

Alkali metal coactivators in SrS: Cu,F thin-film electroluminescent devices

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A unique approach for obtaining bright and efficient saturated green phosphors for alternating-current thin-film electroluminescent (ACTFEL) device applications is presented. The approach involves color-shifting blue SrS:Cu,F ACTFEL phosphors into the green region of the spectrum via the incorporation of alkali metal ions into the SrS lattice. Alkali metals are incorporated into SrS:Cu,F phosphors by using LiF, NaF, KF, RbF, or CsF coactivators. The best result to date is obtained by using a KF coactivator and results in a saturated green brightness and efficiency of 52.7 cd/m² and 0.973 lm/W (at a frequency of 60 Hz and an overvoltage of 40 V). In addition to providing a color shift, the alkali-metal fluorides improve the overall performance of the ACTFEL device by increasing the magnitude of the electric field and its uniformity across the phosphor through suppression of positive space charge. © 1999 American Institute of Physics. [S0003-6951(99)04736-1]

For several decades, the development of alternating-current thin-film electroluminescent (ACTFEL) devices for full-color flat-panel displays has been hampered by the lack of an efficient, saturated blue phosphor.¹ With the recent development of SrS:Cu as a blue ACTFEL phosphor,²⁻⁵ this situation appears to be changing so that the ultimate performance of first-generation full-color commercial ACTFEL displays may actually be established by the performance of the green, not the blue phosphor. The purpose of the work described herein is to report a novel approach for obtaining a bright and efficient green ACTFEL phosphor.

The basic idea is to begin with the efficient, blue SrS:Cu phosphor system and to add appropriate coactivators, i.e., alkali metal ions, to color shift from blue to green. The model underlying this color shift and the procedure for selecting appropriate coactivators via monitoring the photoluminescence (PL) of coactivated phosphor powders is described elsewhere.^{6,7} Briefly, the green-color shift is ascribed to a self-compensation driven process in which S vacancies (double donors) are formed when acceptors (Cu and alkali metal ions) are intentionally incorporated into the SrS host. These S vacancies associate with Cu luminescent impurities to form Cu-S vacancy complexes such that the Cu coordination number is reduced. This reduced coordination leads to green emission, whereas normal sixfold coordinated Cu gives blue emission. The primary focus of this letter is to demonstrate that this color-shift approach, which was first applied to shift the PL spectrum of powder phosphors, is equally viable for shifting the electroluminescence (EL) spectrum of thin-film phosphors.

The ACTFEL devices employed in this study are fabricated as follows. First, a SrS:Cu,F thin-film phosphor layer with a typical thickness of 800–1000 nm is deposited onto a

glass substrate coated with layers of indium tin oxide and aluminum-titanium oxide, which serve as the bottom transparent contact and the bottom insulator, respectively, of the ACTFEL device. The SrS:Cu,F deposition is accomplished by electron-beam evaporation of SrS and simultaneous thermal co-evaporation of CuF₂. Next, a thin layer of the appropriate alkali metal fluoride coactivator, i.e., LiF, NaF, KF, RbF, or CsF, is deposited by thermal evaporation over one half of the sample area. Subsequently, rapid thermal annealing of the sample is performed, typically at 810 °C for 2 min. Finally, a top insulating layer of silicon oxynitride is deposited by plasma-enhanced chemical vapor deposition, and aluminum dots are thermally evaporated as the top contact.

Since the ACTFEL fabrication sequence involves the deposition of the coactivator over only half of the sample area, a direct comparison of the PL and EL performance of the coactivated and noncoactivated portions of the sample is possible.

Figure 1 shows a comparison of the EL spectra of a coactivated SrS:Cu,Na,F (subsequently denoted the “green device”), i.e., this notation implies that NaF is used as the

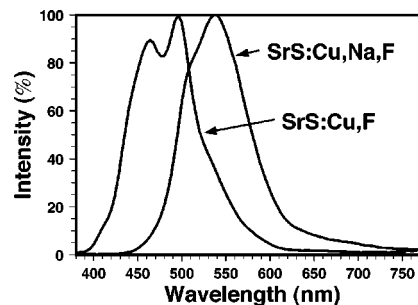


FIG. 1. Normalized electroluminescence spectra for a coactivated SrS:Cu,Na,F (green) and a non-coactivated SrS:Cu,F (blue) ACTFEL device.

