Low-Voltage Cathodoluminescent Phosphors

A 20-year chronology of low-voltage cathodoluminescence efficiency

by Lauren E. Shea

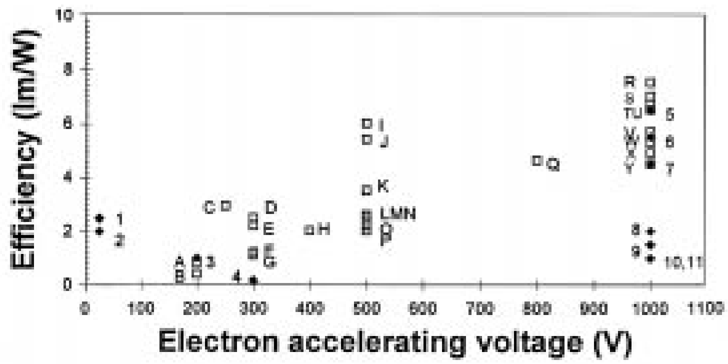

*FIG. 1. Efficiency of red phosphor powders (lettered squares) and screens (numbered diamonds) as a function of electron accelerating voltage. Y_2O_3:Eu - **A, I, S** (12); **G** (13); **N** (20); **O, U, 5, 9** (14); **W** (21); YVO_4:Eu - **B, L, Q** (13); **F** (18); **P, X, 7, 10** (14); Y_2O_2S:Eu - **C, J, R** (22); **D**(12); **H, Y** (20); **K, V** (21); **M, T, 3, 6, 11** (14); **8** (23); ZnCdS:Ag, In - **1** (16); ZnCdS:Ag, In + SnO_2 - **2** (17); $LaInO_3$:Eu - **4** (15); unspecified - **E** (18).*

Phosphors have been used for the display of information since the invention of the cathode-ray tube (CRT) by Karl Ferdinand Braun in 1897 (1). With the development of color television, an effort spanning approximately thirty years, came the most significant advances in phosphor technology. The most noteworthy was the shift to the all-sulfide system, and discovery of the red, rare-earth oxysulfide phosphors (e.g., $Y_2O_2S:Eu^{3+}$) (2). White brightness efficiency of phosphor screens also improved significantly: 15 lm/W in 1951 to over 35 lm/W in 1979, as a result of new phosphor formulations and improved screening techniques (3).

Today, a primary focus of research in the area of luminescence is phosphor development and improvement for low-voltage (≤1 kV) emissive flat-panel displays. An emissive display produces light by excitation of phosphors, whereas non-emissive displays such as liquid crystal displays (LCDs) require a backlight. Flat-panel displays encompass a wide range of devices, which include: electroluminescent (EL) displays, field emission displays (FEDs), plasma display panels (PDPs), and vacuum fluorescent displays (VFDs).

The FED is a promising candidate for the next generation of information display, and has been heavily supported by industry and government in recent years. FEDs, like CRTs are based on cathodoluminescence (CL), the emission of light as a result of excitation by electrons. However, CRTs utilize high-voltage cathodoluminescence (≥10 kV). FEDs are expected to realize the following advantages over other information displays: a thinner, more portable package, wider viewing angle, lower power consumption, higher resolution, and video capability.

The field emitter array was invented by Spindt in 1968 (4). The first realization of a color FED was by the Laboratoire d'Electronique de Technologie et d'Instrumentation (LETI) (5). Many FEDs are being designed for operation in the 5-10 kV range. Operation in the 1-5 kV range or lower is desirable. However, most available phosphors do not have high enough efficiencies at low voltages.

In the literature, the phosphor compositions most widely considered for FEDs have been the conventional CRT phosphors (ZnS:Ag, ZnS:Cu,Al, Y_2O_2S:Eu, Y_2O_3:Eu), VFD phosphors (ZnO:Zn, $ZnGa_2O_4$), thiogallate phosphors ($SrGa_2S_4$:Eu, $SrGa_2S_4$:Ce), and projection TV phosphors ($Y_3Al_5O_{12}$:Tb, Y_2SiO_5:Tb). What has been realized is the difficulty in utilizing high-voltage (>10 kV) CRT and projection TV phosphors in FEDs that will operate at low voltages. Low-voltage excitation of phosphors typically yields lower efficiencies and the mechanism for low-voltage cathodoluminescence is not well understood. The main purpose of examining the phosphor efficiencies reported in the literature over the past twenty years is to obtain a more clear indication of the following: (1) phosphor compositions most often studied, (2) the development of new phosphor compositions, (3) the efficiency values reported now compared to those reported in earlier years, and (4) has progress been made?

