CATHODOLUMINESCENT DISPLAY PHOSPHORS

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ABSTRACT

The past several years rendered a resurgence of interest in phosphors for low-voltage flat panel displays utilizing cathodoluminescence (CL). A major selection criterion for these phosphors is CL efficiency. The objective is to maximize the efficiency at low voltages. This work focuses on understanding the materials properties that influence CL efficiency below 1 kV. Existing high-voltage CL efficiency models take into account intrinsic materials properties such as band-gap energy. Experimental data reveals that the CL efficiency also depends on physical properties such as particle and crystallite size. An updated, predictive model of CL efficiency that includes the effects of crystallite size, radiative recombination probability, and electron accelerating potential was developed. The predicted efficiencies agree very well with experimental results. The experimental data were collected using a hot filament electron gun in a demountable high-vacuum chamber. To obtain measurement accuracy, secondary electrons were collected and the phosphor excited with a uniform beam profile. A CL characterization protocol for display phosphors was established at Sandia National Laboratories and made available to phosphor researchers.

INTRODUCTION

Cathodoluminescence (CL) is the emission of light from a material that is being bombarded by electrons. Familiar displays that utilize cathodoluminescence include cathode-ray tubes (CRTs), vacuum fluorescent displays (VFDs), and field emission displays (FEDs). Typical electron beam energies incident on the phosphors used in these devices are >10 keV for CRTs, <200 eV for VFDs, and 5-8 keV for FEDs. The FED is a hopeful candidate for next generation information display. Typical phosphor compositions considered for FED use include the conventional sulfide-based cathode-ray tube phosphors (ZnS:Ag; ZnS:Cu,Al; Y_2O_2S:Eu), thiogallate phosphors ($SrGa_2S_4$:Eu; $SrGa_2S_4$:Ce), and oxide-based phosphors ($Y_3Al_5O_{12}$:Tb; Y_2O_3:Eu, Y_2SiO_5:Ce; ZnO:Zn; $ZnGa_2O_4$). It is generally accepted that screen luminous efficiencies of 11, 22, and 3 lm/W are required for red, green, and blue phosphor components respectively [1]. In addition, good chromaticity, chemical stability, resistance to Coulombic aging, and small particle size are requirements for FED phosphors.

The selection and development of the appropriate FED phosphor requires an understanding of electron interactions with solids. When electrons impinge on a phosphor, a portion are elastically backscattered from the surface, while others penetrate the host lattice and undergo elastic and inelastic collisions with atoms of the host lattice, generating secondary electrons, Auger electrons, x-rays, phonons, and electron-hole (e-h) pairs. The e-h pairs can recombine radiatively at activator ions and nonradiatively at microstructural features in the phosphor crystal such as point defects, grain boundaries, impurities, and regular ions of the host lattice as shown in Figure 1. The goal is to manipulate these recombination processes to maximize the CL output.

DISCLAIMER

Luminous efficiency and radiant efficiency are commonly used to characterize CL phosphors. The luminous efficiency, ε, is the ratio of the luminance to the input

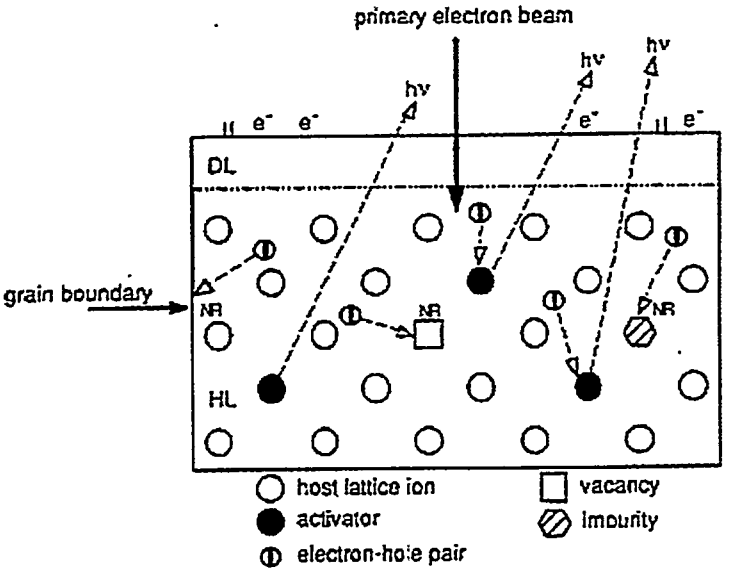

Figure 1. Recombination processes in a phosphor under electron beam excitation. HL: host lattice; DL: dead layer; hν: photon emission; NR: nonradiative recombination; e⁻: surface bound electrons. The parallel lines extending from the surface represent dangling bonds.

