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Effect of Eu^{2+} concentration on afterglow suppression in CsI:Tl, Eu

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Abstract

Combined radioluminescence and thermoluminescence experiments on the co-doped scintillator material CsI:Tl, Eu were extended in the present investigation to a sample with diminished europium concentration. Simulations based on postulated rate equations with empirically adjusted parameters are consistent with observed insensitivity of afterglow suppression to europium concentration for sufficiently short radiation times.

Keywords: Cesium iodide; Radioluminescence; Thermoluminescence; Afterglow simulation

1. Introduction

Experiments that demonstrated the feasibility of suppressing afterglow in CsI:Tl by co-doping with Eu^{2+} revealed that the effect is relatively insensitive to europium concentration within limits (Brecher et al., 2006). A theoretical model for afterglow suppression in CsI:Tl, Eu was developed, based on combined radioluminescence and thermoluminescence experiments on a single crystal of CsI with nominally equal concentrations of Tl^+ and Eu^{2+}, 0.25% (Bartram et al., 2006). Persistent afterglow in CsI:Tl was attributed to thermal ionization of trapped electrons (Tl^0) followed by radiative recombination with trapped holes [V_{KA} (Tl^+)]. Co-doping with europium introduces deeper electron traps with room-temperature glow peaks that effectively scavenge the electrons from shallow traps associated with thallium, thus suppressing afterglow in the time domain of tens of milliseconds, but enhancing afterglow in the longer time domain of seconds and minutes. During radioluminescence most of the energy is transported to activators by excitons that bypass both electron and hole traps. Consequently, scintillation light output is nearly independent of radiation time, even though the traps are far from saturated. For the same reason, long-time afterglow normalized to scintillation is proportional to radiation time but nearly independent of radiation intensity. Radioluminescence and thermoluminescence experiments were extended in the present investigation to a single crystal of CsI:Tl, Eu, provided by RMD, with the same thallium concentration as before, nominally 0.25%, but with diminished europium concentration, nominally 0.05%.

2. Radioluminescence and thermoluminescence

Combined radioluminescence and thermoluminescence measurements were performed at the University of Connecticut. The branching ratio of electron–hole pairs that contribute either to scintillation or thermoluminescence was determined by employing a common apparatus for both measurements. An electron Van de Graaff accelerator operated at a beam voltage of 1.0 MeV and a beam current of 1.0 μA was employed as the primary radiation source with the 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, cooled by nitrogen gas and monitored by a thermocouple. Luminescence was conducted to a photomultiplier by a shielded

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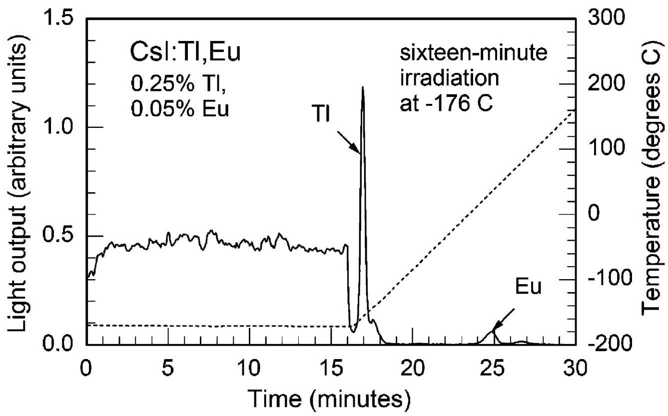

Fig. 1. Recorded light output (continuous curve) and sample temperature (dashed curve) for low-temperature (−176 °C) irradiation of CsI:Tl, Eu with reduced europium concentration for a radiation time of 16 min.

optical fiber. Radioluminescence and thermoluminescence light outputs for irradiation at −176 °C, followed by a temperature ramp with a ramp rate of 25 °C/ min to +275 °C, were recorded for the radiation times ranging from 30 s to 16 min. Light outputs for irradiation at −66 °C were also recorded for the radiation times ranging from 30 s to 16 min. Scintillation was partially quenched at the lowest temperature. Light output for 16-min irradiation at −176 °C is plotted in Fig. 1.