Background

Efficiency.—There are several definitions of the efficiency of a phosphor. The luminous efficiency, ε, is the ratio of the luminance to the input power. Luminance is a measure of the total energy output of a light source emitted in the visible region of the spectrum (6). The subjective sensation produced by this energy is known as brightness. The units of luminance are candelas per meter squared (cd/m^2) in the SI system. The older units of footlamberts (fL), are still used in many cases. The luminous efficiency of a phosphor under electron beam excitation is reported in units of lumens per watt (lm/W) which is obtained by the following equation:

$$\varepsilon = \frac{\pi\, LxA}{P}$$

where L is the luminance in cd/m^2, A is the area of the electron beam spot in m^2, and P is the power of the incident electron beam in watts (W), calculated by multiplying the electron accelerating potential in volts (V) by the current in amperes (A). The factor of π is included since the emission of the phosphor is Lambertian. As a general rule, the luminous efficiency (ε) is used to describe the efficiency of phosphors excited by sources that produce electron-hole pairs in the host lattice (cathode-rays, electric field, X-rays, α-particles, γ-rays). This paper is concerned with luminous efficiency (lm/W), as it is most often used by display manufacturers to assess the potential of a phosphor for use in a cathodoluminescent display such as an FED.

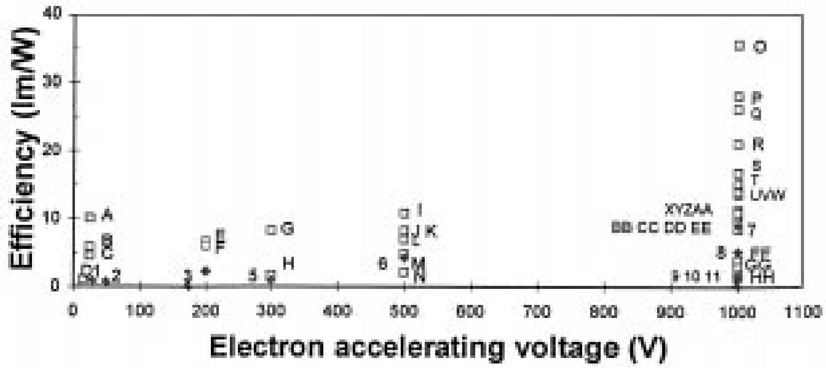

*FIG. 2. Efficiency of green phosphor powders (lettered squares) and screens (numbered diamonds) as a function of electron accelerating voltage. ZnO:Zn - **A** (17); **D** (15); **I, W** (21); ZnO:Zn,Si,Ga - **B** (26); ZnO:Zn,Si - **C** (26); (Zn, Mg)O:Zn - HH, **9** (14); $Gd_3Ga_5O_{12}$:Tb - **E, J, X, 3, 6, 8** (31); $Y_3(Al,Ga)_5O_{12}$:Tb - **Y** (22); **FF, 10** (14); $Y_3Al_5O_{12}$:Tb - **F, L, AA, 4** (31); **BB** (28); **DD** (12); Y_2O_2S:Tb - **H** (20), **K** (21); ZnS:Cu,Al - **P, Q, R** (22); **T** (27); **1** (25); ZnCdS:Cu,Al - **M, EE** (21); $ZnGa_2O_4$:Mn - **N, GG** (21); **2** (24); **5** (30); Zn_2SiO_4:Mn - **Z** (14); Gd_2O_2S:Tb - **O** (22);* U (21); ***V** (27) **CC, 7, 11** (14); $SrGa_2S_4$:Eu - **S** (27); unspecified - **G** (18).*

The intrinsic luminous efficiency is the efficiency of a powder sample of the phosphor. The screen luminous efficiency is the efficiency of a thin layer of phosphor powder deposited onto a substrate. Screen efficiencies are typically lower than intrinsic efficiencies, due to the presence of binders that can absorb portions of the excitation and emitted energy, and may also chemically react with the phosphor. Screen efficiencies can be measured in back reflection mode (light emitted directly from the front of the phosphor screen) or transmission mode (emitted light transmitted through the phosphor layer and the substrate, measured from the back of the phosphor screen). A good phosphor screen should have an efficiency comparable to its intrinsic efficiency.