power, and is expressed in units of lumens per watt (lm/W). The luminous efficiency can be calculated using the following:

$$\varepsilon = \pi \frac{L \times A}{P \times C} \qquad [1]$$

where L is the luminance in cd/m^2, A is the spot area in m^2, P is the power in watts, calculated by multiplying the net electron accelerating potential in volts (V) by the net measured current in amps (A), C is the area coverage, and is only used in calculations of screen luminous efficiency. The luminance is a photometric quantity that is weighted by the human eye response. The peak response occurs at a wavelength of 555 nm. Luminous efficiencies are in general higher for green-emitting phosphors where ε(green)>ε(red)>ε(blue). Display manufacturers most often use the luminous efficiency as a figure-of-merit in phosphor selection. However, the radiant efficiency, η is more symbolic of the materials properties, since it is not corrected for the eye's response. The radiant efficiency is given by the following:

$$\eta = (1-\gamma)\left(\frac{h\nu}{\beta E_g}\right) SQ \qquad [2]$$

where γ is the backscattering coefficient, $h\nu_m$ is the mean energy of the emitted photons, S is the probability of radiative recombination, Q is the quantum efficiency of the activator, E_g is the band gap energy, and β is a constant of the particular material [2]. The maximum conversion efficiency, η_{max}, is attained when S =1, Q = 1, and $\gamma = 0$. For blue-emitting ZnS:Ag, $h\nu = 2.82$ eV, $\beta = 2.9$, $E_g = 3.8$ eV, and $\eta_{max} = 0.25$ (25%). For green-emitting ZnS:Cu, $\eta_{max} = 0.21$ (21%). However, luminous efficiencies at 5 keV are 5 and 40 lm/W for ZnS:Ag and ZnS:Cu respectively. This discrepancy is a result of the eye sensitivity being factored into luminous efficiency calculations. It does not mean that there are significantly more photons being emitted from the ZnS:Cu. The number of photons produced by one 5 keV electron can be calculated by the following:

$$\text{number of photons} = \frac{5000\ \text{eV}}{h\nu}\eta \qquad [3]$$

For ZnS:Ag, one 5 keV electron produces 440 2.82 eV photons, and 450 2.34 eV photons for ZnS:Cu. This amounts to ~2.8×10^{15} photons/s•cm^2 for these two phosphors, assuming a current density of 1 $\mu A/cm^2$.

The assumptions made in equation (2) to obtain η_{max} are often inadequate for phosphors that operate in the low voltage range because nonradiative recombination possibilities are neglected by assuming that S = 1. In addition, backscattered and secondary electrons, variations in phosphor surface potential at different electron accelerating potentials, and the effects of particle and crystallite size are neglected. Crystallites are small, independent single crystals, typically 10 to 200 nm in diameter. The size of the crystallites depends on the annealing temperature, where higher annealing temperatures produce larger crystallites. Particles are comprised of crystallites and typically range in size from 0.5 to 10 μm. The particle size depends on post-synthesis processes such as milling. Small crystallites and small particles both result in an increase in the surface area and surface adsorbed species [3].

Based on the limitations of the CL efficiency model given in equation 2 for phosphors in the low to medium voltage range, a revised model for conversion efficiency was developed which includes the contributions of crystallite size, particle size, and electron accelerating potential. This model was corroborated with experimental data in the low to medium voltage range. Methods to ensure accuracy of experimental data were developed. This paper will address both modeling and CL characterization of FED phosphors.

EXPERIMENTAL

For CL efficiency measurements, phosphor powders were packed into 5 mm diameter stainless steel sample holders and placed into a demountable vacuum chamber. Samples were characterized at a vacuum ambient of 10^{-7} Torr with a hot filament electron gun (Kimball Physics, Inc., Wilton, NH). Both Gaussian and uniform beam profiles were used for the CL measurements. Beam profile was monitored using a BeamView Analyzer (Big-Sky Software Corporation, Bozeman, MT), and solid-state CCD camera (Cohu, Inc., San Diego, CA). Photometric and radiometric data were collected using a spectroradiometer (Oriel Corporation, Stratford, CT). The emitted light from the phosphor was coupled into an optical fiber bundle leading to the

spectroradiometer. The light was dispersed by a 400 line/mm grating and imaged onto a 1024 element linear silicon photodiode array. For luminous efficiency, the resulting spectrum was then weighted by the photopic response of the eye (the relative visual response of the human eye in bright light, as a function of wavelength) and integrated over the range of visible wavelengths. The result of this calculation was the luminous intensity per unit area in cd/m^2. In addition, the chromaticity coordinates were computed by weighting the spectrum with certain color matching functions and similarly integrating.

