

Second-order luminescent saturation effects in SrGa₂S₄:Eu

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This study identified a quadratic energy loss process in europium-doped strontium thiogallate using luminescent decay time analysis. The role of activator–activator cross relaxation in producing the nonlinearity in the luminescent efficiency for SrGa₂S₄:Eu was assessed. Ground-state depletion did not contribute to the observed saturation, which instead was attributed to interionic energy transfer (cross relaxation). This work provides a deeper understanding of the factors contributing to luminescent saturation. The understanding of these mechanisms will contribute to the optimization of phosphors for cathodoluminescent applications. © 2002 American Institute of Physics. [DOI: 10.1063/1.1490398]

Knowledge of the physics contributing to phosphor efficiency under low-energy electron excitation is essential to developing high-power, efficient phosphors for flat-panel displays.¹ Several candidates, including europium-activated strontium thiogallate (SrGa₂S₄:Eu), are in development with this in mind.² In field-emission displays, which operate at lower energies than cathode ray tubes, the excitation dwell time and average current density are increased to achieve the same output. Under these conditions, phosphors have a nonlinear dependence of luminance on excitation energy. The mechanisms contributing to this are ground-state depletion (GSD) (Ref. 3) and second-order saturation (SOS).⁴

Below 5 keV, surface defects dramatically decrease luminescent efficiency. High current excitation increases the number of electron–hole (*e*–*h*) pairs accessible to activators, thus intensifying the light output. However, this can “saturate” by two mechanisms: (1) Activators are excited out of their ground state (GSD). (2) Excited centers exchange energy rather than decay radiatively (SOS). Increasing activator concentration and using fast decaying phosphors reduces GSD by activator recycling.^{3,5} This occurs as long as the decay time is less than the excitation pulse length.

The GSD model has explained saturation in slower decaying phosphors such as Gd₂O₂S:Tb ($\tau_d \sim 0.52$ ms).⁶ However, saturation in fast decaying phosphors such as SrGa₂S₄:Eu²⁺ ($\tau_d \sim 500$ ns) occurs two orders of magnitude earlier than predicted by GSD (Fig. 1), clearly indicating that another mechanism is responsible for the saturation.

In 1983, de Leeuw and 't Hooft² identified nonradiative energy transfer as a superlinear loss process. Activator excited-state absorption and cross relaxation were the mechanisms identified. In excited-state absorption the activators already in excited states are promoted to higher states. When GSD is unlikely due to high activator concentrations and fast decay times, excited-state absorption is ruled out, as in the case of SrGa₂S₄:Eu, however, cross relaxation remains a possibility. Several studies^{4,7,8} have identified second-order energy exchange mechanisms.

Eichenauer⁹ has confirmed that in SrGa₂S₄:Eu luminescence occurs from the lowest 4*f*⁶5*d*¹ state to the ground state. Transitions to other states are largely nonradiative.

Thus, energy transfer to upperlevel nonradiative excited states in the 4*f*⁶5*d* bands is possible.

Figure 2 depicts the processes involved in host–activator excitation and recombination along with activator cross relaxation (recombination energy from an excited activator is transferred to a neighboring excited activator promoting it to a higher level). The excitation rate equations are

$$\frac{d}{dt}n_1 = g - n_1\alpha - n_1\beta(N - n_2), \quad (1)$$

$$\frac{d}{dt}n_2 = n_1\beta(N - n_2) - \gamma n_2 - \alpha_{act}n_2 - \alpha_{act,s}n_2^\lambda, \quad (2)$$

where *g* is the *e*–*h* pair generation rate, *n*₁ the number of *e*–*h* pairs, α the nonradiative transition probability, β the activator excitation probability, and *N* the total number of activators. In Eq. (2), *n*₂ is the number of excited activators with electrons in level 2, γ the radiative recombination rate, α_{act} the first-order nonradiative rate, and $\alpha_{act,s}$ the cross-relaxation energy loss rate. The term $\alpha_{act,s}n_2^\lambda$ represents superlinear energy loss. When $\lambda = 2$, saturation is second order.