Basic Structure and Operation of Field Emission Displays

Field emission displays consist of arrays of microscopic cold cathode emitters that excite a cathodoluminescent phosphor screen. Such arrays can contain as many as 10^7 emitters/cm^2, so that thousands of emitters can be used to excite a single pixel (7). Emitters are typically sharp cones that produce electron emission in the presence of an intense electric field (~10^6 V/cm) required for cold cathode emission. The faceplate of an FED consists of a cathodoluminescent phosphor that is deposited onto a conductive substrate, and the baseplate contains the emitter tips. Mechanical spacers are used to prevent the collapse of the vacuum assembly. The distance between the faceplate and baseplate is typically 1 mm. This eliminates the need for focusing and deflection coils, as are necessary in a CRT. Because the emitters in an FED must be held a short distance from the screen to obtain adequate brightness and resolution, they must be operated at lower voltages to avoid vacuum breakdown. In order to maintain adequate screen brightness, the current density must be increased to compensate for the decreased voltage. A high current density often causes degradation of the phosphor screen due to charge loading at the surface.

Sulfide-based phosphors (e.g., ZnS:Cu,Al), though typically more efficient than oxide phosphors under the same voltages and current densities (8), degrade more dramatically under electron bombardment, and degradation products are known to contaminate the cathode components of displays (9). In view of this, oxide phosphors are preferred in FEDs, provided they meet the efficiency requirements.

Phosphor Requirements for Field Emission Displays

To compete with the liquid crystal display (LCD) on a power consumption level, the phosphors used in an FED must have screen efficiencies of 11, 22, and 3 lm/W for the red, green, and blue components, respectively (10). This corresponds to a display white brightness efficiency of 6 lm/W.

Phosphors used in FEDs must not only be efficient at low voltages, but also be resistant to Coulombic aging and saturation at high current densities. Coulombic aging refers to the permanent loss of efficiency due to prolonged electron bombardment at high current densities. In CRTs, the acceptable time for a phosphor to decrease to one half its original brightness is 10,000 h. This corresponds to 100 C/cm^2. Because the phosphors in FEDs require much higher current densities to achieve adequate brightness, they must withstand >2000 C/cm^2. Coulombic aging has been attributed to the formation of color centers (point defects that act as traps for electron-hole pairs), and surface damage. Electron-stimulated chemical reactions between the phosphor and the constituents of the residual atmosphere in vacuum (H_2, CO, CO_2, H_2O) (11) is another Coulombic aging mechanism.

Methodology

The information compiled for this paper was obtained from a keyword search of 150 databases including DOE, NSF, IEEE, and NIST, as well as domestic and foreign patents, and technical journals. The search was limited to low-voltage cathodoluminescent powders and screens. Most of the published efficiency data in the low-voltage range began appearing in the literature in the 1990s. Only papers that reported absolute efficiencies were used for the data compilation. Many papers reported luminance without giving the conditions for which efficiency could be calculated (e.g., current density, spot size), while others often used relative brightness or "arbitrary units." Arbitrary units are meaningless when assessing the potential of a phosphor for FED use. The inconsistency of data presentation in the literature was partly due to the lack of an accepted characterization protocol and standard for display phosphor characterization. Since there was no protocol, researchers reported their data to the best of their ability, using their best estimate of how to characterize potential display phosphors. 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. Bear in mind also that the data that was available in the literature may not necessarily be accurate

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due to equipment calibration errors, low or unrealistic current densities used for characterization, or poor deposition processes, in the case of screen efficiencies. All of these possible scenarios and data uncertainties make the need for a characterization protocol more apparent. Sandia National Laboratories (SNL) has recently developed a protocol for cathodoluminescence characterization of phosphors for display applications. The establishment of this protocol should result in more accurate and consistent data among different research groups in the future.