Crystallite size was estimated from the width of the (222) line of Y_2O_3 using a LaB_6 standard and employing the Scherrer x-ray line broadening technique.

RESULTS AND DISCUSSION

Cathodoluminescence Efficiency Modeling

A revised equation for the probability of radiative recombination, S, was developed assuming a phosphor of cubic particles and crystallites as shown in Figure 2. Geometric equations were derived for the number of atoms within one cubic particle containing n^3 crystallites. The total number of atoms in the particle is the sum of the atoms in the bulk ($N_b = (p-1)^3n^3$), atoms on the surface ($N_s = [(p+1)^3 - (p-1)^3]n^3$), and atoms in the grain boundary ($N_{gb} = (1/a^3)(na)^2 3\delta(n-1)(p-1)^3$), where $p=a/\ell$ and $n=d/a$ from Figure 2. S, the fraction of radiative sites is given by $N_b/(N_b+N_s+N_{gb})$, assuming the same activator concentration is present in the bulk, surfaces, and grain boundaries and only activators within the bulk are radiative recombination sites. The new expression for S, as a function of crystallite size (a), number of crystallites along a particle edge (n), and grain boundary thickness (δ) appears in the bracketed portion of equation (4).

$$\eta = (1-\gamma)\frac{N_{eh}}{N_a}\frac{h\nu_m}{\beta E_g}\left[\frac{1}{\left(\frac{a+1}{a-1}\right)^3 + \frac{3\delta(n-1)}{na}}\right] \qquad [4]$$

Figure 3 shows a plot of S as a function of crystallite size (25-150 nm) for varying phosphor particle sizes (0.5-10 μm). As $a\rightarrow\infty$, $S\rightarrow 1$, and as $a\rightarrow 0$, $S\rightarrow 0$. As the crystallite size increases, the number of atoms in the grain boundaries and on the surface decreases, leading to an increase in the number of radiative recombination sites, and therefore a higher probability of radiative recombination. This plot suggests that the CL efficiency is independent of particle size but dependent on crystallite size. This result has also been demonstrated empirically for oxide phosphors [4,5]. N_a in equation (4) is the number of primary electrons that penetrate the phosphor host lattice, and N_{eh} is the number of electron-hole (e-h) pairs generated. This equation has been shown to be more accurate in predicting the CL efficiency at low voltages (≤1 kV) [5] as shown in Figure 4 for $Y_2O_3:Eu^{3+}$. The assumptions used in this model may break down above 1 kV, as shown in the figure.

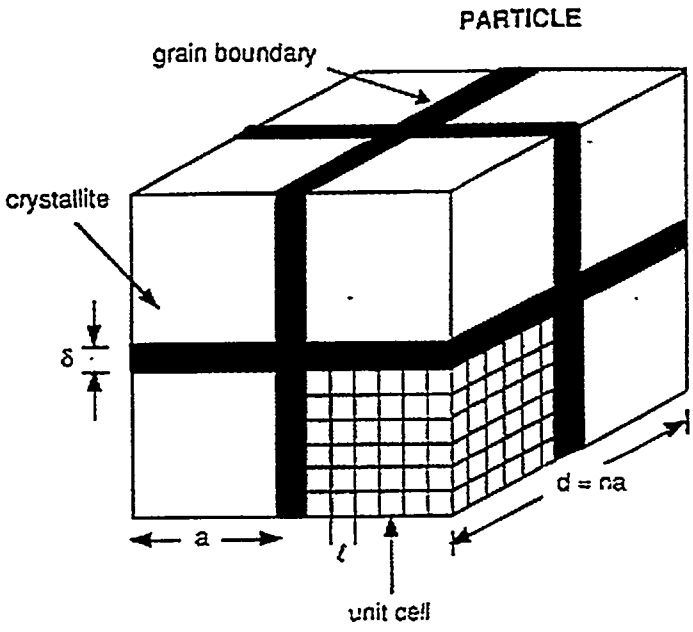

Figure 2. A cubic particle of edge length, d; made up of cubic crystallites of edge length, a, comprised of unit cells with lattice parameter, ℓ; and grain boundary thickness, δ.

