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Fundamental Efficiency Limitations for Low Electron Energy Cathodoluminescence*

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Abstract

The design of field emission displays is severely constrained by the universally poor cathodoluminescence (CL) efficiency of most phosphors at low excitation energies. As part of our effort to understand this phenomenon, we have measured the time decay of spectrally-resolved, pulsed CL and photoluminescence (PL) in several phosphors activated by rare earth and transition metal impurities, including Y_2O_3:Eu, Y_2SiO_5:Tb, and Zn_2SiO_4:Mn. Activator concentrations ranged from ~ 0.25 to 10%. The CL decay curves are always non-linear on a log(CL)-linear(time) plot - i.e. they deviate from first order decay kinetics. These deviations are always more pronounced at short times and larger activator concentrations and are largest at low beam energies where the decay rates are noticeably faster. PL decay is always slower than that seen for CL, but these differences disappear after most of the excited species have decayed. We have also measured the dependence of steady state CL efficiency on beam energy. We find that larger activator concentrations accelerate the drop in CL efficiency seen at low beam energies. These effects are largest for the activators which interact more strongly with the host lattice. While activator-activator interactions are known to limit PL and CL efficiency in most phosphors, the present data suggest that a more insidious version of this mechanism is partly responsible for poor CL efficiency at low beam energies. This "enhanced" concentration quenching is due to the interaction of nearby excited activators. These interactions can lead to non-radiative activator decay, hence lower steady state CL efficiency. Excited state "clustering", which may be caused by the large energy loss rate of low energy primary electrons, appears to enhance these interactions. In support of this idea, we find that PL decays obtained at high laser pulse energies resemble the non-linear decays seen in the CL data.

Most flat panel field emission displays are presently designed with conventional CRT phosphors[1]. Except for ZnO, which has poor chromaticity, essentially all conventional phosphors[2] have efficiencies which decline monotonically as the electron excitation energy drops below 5 keV. Consequently most manufacturers utilize 4-6 keV electrons in prototype field emission displays; these devices have high internal electric fields, a feature that raises cost and complexity and introduces problems with charging of dielectric standoffs.

Conventional explanations for reduced low voltage cathodoluminescence (CL) efficiency focus on energy losses which occur **before** excitation of the activators[2]. For example, beam-created electrons and holes can recombine at phosphor surfaces, before they have a chance to excite the luminescent impurities. In this work we will present both steady state and pulsed CL data which show that non-radiative energy losses ***after activator excitation*** may be equally important for the phosphors that are studied here. Our data indicates that these losses increase markedly at low beam energies, particularly as the activator density is increased. And, it strongly points to an important new type of activator interactions which, at low beam energies, play a role in quenching CL.

All of the CL decay measurements reported here were made on screened commercial[3] and experimental[4] phosphor samples with a conventional Kimball electron gun by pulsing the grid to turn the electron beam on and off. Extensive signal averaging of the spectrally filtered, photomultiplier-detected luminescence was employed to resolve the exact shape of the decay profile, and the beam energy, E_b, was varied from 0.8 to 4 keV. Beam pulses short compared to the activator decay times were generally used. Decay data were directly compared to laser-stimulated PL persistence profiles obtained on the same phosphors. Some dependence of the PL decays on excitation wavelength was observed, and important decay rate changes were seen as the laser excitation power was raised.

In order to analyze the decay of a particular excited state population in cathodoluminescence, we will write an equation which describes the time evolution of the state population, C. The experimentally measured CL brightness is proportional to C and to the radiative decay rate (which is not normally a function of time). We have:

$$\frac{\partial C}{\partial t} = f(t) - \frac{C}{\tau_1} - \frac{C^2}{\tau_2}$$

Eq. (1)

where the first term describes energy feeding into state C from higher excited states and is frequently of minor

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importance in interpreting the data which we will present. The second term describes the decay of state C via radiative and non-radiative pathways, and the third term describes the decay of state C via interactions **with other excited states**, C. Dividing equation 1 by C and inserting a minus sign, we generate an expression for the logarithmic decay rate of CL (or PL) brightness:

$$-\frac{1}{C}\frac{\partial \dot{C}}{\partial t} = -\frac{f(t)}{C} + \frac{1}{\tau_1} + \frac{C}{\tau_2} \qquad \text{Eq. 2)}$$

An example of experimental logarithmic decay rate data for the $^5D_0$ state (at 611nm) of Eu^{3+} in Y_2O_3 is shown in figure 1 for three different activator fractions and two different beam energies. Here we plot this rate versus the remaining fraction of CL, normalized to unity at the CL emission peak. At 1 % Eu (diamonds) the rate is fairly constant over a large range of brightness (1 to 0.06), although there is some decrease at high C values (short times) due to energy entering this state from the decay of higher levels ($^5D_1$,$^5D_2$, etc.). This can be described with the first term of equation 2.

