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Development of Standards for Characterization of Cathodoluminescence Efficiency

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ABSTRACT

Cathodoluminescence (CL) characterization in a demountable vacuum chamber is an important benchmarking tool for flat-panel display phosphors and screens. The proper way to perform these measurements is to minimize the effects of secondary electrons, excite the phosphor/screen with a uniform beam profile, and maintain a clean vacuum environment. CL measurements are important for preliminary evaluation and lifetesting of phosphor powders and screens prior to incorporation into the FPD. A survey of many CL characterization systems currently in use revealed the myriad of spectroradiometers, colorimeters, electron guns, vacuum pumps, mass spectrometers, etc. that introduce many avenues for error that are often difficult to isolate. A preliminary round-robin experiment was coordinated by Sandia and involved five other research groups. The purpose of this experiment was to obtain an indication of equipment capabilities and instrument variations, as well as reliability and consistency of results. Each group was asked to measure the luminance (cd/m^2) and chromaticity coordinates of a $Y_3Al_2Ga_3O_{12}$: Tb pellet and calculate the luminous efficiency. Pellets were chosen in order to reduce errors associated with processing and handling of powders or screens. Some of the data reported in this experiment were in good agreement, while others differed significantly. Determining sources of error in CL measurements is an ongoing effort. By performing this experiment, we were able to identify some of the causes of error and develop a characterization protocol for display phosphors.

Keywords: Cathodoluminescence, flat-panel display, characterization standards, phosphors, cathodoluminescent efficiency

1. INTRODUCTION

Cathodoluminescence (CL) efficiency is an important property used to determine the potential of a phosphor material for use in flat-panel display applications such as field emission displays (FEDs). The CL efficiency of a phosphor is the ratio of its energy output to the energy input. To determine the CL efficiency accurately requires an understanding of the complexities associated with electron interactions with phosphor materials and subsequent emission of cathodoluminescence. When an electron beam bombards a phosphor, a portion of the incident electrons undergo elastic backscattering from the atoms on the phosphor surface. The electrons that penetrate deeper into the phosphor lose their energy by elastic and inelastic collisions with the atoms of the host lattice, generating secondary electrons, Auger electrons, x-rays, electron-hole pairs, and phonons [1]. The secondary electrons can produce other lower energy secondary electrons, initiating a cascade process that results in a plasma of secondary electrons with a corresponding number of positive holes in the same region. The electron-hole (e-h) pairs generated can migrate through the host lattice. CL emission is a result of the radiative recombination of e-h pairs at activator ions.

In general, CL characterization involves measuring (i) variation of luminescence with electron accelerating potential in volts (V) for a given current density ($\mu A/cm^2$) and (ii) variation of luminescence with current density for a given electron accelerating potential. Cathodoluminescence intensity is typically quantified in photometric or luminance units of candela per meter squared (cd/m^2). For a given current density, the luminance of a phosphor increases with the electron accelerating potential and can be represented by the following formula [2]:

$$L = k(V - Vth)^n \qquad (1)$$

where k and n are constants for a particular phosphor material, V is the electron accelerating potential, and V_{th} is the threshold voltage, or voltage at which the luminance goes to zero. Threshold voltage depends on materials and processing parameters.

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DISCLAIMER

Lattice defects (vacancies, dislocations, grain boundaries, impurities, surface recombination sites), electrical/thermal conductivity, band gap energy, particle/crystallite size, activator concentration are examples of intrinsic materials and processing-based parameters that influence a phosphor's cathodoluminescent efficiency. The power deposited by the impinging electron beam must be known in order to calculate the CL efficiency of a phosphor. 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 suppression voltage or bias voltage. The accelerating potential of the incident electron beam does not always represent the actual potential of the 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 [3]. The net beam current is the incident electron beam current minus the backscattered and secondary electron currents.

Backscattered electron emission characteristics depend primarily on density, average atomic number, and molecular weight of the phosphor. Monte Carlo simulation [4] is a useful tool for estimating the electron penetration depth, activation volume, and backscattering coefficient at a given beam energy. Figure 1 illustrates the penetration range and trajectories of 5 kV electrons in a Y_2O_3 host lattice. At 5 kV, the calculated penetration depth is 0.1 μm with a backscatter coefficient (BS) of ~27%. This represents a significant fraction of the primary beam. Consequently, these electrons do not contribute to further phosphor excitation, energy deposition, or charge injection. The backscattered electron (BSE) spatial distribution at the surface of Y_2O_3 at 5 kV is shown in Figure 2. The highest distribution of backscattered electrons is located along the path of the primary beam. Since accurate estimates of the losses associated with backscattered electrons are not easily obtained, it may be difficult to ascertain the actual beam current, and hence, the total injected charge and actual CL efficiency.