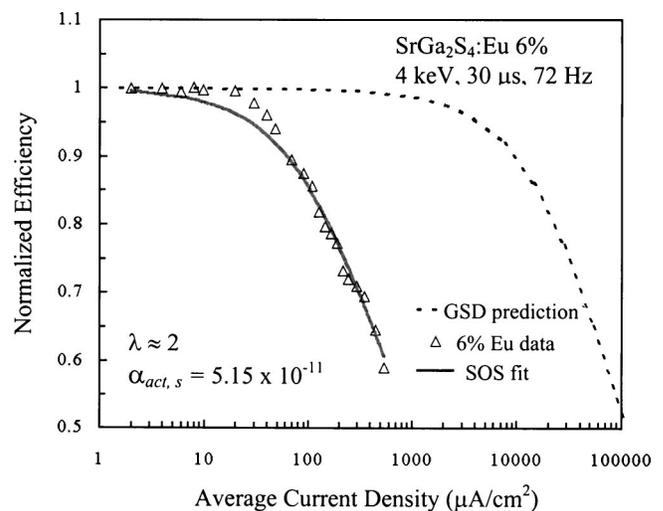


FIG. 1. Saturation of SrGa₂S₄:Eu 6% at 4 keV. Measured data (triangles) are compared to that predicted by ground-state depletion (dotted line). Second-order saturation fit (solid line) is for $\lambda \approx 2$ and $\alpha_{act,s} = 5.15 \times 10^{-11}$.

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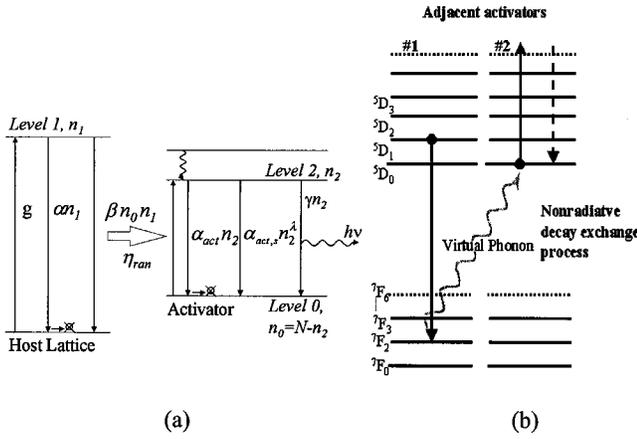


FIG. 2. (a) Two-level excitation model used to analyze saturation, n_1 and n_2 are the host and activator excited-state populations, respectively. The second nonradiative term in level 2 ($\alpha_{act,s}n_2^\lambda$) represents the influence of superlinear energy loss. When $\lambda=2$, the saturation is second order and $\alpha_{act,s}$ is the energy loss rate. (b) Cross relaxation: nonradiative energy exchange between neighboring activators 1 and 2.

The order was determined from analysis of the cathodoluminescence (CL) decay. Under steady-state conditions, the activator efficiency becomes

$$\eta_{act} = \frac{\gamma n_2}{\gamma n_2 + \alpha_{act} n_2 + \alpha_{act,s} n_2^\lambda} = \frac{\gamma}{\gamma_d + \alpha_{act,s} n_2^{\lambda-1}} \quad (3)$$

A relation between η_{act} and the intrinsic quantum activator efficiency $\eta_{act,0}$ is derived by rearranging terms and noting that $\gamma/\gamma_d = \eta_{act,0}$ resulting in

$$\frac{\eta_{act,0}}{\eta_{act}} - 1 = \frac{\eta_{act,0} \alpha_{act,s}}{\gamma} n_2^{\lambda-1} \quad (4)$$

This is related to the optical emission flux by the relation $P_{em} = (\gamma R h \nu \eta_e) n_2$, where the constants in parentheses are lumped into one constant (c_1), and are the probability of radiative decay, electron range, photon energy ($h\nu$), and photon escape efficiency, respectively. By substituting for n_2 , the relation becomes

$$\frac{\eta_{act,0}}{\eta_{act}} - 1 = \frac{\eta_{act,0} \alpha_{act,s}}{\gamma} (c_1 P_{em})^{\lambda-1} = c_s P_{em}^{\lambda-1} \quad (5)$$

λ gives the order and is determined from the initial CL decay time under unsaturated and saturated conditions.

In order to express Eq. (5) in terms of the initial decay time, Eq. (3) is used to express the level 2 rate equation as

$$-dn_2/dt = n_1 \beta (n_2 - N) + \gamma n_2 / n_{act} \quad (6)$$

When the excitation is turned off $n_2 \approx N$, and the first term on the right in Eq. (6) goes to zero. Thus,

$$-\frac{1}{P_{em}} \frac{dP_{em}}{dt} \Big|_{t=0} = \frac{\gamma}{\eta_{act}} = \gamma_i \quad (7)$$

by substituting $n_2 = c_1 P_{em}$. This is the initial decay rate. By substituting $\eta_{act} = \gamma/\gamma_i$ and $\eta_{act,0} = \gamma/\gamma_d$, Eq. (5) becomes

$$D_f = \gamma_i / \gamma_d - 1 = c_s P_{em}^{\lambda-1} \quad (8)$$

This relates the initial decay rates under saturated, and unsaturated conditions, to the CL intensity. Referring to the left side of Eq. (8) as the decay factor (D_f), experimental data for D_f plotted as a function of P_{em} can be fitted using a