3. Rate equations

Additional features of the data can be inferred from postulated model rate equations (Bartram et al., 2006). It has been established that part of the incident energy is transferred directly to excitons rather than to independent electrons and holes. Accordingly, the concentration f of electron–hole pairs generated per unit time is given by

$$f = f_x + f_r, \tag{1}$$

where f_x is the exciton component and f_r is the component of free electrons and holes. The reduction in quantum efficiency at low temperature is attributed to non-radiative recombination of self-trapped excitons. Simplified rate equations are as follows:

$$\frac{\mathrm{d}\tilde{n}_\mathrm{e}^{(i)}}{\mathrm{d}t} \cong \frac{\tilde{f}_r + \sum_i \tilde{n}_\mathrm{e}^{(i)} p_\mathrm{e}^{(i)}}{(1+\tilde{n}_\mathrm{h})}\delta^{(i)} - \tilde{n}_\mathrm{e}^{(i)}\left[p_\mathrm{e}^{(i)} + \frac{\tilde{f}_r}{1+\tilde{n}_\mathrm{h}}\right], \tag{2a}$$

$$\frac{\mathrm{d}\tilde{n}_\mathrm{h}}{\mathrm{d}t} \cong \frac{\tilde{f}_r(1-\tilde{n}_\mathrm{h}) - \tilde{n}_\mathrm{h}\sum_i \tilde{n}_\mathrm{e}^{(i)} p_\mathrm{e}^{(i)}}{(1+\tilde{n}_\mathrm{h})}, \tag{2b}$$

$$\tilde{I} = Q\tilde{f}_x + \tilde{f}_r - \frac{\mathrm{d}\tilde{n}_\mathrm{h}}{\mathrm{d}t} \cong Q\tilde{f}_x + \frac{2\tilde{f}_r\tilde{n}_\mathrm{h} + \tilde{n}_\mathrm{h}\sum_i \tilde{n}_\mathrm{e}^{(i)} p_\mathrm{e}^{(i)}}{(1+\tilde{n}_\mathrm{h})}, \tag{2c}$$

where $n_\mathrm{e}^{(i)}$ is the concentration of electrons at electron traps of the ith type; n_h is the concentration of holes trapped near Tl^+ ions [V_KA (Tl^+) centers]; $N_\mathrm{e}^{(i)}$ is the concentration of electron traps of the ith type; and N_h is the concentration of hole traps. $Q(T)$ is the quantum efficiency of exciton radiative recombination at Tl activators. Normalization in Eqs. (2) is defined by

$$\tilde{n}_\mathrm{e}^{(i)} \equiv n_\mathrm{e}^{(i)}/n_f, \quad \tilde{f} \equiv f/n_f, \quad \tilde{I} \equiv I/n_f, \quad n_f \equiv N_\mathrm{h}A_\mathrm{h}/A_\mathrm{r}. \tag{3a}$$

The parameters A_h, $A_\mathrm{e}^{(i)}$ and A_r govern the rates of hole trapping, electron trapping, and radiative recombination of conduction electrons with trapped holes, respectively. Thermal ionization rates $p_\mathrm{e}^{(i)}$ are assumed to be of Arrhenius form

$$p_\mathrm{e}^{(i)} = s_\mathrm{e}^{(i)}\exp[-E_\mathrm{e}^{(i)}/k_\mathrm{B}T] \tag{3b}$$

and the parameter $\delta^{(i)}$ is defined by

$$\delta^{(i)} \equiv \frac{N_\mathrm{e}^{(i)}A_\mathrm{e}^{(i)}}{N_\mathrm{h}A_\mathrm{h}}, \quad \sum_i \delta^{(i)} = 1. \tag{3c}$$

The rate equations are simplified further by retaining only two types of electron trap in co-doped CsI:Tl, Eu, $\delta^{(\mathrm{Tl})}$ and $\delta^{(\mathrm{Eu})}$. Trap concentrations are assumed to be much larger than trapped charge concentrations; the apparent saturation of traps reflects dynamic equilibrium between trapping and recombination.