During electron bombardment, the absorbed primary electrons tend to charge the phosphor negatively. At least an equal number of secondary electrons must be emitted to prevent the phosphor from charging so negatively that the incident electrons are repelled from the surface. The secondary electron emission ratio (η) is the ratio of the number of emitted secondary electrons to the number of absorbed primary electrons. Figure 3 shows the secondary emission ratio as a function of applied voltage (kV) for two insulating phosphors, neglecting backscattered electrons. Phosphors are typically operated in the accelerating potential region where η is greater than unity (positive surface potential). The first potential region where η is less than unity is due to the low electron penetration depth. Most of the primary beam energy is dissipated as heat in the phosphor surface. The second less-than-unity region is due to secondary electrons produced deep within the phosphor. These secondaries have a higher probability of encountering lattice imperfections that reduce their kinetic energies so that they no longer have sufficient energy to escape the phosphor. Operation of phosphors at accelerating potentials in either of the two less-than-unity regions typically results in negative surface charging.

Based on the aforementioned discussions, it is obvious that the effects of backscattered electrons, secondary electrons, and variations in surface potential limit the accuracy of CL data. This accuracy is further limited by error associated with the type of luminance measuring equipment used. Measurement errors of commercial colorimeters can be greater than 0.01 in x and y chromaticity and as high as 10% in luminance. The accuracy of luminance measurements is related to the wavelength of the emitted light and the shape of the spectral energy distribution. Many colorimeters are designed to give best results when measuring broad band emitters, rather than line emitters. Certain colorimeters require that the emitted light from the sample must completely fill or over-fill the instrument aperture. It is necessary to determine the ratio required for accurate CL measurements by characterizing the sample under the following conditions: $d_{aperture} \leq d_{spot}$ and $d_{aperture} > d_{spot}$. Additional sources of error are typically related to the beam profile (uniform, Gaussian) of the electron gun.

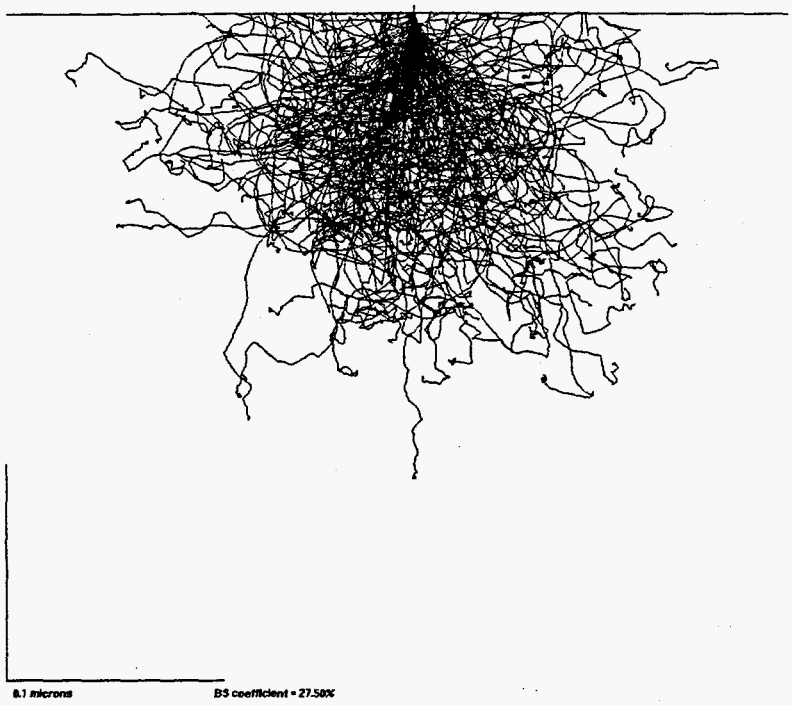

Figure 1 Monte Carlo simulation of electron trajectories in Y_2O_3 at an incident beam energy of 5 kV.