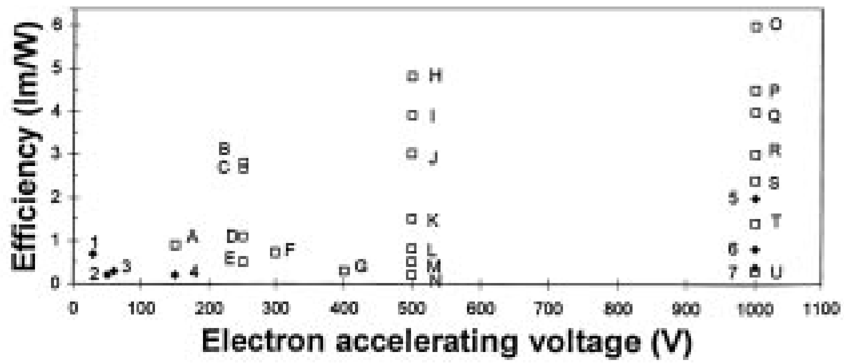

*FIG. 3. Efficiency of blue phosphor powders (lettered squares) and screens (numbered diamonds) as a function of electron accelerating voltage. ZnS:Ag,Cl - **A** (20); **C** (22); ZnS:Ag,Cl,Al - **B, D, E, I, J, K, P, Q, S** (22); ZnS:Ag - **C, H, M, O, 5** (22); **L, T** (21); **R** (14); **6** (20); **7** (14); ZnS:Zn - **2** (9); **4** (34); ZnS:Te - **3** (33); $ZnGa_2O_4$ - **N, U** (21); **1** (32); Y_2SiO_5:Ce - G (29); unspecified - F (18).*

Low-Voltage Efficiency Data

Low-voltage efficiency data for red, green, and blue phosphor powders and screens are shown in FIGURES 1, 2, and 3, respectively. The powder data are represented by squares and labeled with letters. The screen data are represented by diamonds and labeled with numbers. In the figures, data are shown for voltages: 1 kV, 500V, and <500 V. The screen efficiencies reported were all measured in back-reflection mode.

Red Phosphor Powders and Screens.— AS FIG. 1 shows, most of the data for various red-emitting phosphors was found at 500 V and 1 kV. The predominant red phosphor compositions reported are Eu^{3+}-doped Y_2O_2S, Y_2O_3, and YVO_4. The highest efficiency reported for a powder at 1 kV is 7.5 lm/W for Y_2O_2S:Eu in 1997, followed by 7 lm/W at from Y_2O_3:Eu made by combustion synthesis in 1997. Hydrothermally synthesized YVO_4:Eu measured at 800 V is also 7 lm/W, as reported in 1995. At 1 kV, the most efficient screen is 6.5 lm/W from Y_2O_3:Eu, reported in 1997. This screen efficiency is comparable to the intrinsic efficiency of the Y_2O_3:Eu powder, and up to four times more efficient than the other screen efficiencies reported at this voltage. For the powders measured at 500 V, the highest efficiency reported was 6 lm/W for combustion-synthesized Y_2O_3:Eu in 1997.

In the <500 V region of this figure, the powder with the highest efficiency is Y_2O_2S:Eu at 2.94 lm/W, measured at 250 V in 1997. The most efficient screens in this voltage range are sulfides; ZnCdS:Ag,$In^{+}SnO_2$ and ZnCdS:Ag,In measured at 25 V as 2.5 and 2 lm/W, respectively. These screens are twice the efficiency of Y_2O_2S:Eu screens measured at 200 V.

Green Phosphor Powders and Screens.—FIGURE 2 shows that a significantly larger number of phosphor compositions were investigated for efficient low-voltage green emission than for red or blue. At 1 kV, the most efficient powder reported is Gd_2O_2S:Tb, at 35.5 lm/W, in 1997. This reported efficiency is 25% higher than ZnS:Cu,Al and almost a factor of three higher than ZnO:Zn. The highest efficiency reported for an oxide at this voltage is ZnO:Zn, 13.5 lm/W in 1995. At 1 kV, Gd_2O_2S:Tb has the highest screen efficiency, 9 lm/W, reported in 1997.

More data were reported for oxide phosphors at 500 V than for the sulfide-based phosphors. The highest efficiency at this voltage was reported in 1995 for ZnO:Zn, 10.7 lm/W. This is approximately 25 and 35% higher than the data reported for $Gd_3Ga_5O_{12}$:Tb (GGG:Tb) and Gd_2O_2S:Tb powders, respectively.

In the region <500 V, the highest reported efficiency was 10 lm/W at 25 V, reported in 1993 for ZnO:Zn. The most efficient screen reported in this voltage range was GGG:Tb, 2.36 lm/W at 200 V, reported in 1995.