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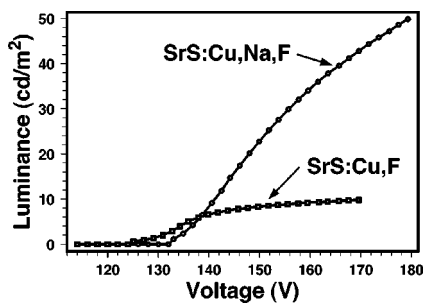


FIG. 2. Luminance–voltage (L – V) curves (60 Hz) for a coactivated SrS:Cu,Na,F (green) and a non-coactivated SrS:Cu,F (blue) ACTFEL device.

coactivator, and a noncoactivated SrS:Cu,F ACTFEL device (subsequently denoted the “blue device”), which are prepared on the same sample substrate. Note the dramatic green shift in the spectrum for the coactivated sample. The Commission Internationale de l’Eclairage (CIE) color coordinates for the coactivated sample are $CIE_x=0.317$ and $CIE_y=0.585$, which are very close to that desired for an ideal green phosphor (i.e., $CIE_x=0.30$, $CIE_y=0.60$).¹ In contrast, the noncoactivated EL CIE color coordinates of the SrS:Cu,F phosphor are $CIE_x=0.164$ and $CIE_y=0.268$, which is in the blue region of the spectrum. However, these values are not quite those desired for an ideal, fully-saturated blue phosphor, which would have $CIE_x=0.15$ and $CIE_y=0.10$.

Comparisons of the EL luminance–voltage (L – V) and efficiency–voltage (E – V) characteristics for green and blue ACTFEL devices, each prepared on the same sample substrate, are shown in Figs. 2 and 3. The dramatic increase in brightness and improvement in efficiency from coactivation is clearly evident from these figures. All of the L – V and the E – V results reported herein are obtained at 60 Hz by using bipolar trapezoidal voltage pulses with 5 μ s rise and fall times and a pulse width of 30 μ s.

A summary of the better brightness and efficiency results obtained to date, with corresponding CIE color coordinates, is collected in Table I for each of the five green alkali metal coactivators employed in this study and for the blue SrS:Cu,F reference. Note that all of the alkali metal atoms employed in this study, except for Li, provide excellent color shifting so that CIE color coordinates very close to those desired for saturated green emission are obtained. We believe that the SrS:Cu,K,F efficiency reported in Table I is equal to the highest ever reported [i.e., ~ 1 lm/W for sputtered ZnS:TOF (Ref. 1)] for a saturated green ACTFEL

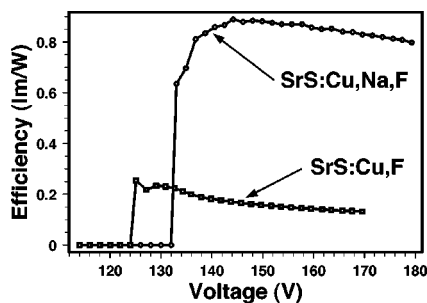


FIG. 3. Efficiency–voltage (E – V) curves (60 Hz) for a coactivated SrS:Cu,Na,F (green) and a non-coactivated SrS:Cu,F (blue) ACTFEL device.

TABLE I. Performance comparison of coactivated SrS:Cu,F ACTFEL devices. L40 and E40 corresponds to the EL luminance and efficiency at 40 V above threshold at a frequency of 60 Hz. CIE $_x$ and CIE $_y$ correspond to the x and y CIE color coordinates.

Phosphor	L40 (cd/m ²)	E40 (lm/W)	CIE $_x$	CIE $_y$
SrS:Cu,F	9.57	0.136	0.164	0.268
SrS:Cu, Li,F	4.53	0.054	0.293	0.561
SrS:Cu,Na,F	45.8	0.819	0.317	0.585
SrS:Cu,K,F	52.7	0.973	0.289	0.596
SrS:Cu,Rb,F	30.6	0.193	0.285	0.577
SrS:Cu,Cs,F	21.6	0.138	0.291	0.577

phosphor operating under realistic waveform driving conditions, i.e., 40 V above threshold at 60 Hz.