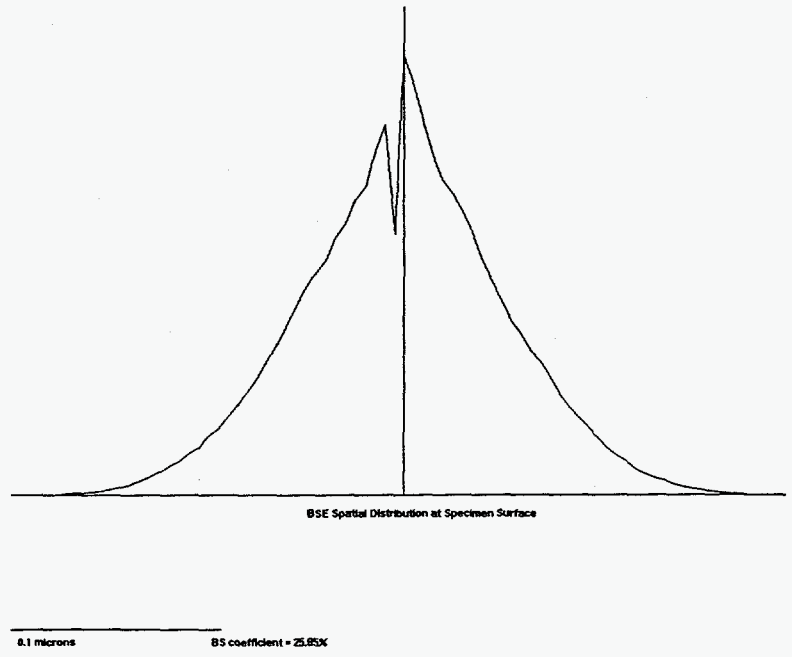

Figure 2 Spatial distribution of backscattered electrons at the surface of a Y_2O_3:Eu phosphor at 5 kV. Electron penetration depth = 0.1 μm. BS coefficient = 25.8%.

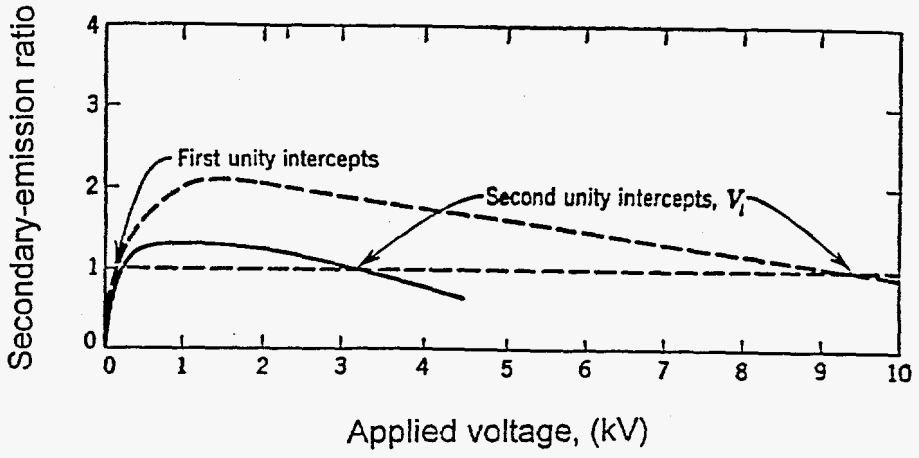

Figure 3 Secondary emission ratio as a function of applied voltage (kV) for two insulating phosphors [5].

The resurgence of interest in phosphor materials for flat-panel display applications has produced a great deal of luminescence data collected under many different experimental conditions, using different instrumentation. As a result, it was very difficult to trace the progression of a particular phosphor through history, and to directly compare data from different research groups. Many papers in the literature report luminance without giving the conditions for which luminous efficiency (lm/W) could be calculated (e.g., current density, spot size), others often use relative brightness or "arbitrary units". The inconsistency of data presentation in the literature and skepticism regarding result comparisons may be alleviated with accepted standards and protocols for display phosphor characterization. Since a protocol was not available in the past, researchers reported their data to the best of their ability, using their best estimate of how to characterize potential display phosphors. Sandia has recently developed a protocol for cathodoluminescence characterization of phosphors for display applications. A preliminary round-robin cathodoluminescence characterization experiment was coordinated by Sandia and involved five other research groups [6]. Each group was given a terbium-doped yttrium aluminum gallium garnet ($Y_3Al_2Ga_3O_{12}$:Tb) pellet to characterize and use as a system calibration standard. $Y_3Al_2Ga_3O_{12}$:Tb (YAGG:Tb) was chosen as a standard because of its yellow-green emission color (λpk = 544 nm, x = 0.348, y = 0.542) and its saturation resistance under prolonged electron bombardment. Photometric measurements of yellow-green sources tend to have less error [7].