Blue Phosphor Powders and Screens.—FIGURE 3 shows that the most predominant blue phosphor compositions investigated were ZnS:Ag, ZnS:Ag,Cl,Al, and $ZnGa_2O_4$. At 1 kV, the highest efficiency reported for a powder was 6 lm/W from ZnS:Ag in 1997. This is 35% higher than the reported ZnS:Ag,Cl,Al, efficiency and a factor of twenty higher than $ZnGa_2O_4$ at this voltage. The most efficient screen reported at 1 kV was ZnS:Ag, 2 lm/W, reported in 1997. At 500 V, the powder with the highest efficiency was ZnS:Ag at 4.8 lm/W, reported in 1997. This efficiency exceeds ZnS:Ag,Cl,Al by about 20% and $ZnGa_2O_4$ by a factor of six.

At <500 V, ZnS:Ag,Cl,Al and ZnS:Ag efficiencies are 2.8 and 2.7 lm/W, respectively at 250 V. These data were reported in 1997 and exceed the efficiencies of the other powders reported by a factor of two or more. For screens, $ZnGa_2O_4$ had the highest efficiency, 0.7 lm/W, measured at 30 V, and reported in 1991.

Summary and Conclusions

The compositions most often represented in the literature over the span of twenty years are the sulfides and oxysulfides. Many more papers are now available that report the absolute efficiencies of phosphor powders and screens than there were in the 1970s and 1980s. Few papers were found in the 1970s that reported absolute efficiencies. More papers began appearing in the 1980s, when VFD research was widespread. These papers focused on oxides such as ZnO:Zn and $ZnGa_2O_4$, measured at voltages <500 V. Late in the 1980s, and early in the 1990s, papers that reported studies of cathodoluminescence in this voltage range became more scarce.

Toward the middle of the 1990s, there was a resurgence of interest in low-voltage phosphor research. However, the prevailing focus was not on the development of new low-voltage phosphor materials, but on trying to get high-voltage, sulfide-based CRT phosphors to operate at lower voltages. Due to the aforementioned degradation problems with sulfides, oxide phosphors are beginning to receive more attention. In addition to ZnO:Zn and $ZnGa_2O_4$, phosphors such as yttrium aluminum garnet, Y_3AlO_{12} (YAG:Tb), GGG:Tb, and Y_2O_3:Eu, are being synthesized using new techniques and characterized at low-voltages. Combustion synthesis and hydrothermal synthesis have been used to produce these and several other multicomponent oxide phosphors, and appear to be promising techniques.

The low screen efficiencies for certain phosphors reported in the 1970s and

1980s were for screens made by conventional gel settling techniques. Data from the 1990s show that certain screens had efficiencies comparable to their intrinsic efficiencies. This can be attributed to recent improvements in deposition techniques. Improvements in particle size and morphology may also play a role. Smaller, more uniform particle size phosphors can now be synthesized, and may result in improved packing densities and more uniform phosphor layers, minimizing light scattering. Researchers have recently been investigating methods for producing spherical phosphors for ease of deposition and improved packing density (36,37). Recently developed nanocrystalline phosphors offer a potential improvement in efficiency at very low voltages <250 V (38,39).

At this point in time, the strategies used in phosphor research for FEDs have not resulted in major breakthroughs in phosphor performance. Based on the openly available data in the literature to date, the required screen efficiencies of 11, 22, and 3 lm/W for red, green, and blue phosphors, respectively, have not been achieved. However, the status of phosphor technology for the flat-panel display industry based on observations of these data, appears to be improving, with more reports available on the efficiency of materials over a range of voltages. Based on an analysis of the available data, it is difficult to determine whether or not improvements in actual phosphor performance have been made over the last twenty years. As previously mentioned, a standard characterization protocol was not used and therefore the accuracy of reported data is questionable. Differences in reported efficiencies of 20-40% may not actually be differences in the phosphor performance, but differences in measurement technique and phosphor handling conditions. When a standard protocol for phosphor characterization and data presentation is followed, a more realistic assessment of phosphor performance and progress in phosphor research can be made. SNL has established a characterization protocol that was distributed to members of the phosphor community early this year. Methods for improving this protocol are currently being investigated. SNL also provides a benchmarking service to researchers for analysis and evaluation of new and existing phosphor powders and screens. ■

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