Some of the coactivator-induced L – V and the E – V improvement shown in Figs. 2 and 3 and in Table I is a simple consequence the color shift and of the the human eye’s greater sensitivity to the green portion of the visible spectrum. However, there appear to be other factors inherent in the coactivator processing procedure which also contribute to the improvement in the phosphor performance. There are two primary observations that point to coactivator improvement of the phosphor performance.

First, the coactivator treatment leads to an improvement in the phosphor crystallinity and diffuse reflectance. This may be deduced visually by the rather milky appearance of the coactivated portion of the phosphor. Additionally, the improvement in crystallinity is confirmed by x-ray diffraction. Improved crystallinity leads to more efficient electron transport and radiative recombination in the phosphor. The increased diffuse reflectance improves the optical outcoupling.

The second aspect of the coactivator treatment is that there is a noticeable improvement in the electrical characteristics of the coactivated, green ACTFEL device. For example, the internal charge-phosphor field (Q – F_p) characteristics⁸ of a blue and a green ACTFEL device prepared on the same sample substrate are compared in Fig. 4. There are four trends of importance that should be noted from Fig. 4. (i) In comparison to the blue device, less charge is transported across the phosphor of the green device (even though the luminance of this device is greater). (ii) Less power is dissipated in the green ACTFEL device (as established by the fact that this Q – F_p curve encloses less area⁸). (iii) The steady-state phosphor field of the green device is greater than that of the blue device (i.e., ~ 1.7 MV/cm versus

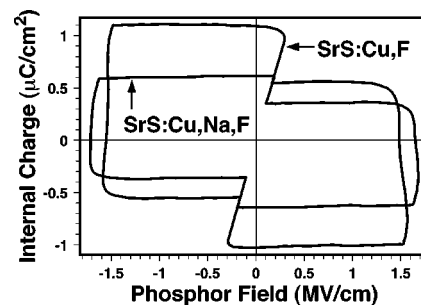


FIG. 4. Internal charge–phosphor field (Q – F_p) curves (60 Hz at an over-voltage of 40 V above threshold) for a coactivated SrS:Cu,Na,F (green) and for a non-coactivated SrS:Cu,F (blue) ACTFEL device.

~ 1.5 MV/cm); this larger phosphor field leads to a more energetic hot electron distribution, more efficient impact excitation of the Cu luminescent impurities, and, hence, greater luminance. (iv) More overshoot is present in the Q - F_p characteristics of the blue device; overshoot is more clearly evident in corresponding capacitance-voltage (C - V) curves (not shown) or in the transferred charge capacitance curves ($dQ_{\max}/dV_{\max}-V_{\max}$) (not shown);⁸ the presence of overshoot implies the existence of positive space charge within the phosphor layer and a corresponding nonuniform electric field across the phosphor layer. Observations (iii) and (iv) taken together imply that the electric field is larger and more uniform across the phosphor for the green device, which leads to a greater luminance.

Note that our original purpose for adding alkali metal ions to the SrS:Cu,F phosphor was to color shift from blue to green. The fact that the alkali metal fluorides employed lead to additional improvements in the phosphor performance implies that these coactivators behave as flux agents. Note that other researchers have recently used chloride flux agents to improve the performance of ZnS:Mn ACTFEL devices.⁹ These flux agents are incorporated into the phosphor layer after deposition of the phosphor in a manner similar to that employed here. Additionally, a reduction of positive space charge and a concomitant increase in the phosphor field has been proposed to explain the observed flux agent induced performance improvement.

In summary, the incorporation of alkali metal ions into SrS:Cu,F phosphors is demonstrated as a new methodology for obtaining bright and efficient green ACTFEL phosphors. In addition to providing a color shift from blue to green, the alkali metal fluorides are found to act as flux agents that improve the ACTFEL device performance by increasing the magnitude and uniformity of the electric field across the

phosphor through the suppression of positive space charge in the phosphor.

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