4. Low and intermediate temperature irradiation

Since the thermal ionization rates $p_\mathrm{e}^{(i)}$ are negligible at −176 °C for traps of interest, Eqs. (2) are reduced to

$$\frac{\mathrm{d}\tilde{n}_\mathrm{e}^{(i)}}{\mathrm{d}t} \cong \frac{\tilde{f}_r(\delta^{(i)} - \tilde{n}_\mathrm{e}^{(i)})}{(1+\tilde{n}_\mathrm{h})}, \tag{4a}$$

$$\frac{\mathrm{d}\tilde{n}_\mathrm{h}}{\mathrm{d}t} \cong \frac{\tilde{f}_r(1-\tilde{n}_\mathrm{h})}{(1+\tilde{n}_\mathrm{h})}, \tag{4b}$$

with solutions

$$\tilde{f}_r t = -\tilde{n}_\mathrm{h} - 2\ln(1-\tilde{n}_\mathrm{h}), \tag{5a}$$

$$\tilde{n}_\mathrm{e}^{(i)} = \delta^{(i)}\tilde{n}_\mathrm{h} \tag{5b}$$

Eqs. (2) can be specialized to the radiation phase at −66 °C by adopting the following approximations:

$$\frac{\mathrm{d}\tilde{n}_\mathrm{e}^{(\mathrm{Tl})}}{\mathrm{d}t} \cong \tilde{n}_\mathrm{e}^{(\mathrm{Tl})} \cong p_\mathrm{e}^{(\mathrm{Eu})} \cong 0, \quad \tilde{n}_\mathrm{e}^{(\mathrm{Eu})} \cong \tilde{n}_\mathrm{h}. \tag{6}$$

It then follows from Eqs. (2) that

$$\frac{\mathrm{d}\tilde{n}_\mathrm{h}}{\mathrm{d}t} \cong \frac{\tilde{f}_r(\delta^{(\mathrm{Eu})} - \tilde{n}_\mathrm{h}^2)}{(1+\tilde{n}_\mathrm{h})(\delta^{(\mathrm{Eu})} + \tilde{n}_\mathrm{h})}, \tag{7}$$

$$\tilde{f}_r t \cong -\tilde{n}_\mathrm{h} + 2\sqrt{\delta^{(\mathrm{Eu})}}\tanh^{-1}\left(\frac{\tilde{n}_\mathrm{h}}{\sqrt{\delta^{(\mathrm{Eu})}}}\right) - \frac{(1+\delta^{(\mathrm{Eu})})}{2}\ln\left(1 - \frac{\tilde{n}_\mathrm{h}^2}{\delta^{(\mathrm{Eu})}}\right). \tag{8}$$

The integrated thermoluminescence light output G and integrated scintillation light output S satisfy

$$(G/G_\mathrm{max})_\mathrm{theory} = \tilde{n}_\mathrm{h}/\tilde{n}_\mathrm{h\ max} \tag{9}$$

Table 1
Parameter values vs. irradiation temperature

Parameter\Rad. Temp.	−176 °C	−66 °C
$\delta^{(\mathrm{Eu})}$	0.1	0.1
$\tilde{f}_r$ (min^{-1})	0.8	0.28
$Q(T)/R$	0.15	8.5
$R \equiv \tilde{f}_r/\tilde{f}_x$	–	0.118
$Q(T)$	–	1.0

$$\left(\frac{G}{S}\right)_{\text{theory}} = \frac{\tilde{n}_{\mathrm{h}}}{[1+Q(T)/R]\tilde{f}_r t - \tilde{n}_{\mathrm{h}}}, \quad R \equiv \tilde{f}_r/\tilde{f}_x. \tag{10}$$

Eqs. (9) and (10) were fitted to the experimental data to obtain the adjusted parameter values listed in Table 1.

5. Room temperature irradiation

The following inequalities apply for co-doped CsI:Tl, Eu in the room-temperature radiation phase:

$$\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})} p_{\mathrm{e}}^{(\mathrm{Tl})} \gg \tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})} p_{\mathrm{e}}^{(\mathrm{Eu})}, \quad \tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})} \ll \tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})}. \tag{11}$$

Of particular interest in the present application is the limit of short radiation time, $\tilde{f}_r t_{\mathrm{rad}} \ll 1$:

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})}}{\mathrm{d}t} \cong \tilde{f}_r \delta^{(\mathrm{Tl})} - \tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})} p_{\mathrm{e}}^{(\mathrm{Tl})}(1-\delta^{(\mathrm{Tl})}) + \tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})} p_{\mathrm{e}}^{(\mathrm{Eu})} \delta^{(\mathrm{Tl})} \cong 0, \tag{12a}$$