2. EXPERIMENTAL MATERIALS AND PROCEDURES

2.1 Phosphors

The following commercially available phosphors were used in this study: Y_2O_3:Eu[+], ZnS:Ag[+], and $Y_3Ga_3Al_2O_{12}$:Tb[%]. Y_2O_3:Eu and ZnS:Ag were characterized in powder form in the Phosphor Characterization Facility (PCF) at Sandia National Laboratories in investigations of cathodoluminescent properties. For the round-robin characterization experiment, YAGG:Tb powder was dry pressed into pellets of 0.5 inch diameter. Pellets were chosen in order to reduce experimental errors associated with processing and handling of powders or screens. Each pellet was dry pressed at 30,000 psi, annealed for 2h in air at 1400°C, and argon plasma cleaned on the surface. The pellets were pre-characterized at Sandia to ensure consistency. Each group was then asked to measure the luminance in candelas per unit area (cd/m^2) and chromaticity coordinates of the pellet at 250, 500, 750, 1000, and 3000 V, at a constant power density of 5 mW/cm^2.

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%Osram Sylvania, Towanda, PA 18848
[$] Kimball Physics Inc., Wilton, NH 03086
[•] Big Sky Software Corporation, Bozeman, MT 59772

2.2 Cathodoluminescence Measurements

Cathodoluminescence measurements at Sandia were performed in a stainless steel demountable vacuum chamber with a hot filament electron gun[$]. Powder samples were packed into stainless steel cups, placed inside the vacuum chamber, and evacuated to $\leq 10^{-7}$ Torr. The electron beam was deflected through a 90-degree angle to bombard the phosphor normal to the surface. The magnetic deflection of the beam minimizes filament light contamination, avoids filament evaporation products and separates electrons from possible negative ions. The electron beam was focused to a spot size of 5 mm in diameter. To collect secondary electrons, the samples were held at a potential of +50 V relative to ground. An aluminum shield with a 5 mm diameter aperture was placed above the powder samples to prevent bombardment by secondary electrons originating from the walls of the chamber. Both Gaussian and uniform beam profiles were used for the CL measurements. Beam profile was monitored using a BeamView Analyzer[♣], and solid-state CCD camera[♠]. Photometric data were collected using a spectroradiometer[°]. 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. 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. The luminous efficiency (ε) in lumens per watt (lm/W) was calculated using the following formula:

$$\varepsilon = \pi \frac{L \times A}{P} \tag{2}$$

where L is the luminance (cd/m^2), A is the area of the spot (m^2), and P is the power in watts (W), calculated by multiplying the net electron accelerating potential in volts (V) by the net measured current in amperes (A). The net electron accelerating potential is given by the following:

$$\text{Net electron accelerating potential (V)} = (\text{electron accelerating voltage} + \text{bias voltage}) \tag{3}$$

The net measured current (I_{net}) can be expressed by the following:

$$I_{net} = I_{in} - I_{bs} - I_{sec} \tag{4}$$

I_{in} represents the beam current of the incident electrons, I_{bs} is the backscattered electron current, and I_{sec} is the secondary electron current. I_{bs} and I_{sec} were not measured quantities in these experiments. Equation (4) is a qualitative representation.

3. RESULTS AND DISCUSSION

Figure 4 shows the CL efficiency as a function of electron accelerating potential (200 V to 1 kV) at constant power density for commercially available and experimental blue-emitting ZnS-based phosphors. This figure illustrates the effects of materials and processing parameters on CL efficiency. The phosphors all have the same general composition, yet vary significantly in both their numerical values of CL efficiency and their CL efficiency vs. accelerating potential behavior. Samples 3-5, 7 have relatively flat accelerating potential dependencies compared to samples 1, 2, and 6. The different accelerating potential dependencies are most likely due to materials and processing parameters such as surface coating, crystallite size/morphology/orientation, and electrical conductivity. Experimental parameters associated with this experiment were not expected to affect these data since all samples were characterized in the same system at the same time.