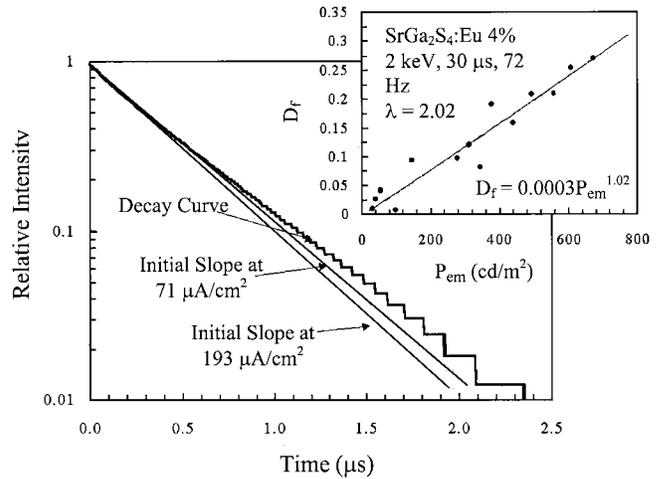


FIG. 3. CL transient response for SrGa₂S₄:Eu 4% excited at 2 keV. Semilog plot illustrates for the change in the initial slope of the decay curve at 71 and 193 $\mu\text{A}/\text{cm}^2$. Inset: dependence of CL decay factor D_f on CL intensity. The order λ was determined from a power-law fit to the experimental data.

power law. The fitted value for the exponent ($\lambda - 1$) reveals the order of the decay. A slope of unity indicates that an energy loss process dominates the saturation, whose probability is proportional to the density of activators squared.

In this study, concentrations of 0.5, 1, 3, 4, 5, and 6% were investigated. Samples were screened on conducting indium–tin–oxide-coated glass substrates to minimize charging and heating. A 2 keV electron beam pulsed at 30 μs and refreshed at 72 Hz induced the CL excitation from which the transient data (pulse averaged 500 times) was obtained. Thermal quenching effects were negligible. Figure 3 displays the CL decay curve for SrGa₂S₄:Eu 4% corresponding to the broadband emission spectra centered at 545 nm. Fits to the initial slope at current densities of 71 and 193 $\mu\text{A}/\text{cm}^2$ illustrate the decrease in the initial CL decay time with increasing excitation density. This trend was observed for all samples at 1, 2, and 4 keV.

Once the current-dependent initial decay times and emitted optical intensities were determined, the decay factor was calculated (inset, Fig. 3). The data were fit by a power law of the form $D = c P^{(\lambda-1)}$. The value of the exponential ($\lambda - 1$) ≈ 1 showed that the saturation order was $\lambda \approx 2$, providing strong evidence of quadratic energy loss. Figure 4 plots the saturation order values obtained as a function of Eu concentration from 0.5–6% for excitation voltages of 1, 2, and 4 keV. The saturation order was ≈ 2 in all samples investigated.

The second-order cross-relaxation energy loss rate $\alpha_{act,s}$ was determined by best fitting an expression for the radiant efficiency under cross-relaxation conditions to the saturation data. The efficiency was derived as follows: For $\lambda=2$, the level 2 rate equation under steady-state conditions is

$$-\frac{dn_2}{dt} = 0 = n_1 \beta (n_2 - N) + \gamma_d n_2 + \alpha_{act,s} n_2^2 \quad (9)$$

When there is no ground-state depletion ($N - n_2 \gg n_1$), then

$$n_1 = \frac{g}{\alpha + \beta N} \quad (10)$$

The fraction of pairs to excite activators is

$$\eta_0 = \frac{\beta N}{\alpha + \beta N} \quad (11)$$

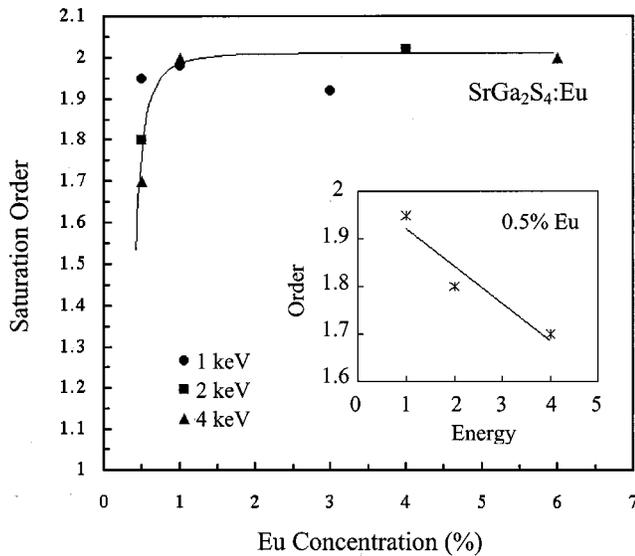


FIG. 4. Saturation order parameter λ as a function of europium concentration for $\text{SrGa}_2\text{S}_4:\text{Eu}$. Inset plots λ vs energy for 0.5% Eu-doped sample.

