calculated values for the separation of initial and final sites are plausible for the nearest dopant sites but not for a random distribution of trapped charges substantially less than the dopant concentration. However, the overlap of 6s orbitals on nearby samarium sites is substantial and the energy barrier for tunneling between them should be relatively small. Accordingly, the promoting-interaction model can be extended to incorporate the assumption that electrons tunnel freely between samarium ions and are trapped preferentially near \(V_{KA}(Tl^+)\) centers where non-radiative recombination is the rate-limiting step, thus explaining the single non-radiative transition rate for fixed temperature and dopant concentration.

7. Acknowledgement
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References
[1] V. V. Nagarkar, C. Brecher, E. E. Ovechkina, V. Gaysinskiy, S. R. Miller, S. Thacker, A. Lempicki and R. H. Bartram, “Scintillation properties of CsI:Tl crystals codoped with Sm\(^{2+}\)”, IEEE Transactions on Nuclear Science 55, 1270-1274 (2008)
[2] R. H. Bartram, L. A. Kappers, D. S. Hamilton, A. Lempicki, C. Brecher, V. Gaysinskiy, E. E. Ovechkina and V. V. Nagarkar, “Afterglow suppression and non-radiative charge-transfer in CsI:Tl,Sm”, IEEE Transactions on Nuclear Science 55, 1232-1236 (2008)
[3] CRC Handbook of Chemistry and Physics, 77th Edition, Ed. David R. Lide (CRC Press, Boca Raton, 1996), p.12-47
[4] C. J. Delbecq, Y. Toyozawa and P. H. Yuster, “Tunneling recombination of trapped electrons and holes in KCl:AgCl and KCl:TlCl”, Phys. Rev. B 9, 4497 (1974)