♠ Cohu Inc., San Diego, CA 92186

° Oriel Corporation, Stratford, CT 06497

To illustrate the effects of experimental parameters on the CL efficiency, a round-robin characterization study was performed. The results of this study appear in Figure 5. The CL efficiency is plotted as a function of electron accelerating

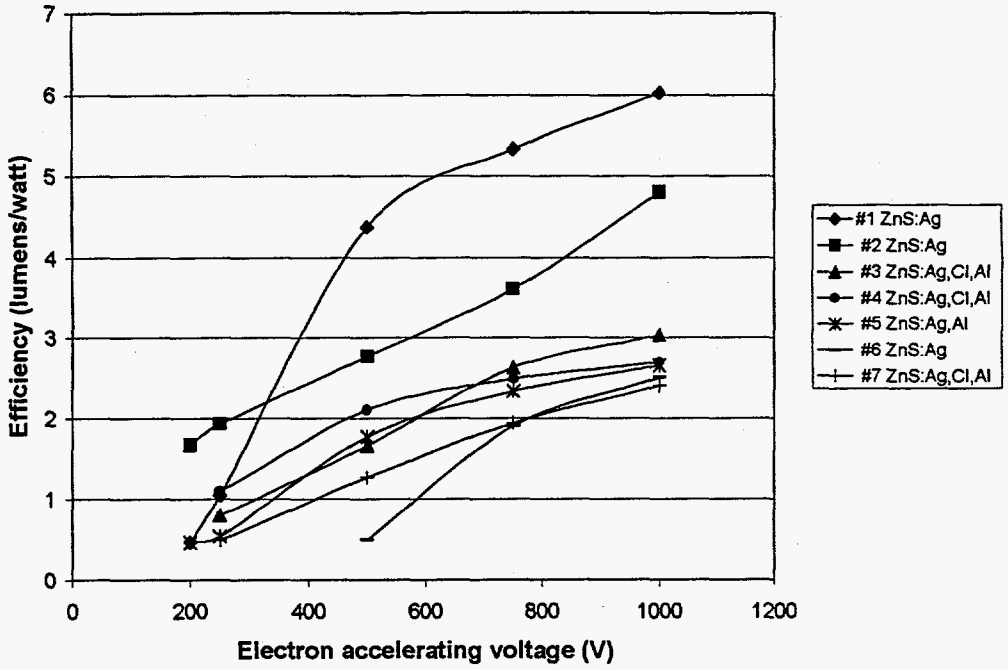

Figure 4 CL efficiency in lumens per watt (lm/W) as a function of electron accelerating potential (V) for ZnS-based phosphors. Power

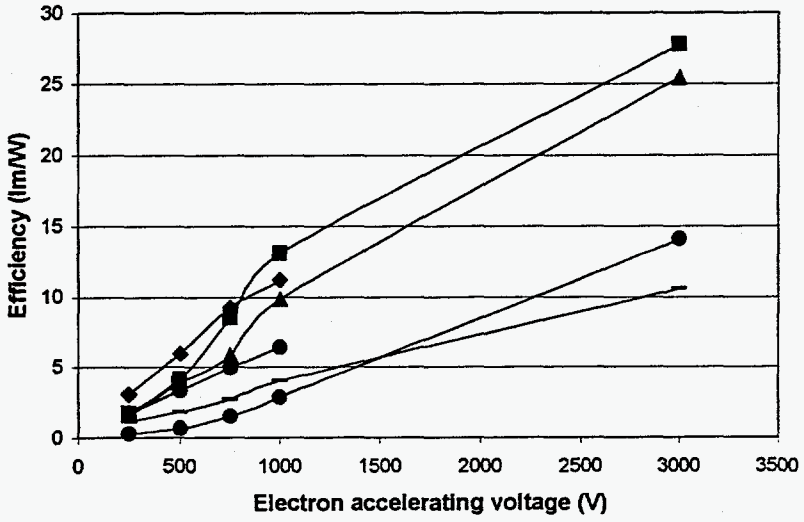

Figure 5 CL efficiency (lm/W) as a function of electron accelerating potential (V) for YAGG:Tb pellets measured in different characterization systems. Symbols represent different research groups. Power density = 5 mW/cm^2.

potential at constant power density for YAGG:Tb pellets measured in six different characterization systems. The results reported by some of the groups were in close agreement (within 10% or less), while others differed more significantly (>50%). The primary parameters that seem to have the largest effect on the final results were: instrument aperture size:spot size ratio, beam profile, and collection of secondary electrons.