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})}}{\mathrm{d}t} \cong \tilde{f}_r \delta^{(\mathrm{Eu})} - \tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})} p_{\mathrm{e}}^{(\mathrm{Eu})}(1-\delta^{(\mathrm{Eu})}) + \tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})} p_{\mathrm{e}}^{(\mathrm{Tl})} \delta^{(\mathrm{Eu})}, \tag{12b}$$

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t} \cong \tilde{f}_r, \tag{12c}$$

with solutions

$$\tilde{n}_{\mathrm{h}}(t_{\mathrm{rad}}) \cong \tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})}(t_{\mathrm{rad}}) \cong \tilde{f}_r t_{\mathrm{rad}}, \tag{13a}$$

$$\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})}(t_{\mathrm{rad}}) \cong \frac{\tilde{f}_r}{p_{\mathrm{e}}^{(\mathrm{Tl})}} \left(\frac{\delta^{(\mathrm{Tl})}}{1-\delta^{(\mathrm{Tl})}}\right), \tag{13b}$$

$$\tilde{I}(t_{\mathrm{rad}}) = \tilde{f}_x + \tilde{f}_r - \frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t} \cong \tilde{f}_x. \tag{13c}$$

The relevant equations for CsI:Tl without the europium co-dopant are

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t} \cong \frac{\tilde{f}_r(1-\tilde{n}_{\mathrm{h}}) - \tilde{n}_{\mathrm{h}}^2 p_{\mathrm{e}}^{(\mathrm{Tl})}}{(1+\tilde{n}_{\mathrm{h}})}, \tag{14}$$

$$\tilde{n}_{\mathrm{h}}(t_{\mathrm{rad}}) \cong \sqrt{\frac{\tilde{f}_r}{p_{\mathrm{e}}^{(\mathrm{Tl})}}} \ll 1.0, \tag{15}$$

with saturation light output

$$\tilde{I} = \tilde{f}_x + \tilde{f}_r. \tag{16}$$

6. Afterglow

With the assumption that $A_{\mathrm{e}}^{(\mathrm{Eu})}$ is negligible in the absence of ionizing radiation, the approximate rate equations for co-doped CsI:Tl, Eu in the afterglow phase in the limit of short radiation time are

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})}}{\mathrm{d}t} \cong -\frac{\tilde{n}_{\mathrm{h}}\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})} p_{\mathrm{e}}^{(\mathrm{Tl})}}{\delta^{(\mathrm{Tl})}} + \tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})} p_{\mathrm{e}}^{(\mathrm{Eu})}, \tag{17a}$$

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})}}{\mathrm{d}t} \cong -\tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})} p_{\mathrm{e}}^{(\mathrm{Eu})}, \tag{17b}$$

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t} \cong -\frac{\tilde{n}_{\mathrm{h}}\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})} p_{\mathrm{e}}^{(\mathrm{Tl})}}{\delta^{(\mathrm{Tl})}}, \tag{17c}$$

with the approximate solution

$$\begin{aligned}\frac{\tilde{I}(t)}{\tilde{I}(0)} &\cong -\frac{1}{\tilde{f}_x}\frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t} = -\frac{1}{\tilde{f}_x}\left(\frac{\mathrm{d}\tilde{n}_{\mathrm{e}}^{(\mathrm{Tl})}}{\mathrm{d}t} + \frac{\mathrm{d}\tilde{n}_{\mathrm{e}}^{(\mathrm{Eu})}}{\mathrm{d}t}\right) \\ &\cong R t_{\mathrm{rad}}\left[\left(\frac{\tilde{f}_r}{1-\delta^{(\mathrm{Tl})}} - p_{\mathrm{e}}^{(\mathrm{Eu})}\right)\exp\left(-\frac{\tilde{f}_r t_{\mathrm{rad}} p_{\mathrm{e}}^{(\mathrm{Tl})} t}{\delta^{(\mathrm{Tl})}}\right)\right] \\ &\quad + R t_{\mathrm{rad}} p_{\mathrm{e}}^{(\mathrm{Eu})} \exp\left(-p_{\mathrm{e}}^{(\mathrm{Eu})} t\right).\end{aligned} \tag{18}$$