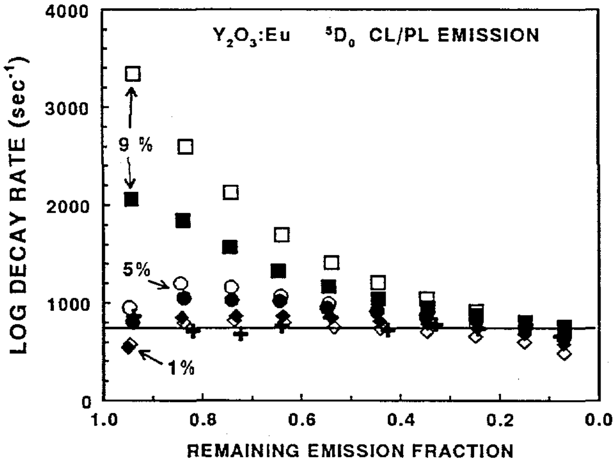

Figure 1. CL and PL logarithmic decay rates (see Eq. 2) as a function of the CL/PL brightness normalized to the maximum brightness value. CL data obtained with a 10 μsec wide pulse of electrons at either 0.8 (open symbols) or 4 keV (filled symbols) electrons. The luminescence was detected at the $^5D_0 \rightarrow {}^7F_2$ (at 611 nm) transition of Eu^{3+} in Y_2O_3. CL Data is shown at 1% (diamonds), 5% (circles), and 9% Eu (squares). Decay rates derived from PL persistence data at 9% Eu are shown as crosses. The solid line denotes the 1st order-like kinetic behavior seen at low Eu concentrations in both the CL and PL data. This corresponds to a lifetime of ~1.5 msec.

At 5% Eu (circles) there is a slight increase of the decay rate at large C values and a noticeable dependence on beam energy appears. At 9% Eu (squares) the decay rate is drastically increased at large C and the beam energy dependence also increases.This dependence on C suggests a contribution to CL decay from the third term in equation 2. The PL data for 5 (not shown) and 9% (crosses) agree well with the 1% CL data and do not show any increase with C, the remaining emission fraction. This illustrates that the type of excitation has a strong influence on the decay of the excited activators.

A second example of experimental decay rate data is shown in figure 2 for emission from the 2nd excited state of Tb^{3+} in Y_2SiO_5 ($^5D_3$). Here we have plotted both C and the decay rate on log scales to encompass the large variations of rate with Tb concentration. Notice that, even at 0.2% Tb, there is a dependence of the rate on C and E_b for C>0.5 (short times). At 1% Tb the decay rate varies with C and E_b over the entire brightness range, and at 5% Tb, the log rate has a second order dependence (the third term in equation 2) over the entire range of C. While the log scale of figure 2 de-emphasizes the beam energy dependence seen in this data, it is actually comparable to that seen for the 9% Eu emission in figure 1. In figure 2, not only is there a strong C dependence of the decay rate, but these rates vary significantly with

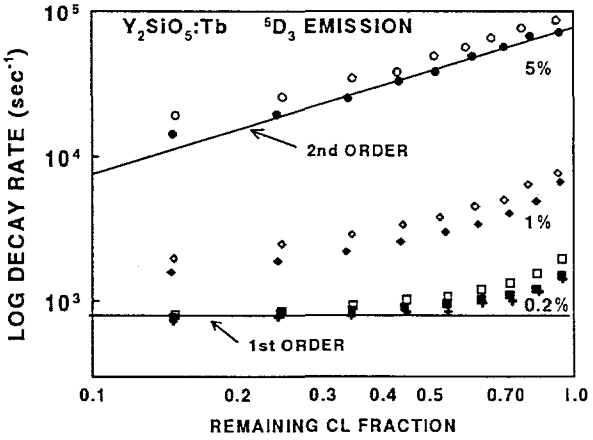

Figure 2. CL and PL logarithmic decay rates (see Eq. 2) as a function of the CL/PL brightness normalized to the maximum brightness value for the $^5D_3 \rightarrow {}^7F_5$ (blue) transition of Tb^{3+} in Y_2SiO_5. In contrast to figure1 log scales are used for both ordinate and abscissa. CL data obtained with a 10 μsec wide pulse of electrons at either 0.8 (open symbols) or 4 keV (filled symbols). CL Data is shown at 0.2% (squares), 1% (diamonds), and 5% Eu (circles). Decay rates derived from PL persistence data at 0.2% Tb are shown as crosses. The upper solid line is behavior expected for 2nd order kinetics (3rd term in equation 2).