Figure 6 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 resulted in lower luminance values and subsequently lower values of calculated efficiency than the same sample excited with a Gaussian beam. Since equation (2) for calculating the CL efficiency from luminance data assumes uniform power density, the luminance data obtained from a uniform beam should be more accurate for calculating the true luminous efficiency.

The collection of secondary electrons is an important component of the CL characterization process. Figure 7 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. The accelerating potential was ~1 kV. Proper secondary electron collection should yield a curve similar to (1), with a leveling off of the current at bias voltages of ~30 V. It should be noted that this procedure and modification was required for the system utilized at Sandia. Other systems may not require such a configuration. However, it is necessary to obtain net measured current vs. bias voltage data to ensure that all secondary electrons are being collected. Figure 8shows a plot of the net measured current (μA) as a function of bias voltage for a metal (stainless steel sample holder), a loosely-packed YAGG:Tb powder, and a YAGG:Tb pellet. Conductive materials typically have lower secondary electron emission coefficients. This is why the net measured current is greater for the metal than for the YAGG:Tb samples. All three curves level-off at approximate the same bias voltage, and eventually merge as the bias voltage approaches 100 V. When the bias voltage exceeds a threshold of ~30 V, the secondary collection efficiency is independent of bias voltage for conducting and insulating materials.

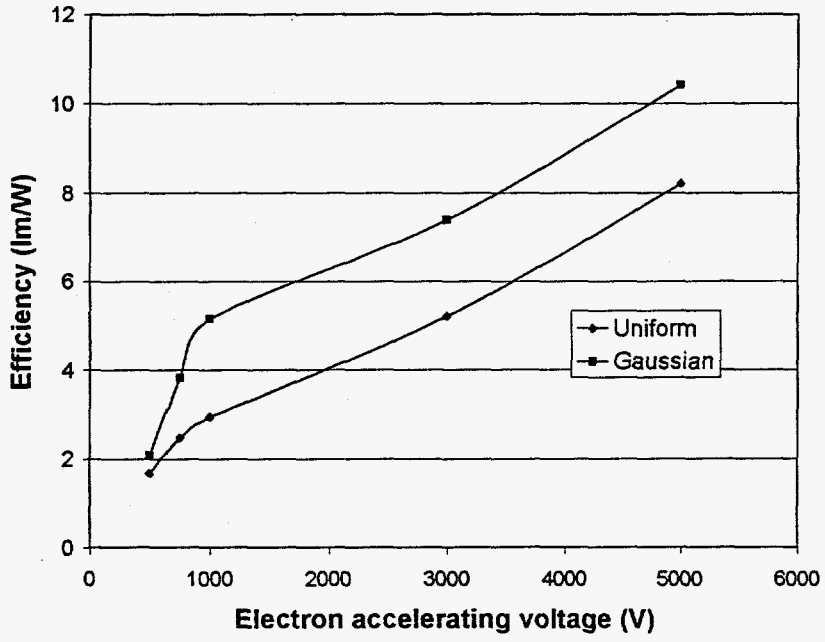

Figure 6 CL efficiency (lm/W) as a function of electron accelerating potential (V) and beam profile. Current was held constant at 1 μA.

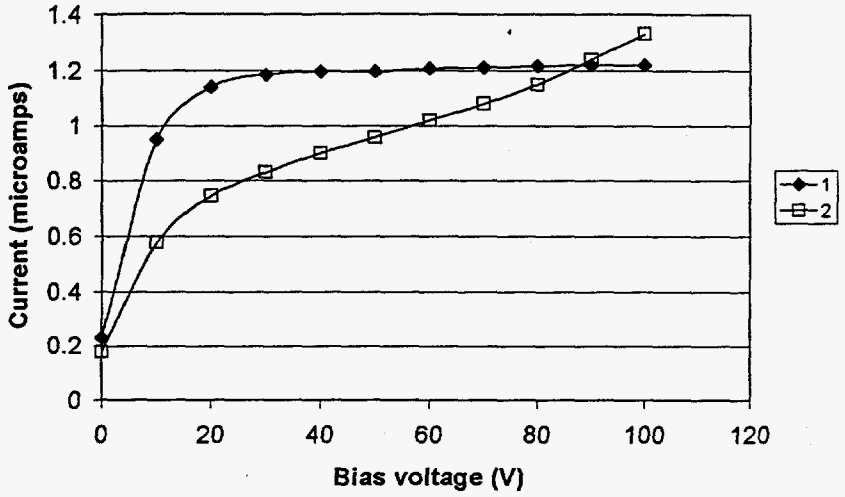

Figure 7 Net measured current (μA) as a function of bias voltage (V) for Y_2O_3:Eu (1) with and (2) without shielding of secondary electrons. Electron accelerating potential ~1 kV.