the rate equation is

$$n_2^2 \alpha_{\text{act},s} + n_2 \gamma_d + g \eta_0 / N - g \eta_0 = 0. \quad (12)$$

Neglecting GDS, the third term in Eq. (12) goes to zero ($N \gg g \eta_0$). Putting $\gamma_d = 1/\tau$, and solving for the level 2 population n_2 gives

$$n_2 = \frac{1}{2 \alpha_{\text{act},s} \tau} (\sqrt{1 + 4 \alpha_{\text{act},s} \tau^2 g \eta_0} - 1). \quad (13)$$

Then under low-excitation conditions,

$$n_{2,0} = \frac{N}{(\alpha + \beta N)(\gamma + \alpha_{\text{act}})/\beta g} = \tau g \eta_0. \quad (14)$$

The normalized efficiency is expressed as the ratio between the emitted optical flux and the low-excitation flux,

$$\varepsilon = \frac{n_2 \gamma R h \nu}{n_{2,0} \gamma R h \nu}, \quad (15)$$

thus, the efficiency under cross-relaxation conditions is

$$\varepsilon_{\text{cr}} = \frac{n_2}{n_{2,0}} = \frac{\sqrt{1 + 4 \alpha_{\text{act},s} \tau^2 g \eta_0} - 1}{2 \alpha_{\text{act},s} \tau^2 g \eta_0} = \frac{2}{X_{\text{cr}}} (\sqrt{1 + X_{\text{cr}}} - 1), \quad (16)$$

where the cross-relaxation variable X_{cr} is defined as

$$X_{\text{cr}} = 4 \alpha_{\text{act},s} \tau^2 \eta_0 \frac{E_0 J (1 - \eta_b)}{E_i R_e}. \quad (17)$$

In Eq. (17), τ is the decay time measured at the $1/e$ point, η_0 the low-excitation quantum efficiency, E_0 the electron beam energy, J the current density, η_b the backscattering coefficient, $E_i = \beta_g E_g$ the ionization energy, and R_e the electron penetration depth. J is the only variable except for the fitting parameter, $\alpha_{\text{act},s}$. Figure 1 illustrates the second-order saturation fit to $\text{SrGa}_2\text{S}_4:\text{Eu}$ 6% data at 4 keV that could not be fitted by GSD theory. Second-order theory fits the data well. The relaxation rate decreases with increasing excitation energy and Eu concentration. This trend suggests increased interionic energy transfer for high-Eu concentrations at low-excitation volumes.

Furthermore, Fig. 4 shows order values of 1.95, 1.8, and 1.7 for the sample with 0.5% Eu at voltages of 1, 2, and 4 keV, respectively. (The inset shows the order parameter λ as a function of energy for this sample.) The decrease in λ with increasing energy indicates a slight weakening in SOS due to cross relaxation. The larger volume excited at higher energies reduced the saturation rate most in the 0.5% sample. Physically, as the exciton interaction volume increases, the interionic energy exchange was reduced, thus weakening the saturation.

The average distance between activators is calculated¹⁰ to be 5.22 nm for the 0.5% sample and decreases to 2.3 nm in the 6% sample. Thus the majority of excited activators remain involved in cross-relation even for the larger excitation volumes resulting at higher excitation voltages. For optically active ions, the probability of interionic energy transfer^{11,12} due to electric dipole-dipole interactions is proportional to R^{-6} , and therefore, is two orders of magnitude higher in the 6% than in the 0.5% sample. The decrease in λ to 1.7 for the 0.5% sample at 4 keV shows a lower, but still strong contribution of cross relation to saturation and implies a threshold for interionic energy loss. However, only for concentrations $< 0.1\%$ are cross relation effects expected to be reduced such that $\lambda = 1$.

In summary, the dependence of the CL efficiency of $\text{SrGa}_2\text{S}_4:\text{Eu}$ on electron current density for Eu concentrations ranging from 0.5 to 6% demonstrated the importance of activator-related efficiency loss mechanisms. Substitution of phosphor properties into the GSD model predicted saturation in $\text{SrGa}_2\text{S}_4:\text{Eu}$ at current densities two orders of magnitude larger than experimentally observed. Transient analysis identified second-order cross relaxation between activator ions as a dominant energy loss process. Good fits to the data were obtained for relaxation energy loss rates $\alpha_{\text{act},s} \sim 5 \times 10^{-11} \text{ cm}^3/\text{s}$. In addition to using phosphors with short luminescent decay times and high activator concentrations, phosphor selection criteria for high-current-density applications should incorporate activator-activator energy loss as a limiting parameter to saturation reduction.

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