The rate equation for CsI:Tl without Eu in the afterglow phase is

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t} \cong -\tilde{n}_{\mathrm{h}}^2 p_{\mathrm{e}}^{(\mathrm{Tl})}, \tag{19}$$

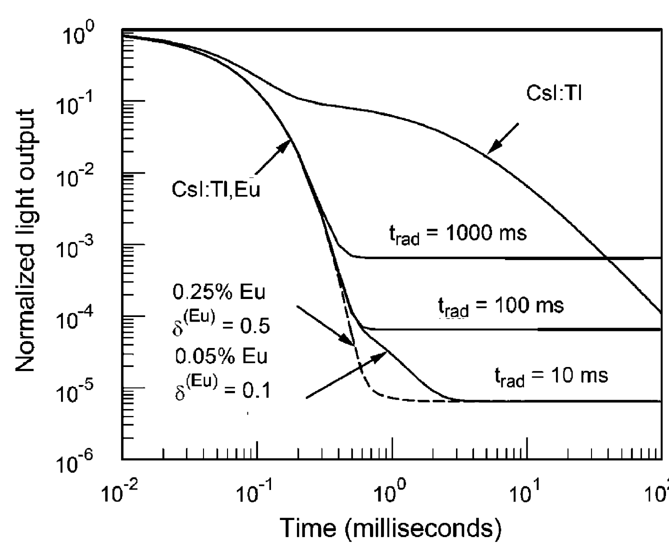

Fig. 2. Simulated afterglow of co-doped CsI:Tl, Eu for two europium concentrations and several radiation times from Eq. (18), compared with that of singly doped CsI:Tl from Eq. (21).

with solution

$$\tilde{n}_{\mathrm{h}} \cong \sqrt{\frac{\tilde{f}_r}{p_{\mathrm{e}}^{(\mathrm{Tl})}}}\left(\frac{t_{0\mathrm{e}}}{t_{0\mathrm{e}}+t}\right), \quad t_{0\mathrm{e}} \equiv \frac{1}{\sqrt{p_{\mathrm{e}}^{(\mathrm{Tl})}\tilde{f}_r}}, \tag{20}$$

$$\frac{\tilde{I}(t)}{\tilde{I}(0)} \cong -\left(\frac{1}{\tilde{f}_x+\tilde{f}_r}\right)\left(\frac{\mathrm{d}\tilde{n}_{\mathrm{h}}}{\mathrm{d}t}\right) \cong \left(\frac{R}{1+R}\right)\left(\frac{t_{0\mathrm{e}}}{t_{0\mathrm{e}}+t}\right)^2. \tag{21}$$

Simulated afterglow is plotted in Fig. 2 from Eqs. (18) and (21) for $\tilde{f}_r = 1.0$, with the thermal ionization rates $p_{\mathrm{e}}^{(\mathrm{Tl})}$ and $p_{\mathrm{e}}^{(\mathrm{Eu})}$ calculated from Eq. (3b) and parameters inferred from thermoluminescence glow curves in Bartram et al. (2006). Scintillation decay of the form $\exp(-qt)$, $q = 20\,\mathrm{ms}^{-1}$, is incorporated in Fig. 2 to simulate the fall time of the radiation source.

7. Discussion

Reduction of europium concentration increases the number of electrons trapped on thallium ions after short-pulse excitation, but the resulting enhanced afterglow decays very rapidly with nearly first-order kinetics by virtue of the large trapped-hole concentration, $n_{\mathrm{h}} \gg n_{\mathrm{e}}^{(\mathrm{Tl})}$. Consequently, the effect of reduced europium concentration is obscured by the fall time of the radiation source for all but the shortest excitation pulse, 10 ms, in the simulations displayed in Fig. 2. Thus, these simulations are compatible with the observed insensitivity of afterglow suppression to europium concentration following a 100 ms radiation pulse (Brecher et al., 2006). The upper curve in Fig. 2 applies to the total absence of europium. In that case, many more electrons are trapped by thallium and the corresponding afterglow decays much more slowly as well, since Eq. (19) implies second-order kinetics.

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