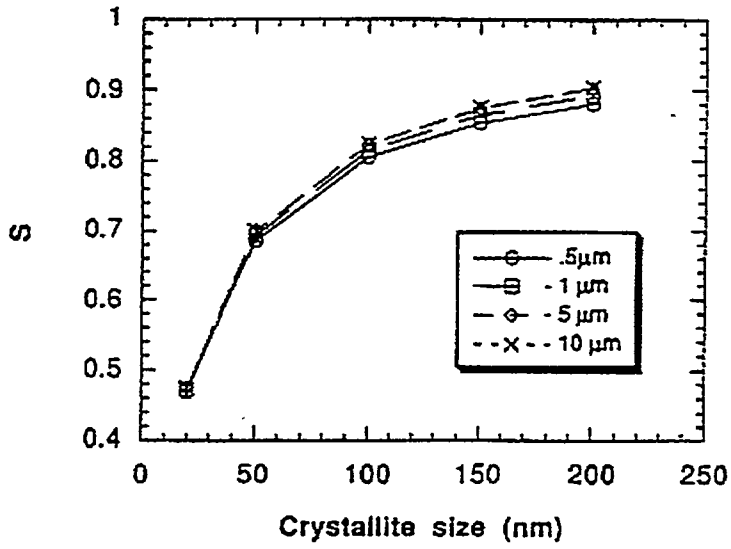

Figure 3. Fraction of radiative recombination sites (S), as a function of crystallite size for different particle sizes.

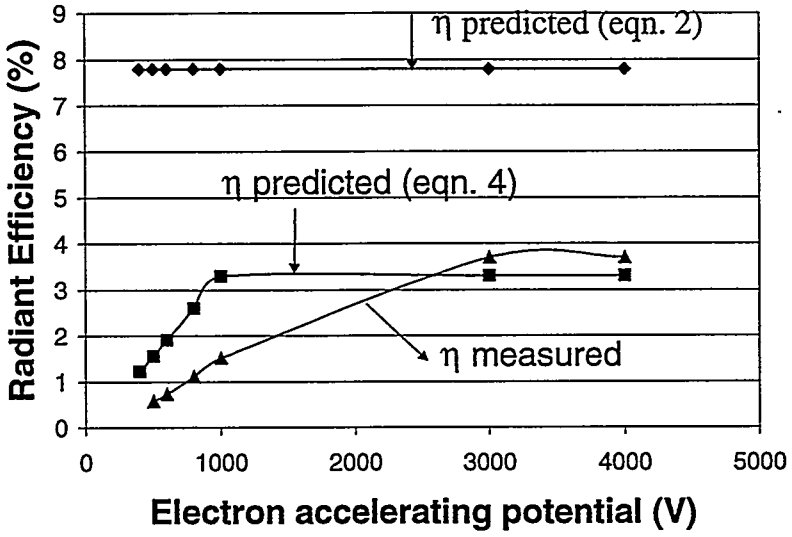

Figure 4. Predicted and measured conversion efficiencies as a function of electron accelerating potential (V) for $Y_2O_3:Eu^{3+}$ where hν=2.03 eV , a=150 nm, d=1.75 μm, δ=5 nm, βEg=25.8 eV, γ=0.52, and N_{eh}/N_a varies with accelerating potential [5].

Cathodoluminescence Efficiency Characterization

Corroboration of predictive models of CL conversion efficiency with experimental data requires measurement accuracy. Achieving this accuracy has been a recent focus of work at Sandia National Laboratories, due to the need to compare data presented and published by many different research groups. The power deposited by the impinging electron beam must be known in order to calculate the CL efficiency. This power can be estimated as the product of the net accelerating potential and the net beam current. The net accelerating potential is the sum of the electron accelerating voltage and the secondary electron voltage or bias voltage. The accelerating potential of the incident electrons does not always represent the actual potential of electrons that penetrate the phosphor, due to variations in the surface potential. Shifts in the phosphor surface potential can be measured by monitoring secondary and Auger electron spectra during electron bombardment [6]. Figure 5 shows plots of CL efficiency of Y_2O_3:Eu powder as a function of electron accelerating potential (500 V to 5 kV) at 1 μA and beam profile. Irradiating the sample with a uniform beam profile ensures a uniform power density distribution across the bombarded area. The power density is not uniform when the beam has a Gaussian profile. Because of this nonuniformity, the luminous efficiency (equation 1) calculated for a phosphor irradiated with a Gaussian beam will not be accurate.