activator fraction at low C values. This corresponds to the well-known concentration quenching of the steady-state blue emission $({}^5D_3 \rightarrow {}^7F_2)$ reported in the literature[5].

Finally, figure 3 shows log rate data for green luminescence $({}^4T_1 \rightarrow {}^6A_1)$ in Mn-doped Zn_2SiO_4. Because this transition involves d electrons, it has a much broader spectral band than the highly shielded f electron transitions in the Y_2O_3:Eu and Y_2SiO_5:Tb systems. The results here are similar to the ${}^5D_3$ Tb^{3+} emission data, but the dependence on C is even steeper than second order at large Mn concentrations. To address the issue of concentration dependent kinetics, we deliberately varied the intensity of the exciting laser at the highest Mn concentration to examine whether the PL decay rates increase as the starting C values are raised. Figure 4 shows some of this data and compares it to CL results at high and low beam energies. The time-integrated values of the intensity are also shown on the graph; these demonstrate that non-radiative losses that are peculiar to the cathodoluminescence process reduce the radiative efficiency of pulsed light output by at least a factor of two at 0.8 keV.

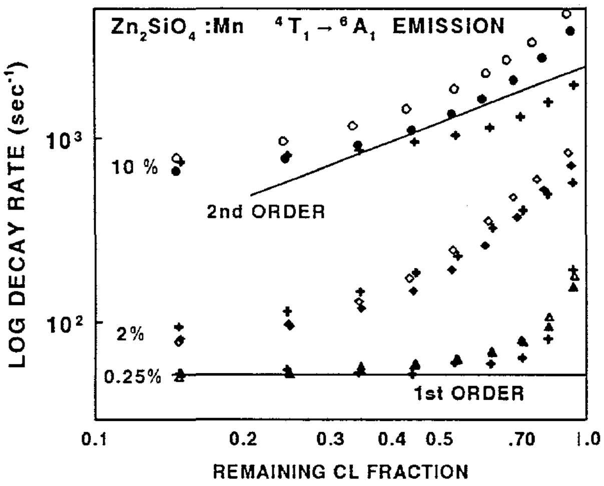

Figure 3. CL and PL logarithmic decay rates (see Eq. 2) as a function of the CL/PL brightness normalized to the maximum brightness value for the ${}^4T_1 \rightarrow {}^6A_1$ (green) transition of Mn^{2+} in Zn_2SiO_4. As in figure 2 log scales are used for both ordinate and abscissa. CL data obtained with a 10 µsec wide pulse of electrons at either 0.8 (open symbols) or 4 keV (filled symbols). CL Data is shown at 0.25% (triangles), 2% (diamonds), and 10% Mn (circles). Decay rates derived from PL persistence data at all three activator fractions are shown as crosses. The upper solid line is behavior expected for 2nd order kinetics (3rd term in equation 2).

The fact that that varying our laser excitation power seems to replicate the effects of beam energy changes in figure 4, strongly suggests that these beam energy effects are caused by changes in the density of excited activators. By contrast, our pulsed CL data show almost no dependence of log decay rates on beam current in any of these systems. However, to enhance the effect of the high excited activator density that ***already exists along the path of a single primary electron*** we would have to raise our pulsed-electron beam current to values so large that excited activators from successive primary electrons overlap spatially.

Recently, we have published measurements of the activator density dependence of CL efficiency at different beam energies for the Y_2O_3:Eu and Y_2SiO_5:Tb systems[6]. In both cases the rate of decline of efficiency with E_b decreases substantially as the activator density is reduced. Figure 5 shows similar data for Zn_2SiO_4:Mn; here we plot the log-slope of efficiency vs. E_b as a function of activator concentration. This slope is reduced by a factor of two as the Mn concentration is reduced from 0.1 to .0025, illustrating that the beam energy effects seen in Figures 3 and 4 are also evident in the steady-state CL efficiency.