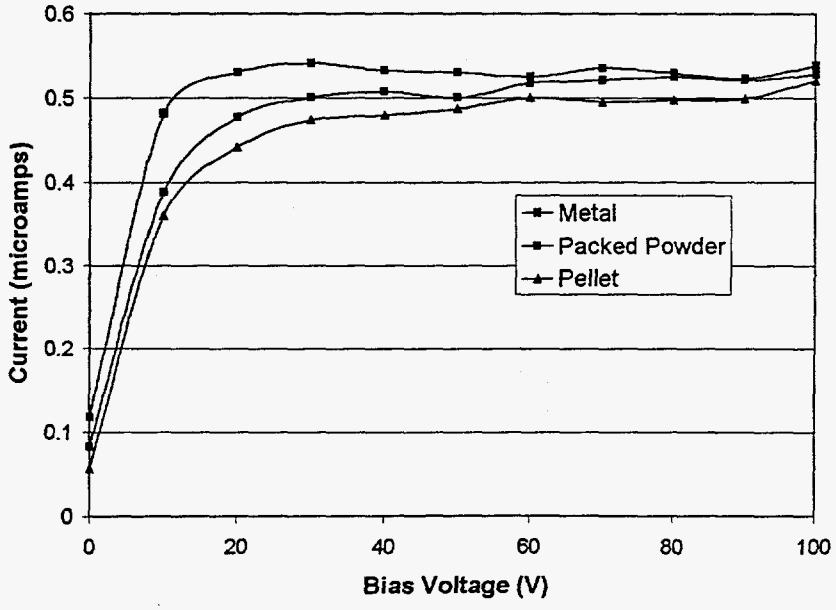

Figure 8 Net measured current (μA) as function of bias voltage (V) for conductive and insulating materials. Electron accelerating potential ~1 kV.

When trying to establish appropriate standards and protocols for display phosphor characterization it is important to not only have a good understanding of the many sources of error associated with conventional CL characterization systems and methods, but also determine the most logical experimental conditions for characterization (e.g., electron accelerating potential, current density). For example, FEDs are being designed for operation in the 5-10 kV range. Operation in the 1-5 kV range or lower would be desirable if the phosphor components met the efficiency requirements at these voltages. Phosphors used in FEDs must not only have high efficiency, but also be resistant to Coulombic aging and saturation at high current densities. For certain materials, the efficiency versus accelerating potential behavior increases proportionally with current density. However, as current density increases, a saturation effect is observed. The value of current density for which saturation occurs depends on the particular phosphor. As shown in Figure 9 for Y_2O_2S:Eu, an increase in the current density is accompanied by a flattening of the CL efficiency vs. accelerating potential curve, indicating saturation. Therefore, characterization over a wide range of current densities and accelerating potentials would provide useful information about CL degradation of a particular phosphor under prolonged high current density operation.