The collection of secondary electrons is an important component of the CL characterization process. Figure 6 shows the net measured current (μA) as a function of sample bias voltage (0 to 100 V) with (curve 1) and without (curve 2) modifications for preventing bombardment from secondary electrons originating from the walls of the

stainless steel vacuum chamber using a shield and aperture. The techniques utilized at Sandia National Laboratories for the accurate characterization of CL display phosphors have been developed into a protocol for the phosphor community [7].

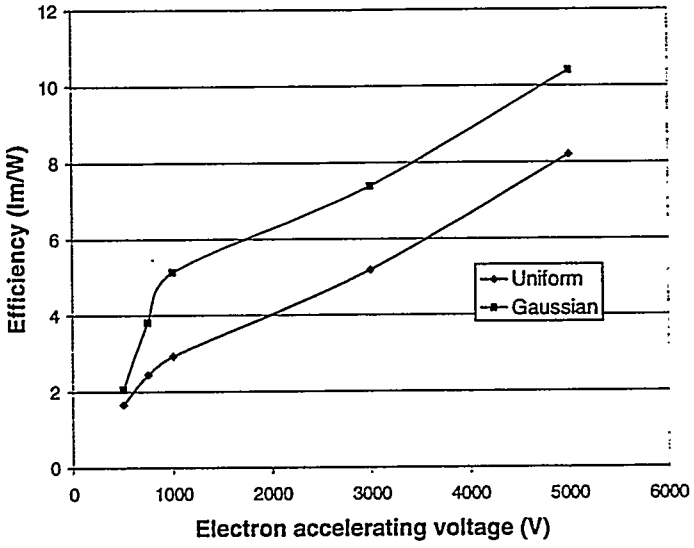

Figure 5. CL efficiency (lm/W) as a function of electron accelerating potential (V) and beam profile. Current was held constant at 1 μA.

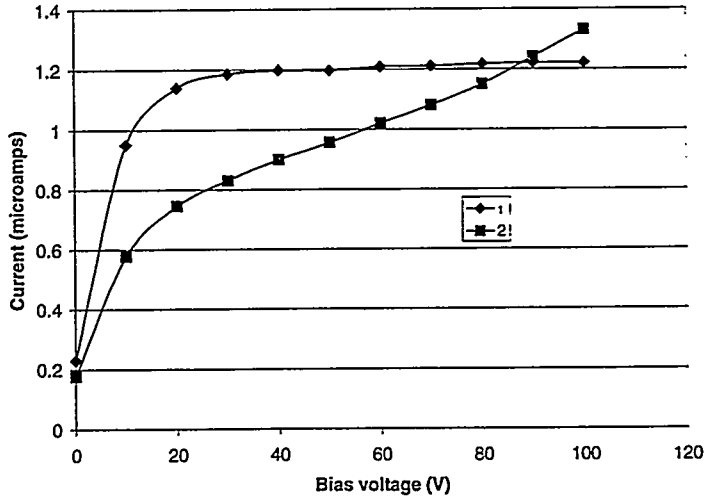

Figure 6. Net measured current (μA) as a function of bias voltage (V) for Y_2O_3:Eu (1) with and (2) without shielding of secondary electrons. Electron accelerating potential ~1 kV.

CONCLUSIONS

Cathodoluminescent displays such as the FED require phosphors that have high efficiencies at low voltages. The CL efficiency can be predicted using a recently-developed model that includes the effects of particle size, crystallite size, and electron

accelerating potential. This model provides a clearer picture of the factors influencing CL efficiency at low voltages (≤1 kV) and agrees well with experimental data. The accuracy of the experimental data is crucial when choosing the appropriate phosphor for FED use. The resurgence of interest in phosphor materials for FEDs resulted in a great deal of data collected under many different experimental conditions, using different instrumentation. As a result, it is difficult to trace the progression of a particular phosphor through history, and to directly compare data from different research groups. A protocol has recently been developed for cathodoluminescence characterization of display phosphors and may allow for more reliable comparison of results among researchers in the field.

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