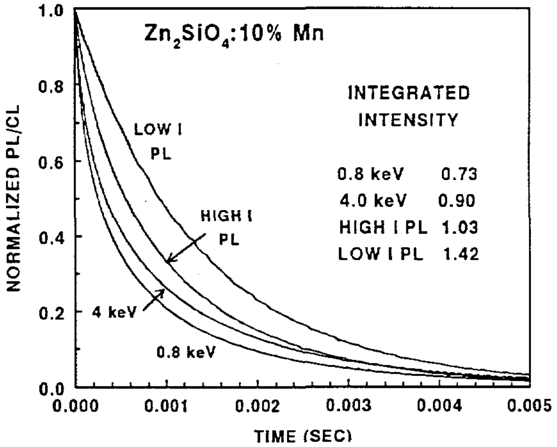

Figure 4. CL and PL intensity values measured for the ${}^4T_1 \rightarrow {}^6A_1$ (green) transition of Mn^{2+} in Zn_2SiO_4 plotted versus time after the end of electron or laser excitation. PL excitation power was varied by a factor of 10 for the two upper decay curves. The tabulated values for the time integrals of these curves (arb. units) are also listed. These values are a measure of the radiative efficiency under pulsed conditions for the four excitation conditions. Raising the PL excitation power (initial excited state density) produces alterations in the decay kinetics which are like those observed when the beam energy is reduced in CL.

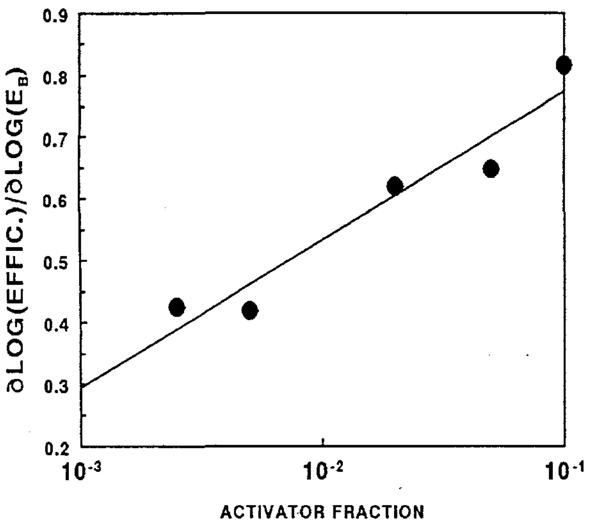

Figure 5. Experimentally measured variation of the beam energy dependence of CL as the Mn activator fraction is varied in Zn_2SiO_4. The quantity plotted is the slope of the log(CL efficiency)-log (beam energy) plot measured under constant current density conditions from 0.75 to 3.0 keV. Similar reductions in beam energy dependence are seen for Y_2O_3:Eu and Y_2SiO_5:Tb (see reference 6).

In conclusion, we have demonstrated that CL decay processes which display non-first order characteristics are important for several common phosphor systems. These enhanced decay processes are always more evident at high activator densities and low beam energies. Correlation of decay rate differences with actual changes in steady state CL efficiencies is difficult because of the multi-state cascade process that is likely in rare-earth spin state manifolds[2]. In the simplest model for de-excitation, the non-radiative energy losses in a sequential de-excitation sequence are additive; thus the loss in any particular transition is expected to be considerably smaller than for the whole multi-state sequence. Thus, it may not be surprising that decay rates only change ~30-50% between 0.8 and 4 keV, while the efficiency difference is a factor of 2-3 over this beam energy range. While the excited state interactions that we have quantified in this work play a significant role in reducing low voltage efficiency, it is also clear from the fact that the CL beam energy dependence does not vanish completely at low activator densities that other mechanisms must be important as well.

The precise physical picture for enhanced non-radiative loss due to excited state interactions remains unexplained. The standard picture of concentration quenching involves the migration of energy from an excited activator to another activator via multipolar electrostatic interactions, with the excitation terminating at a lattice defect where energy is then lost to the phonon bath. It is clear that interactions between **nearby excited states** could lead to immediate phonon emission, if one of the activators de-excites non-radiatively to the ground state, while the second one is promoted to a much higher excited state, where de-excitation is most certainly non-radiative because of the decreased energy spacing in the upper half of the 4f manifold. More experiments will be necessary to firmly establish the nature of these non-radiative losses.

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