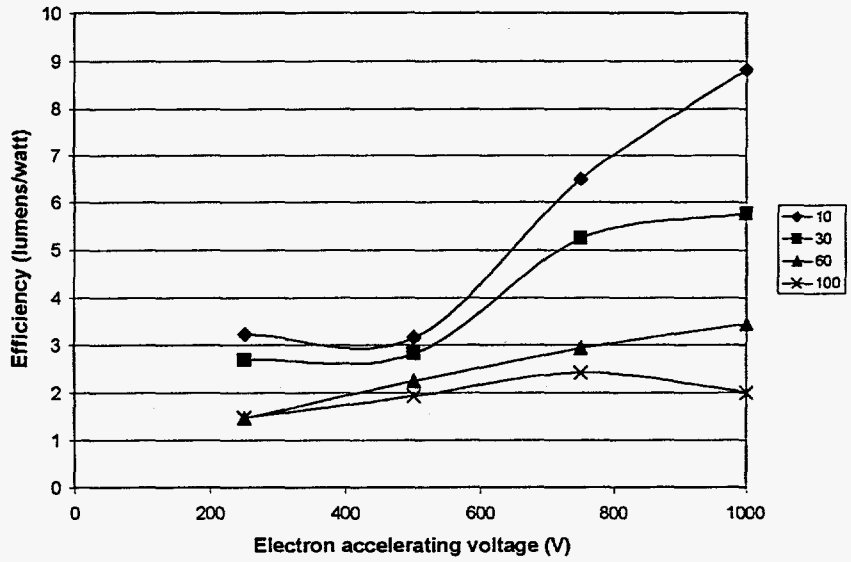

Figure 9 CL efficiency (lm/W) as a function of electron accelerating voltage (V) for Y_2O_2S:Eu measured at 10, 30, 60, and 100 $\mu A/cm^2$.

Considering the aforementioned experimental parameters, the following preliminary protocol was developed for characterizing phosphors for use in flat-panel displays:

Part I – System Optimization.

1. Obtain a YAGG:Tb pellet for use as a standard.
2. Measure the luminance of the pellet under the following conditions: $d_{aperture} > d_{spot}$ and $d_{aperture} \leq d_{spot}$ to determine the optimal condition for the particular instrument being used.
3. Plot sample current as a function of sample bias voltage to ensure adequate collection of secondary electrons.

Part II – Efficiency as a function of voltage at constant power.

1. Place samples and pellet in chamber.
2. Evacuate chamber to $\leq 10^{-7}$ Torr.
3. Set voltage and current.
4. Focus a uniform beam on pellet to the appropriate spot size to achieve a power density of 5 mW/cm^2.
5. Turn room lights off to minimize background light.

6. Measure the luminance of the pellet.
7. If expected luminance is obtained, proceed to the other samples. If expected luminance is not obtained, determine the cause.
8. Move sample into position under the electron beam.
9. Collect luminance data and chromaticity coordinates at the following voltages: 5 kV, 3 kV, 1 kV, 750 V, 500 V, and 250 V, and determine the threshold voltage of each sample. Keep the power density constant at 5 mW/cm^2 based on your chosen spot size.
10. Using the luminance data, calculate the luminous efficiency (lm/W) at each voltage.

Part III – Efficiency as function of current density at constant voltage.

1. Follow steps 1-8 from part II.
2. Collect luminance data and chromaticity coordinates at each voltage for the following current densities: 1, 10, 30, 60, and 100 $\mu A/cm^2$.
3. Calculate the luminous efficiency (lm/W) at each current density.

Part IV – System Calibration

The pellet is to be used as an equipment calibration standard. Be sure to perform the entire protocol on the pellet and determine the experimental standard deviations. Make sure that the results are reproducible. An instrument calibration should be performed at least every three months.

4. CONCLUSIONS

The general procedure for performing cathodoluminescence measurements of phosphors in stainless steel demountable vacuum chambers with hot filament electron guns was analyzed to identify sources of error. A round-robin experiment involving the characterization of a $Y_3Al_2Ga_3O_{12}$:Tb pellet by six different research groups provided further insight into system variations. The luminance and chromaticity coordinates of the pellet were measured at 250, 500, 750, 1000, and 3000 V. Some results were in very good agreement while others were not. The importance of secondary electron collection and beam profile when making CL measurements was presented. A plot of current through the sample versus sample bias voltage is useful for determining if the secondary electrons are being collected. In general, sample bias voltages of ~50 V are appropriate. The luminance and CL efficiency of a Y_2O_3:Eu phosphor were found to depend on the beam profile. A lower luminance was obtained when the sample was excited with a uniform beam profile. The Gaussian beam profile resulted in higher luminance values, presumably due to non-uniformity of the power density.

There are many materials and processing parameters that influence cathodoluminescence efficiency. It would be useful to know that when phosphors from different sources are characterized, the observed variations in data are a result of these materials properties rather than several experimental parameters associated with measurement inaccuracies. A four-part CL characterization protocol was established which includes procedures for system optimization; performing luminance measurements over a range of voltages at constant power density and over a range of current densities at constant voltage; and equipment calibration. If followed by a number of groups, the protocol is expected to mitigate some of the inconsistencies in data presentation and allow for more reliable comparison of results among researchers in the field.

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