Color Control in Sulfide Phosphors: Turning up the Light for Electroluminescent Displays

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At present, commercial flat-panel electroluminescent (EL) displays operate on the basis of the amber emission from thin films of the phosphor ZnS:Mn. Despite the absence of full-color output, the high-performance characteristics of these monochrome displays have led to their use in a variety of niche-market applications. Of course, a greater utility is envisioned for a full-color device. Two methods are currently being examined to realize this color output. In the *color-by-white* method, suitable phosphors broadly emitting in the blue and yellow portions of the spectrum are combined to produce a solid-state EL source of white light; this light is then passed through a set of color shutters. The phosphor ZnS:Mn is under investigation for this application, but much improved performance could be realized by inducing the material to luminesce at a slightly longer wavelength. To replicate the full RGB performance of a cathode-ray tube, efficient EL-active red, green, and blue phosphors having specific emission colors (chromaticity) must be available. To date, such a color set has not been demonstrated, but recently the prospects for production of a full-color EL display, have brightened considerably, following the discovery and efficient operation of the *blue*-emitting phosphor SrS:Cu[1] and its modifications.[2]

In this contribution, we describe results on controlling the emission colors of the phosphors ZnS:Mn and SrS:Cu and on the performance characteristics of new red- and green-emitting EL devices. By manipulating the defect chemistry and crystal properties in the stated materials, essentially any color can be specified across the entire portion of the visible spectrum important for display applications. For the first time, true, chromatically red emission is observed from ZnS:Mn with Ga_2S_3 doping, and chromatically green emission is observed in SrS:Cu, M (M = alkali metal) systems.

Color tuning of emission wavelengths for ZnS phosphors has previously been accomplished by altering energy gaps of materials. For example, a progressive increase in the concentration of Cd in the series $Zn_{1-x}Cd_xS$:Ag ($0 < x < 1$) leads to longer wavelength emission: ZnS:Ag, blue; $Zn_{0.68}Cd_{0.32}S$:Ag, green; and $Zn_{0.13}Cd_{0.87}S$:Ag, red. The emission color is primarily determined by the magnitude of the band gap rather than the intrinsic nature of the dopant atom (Ag,) and the resulting donor−acceptor emission is not EL active. In much the same way, quantum-size effects have been used in nanocrystalline II−VI materials to adjust energy gaps and affect emission colors.[3−6]

Various electronic and structural features can be considered for inducing a red shift to the luminescence of Mn in crystalline ZnS while retaining potential EL activity. From consideration of the Tanabe−Sugano diagram for the d^5 cation Mn^{2+}, such a shift will be produced on increasing the crystal-field strength. Shrinkage of the lattice and associated interatomic distances should increase the crystal field. Such a shrinkage is expected to occur by substitution of smaller or more highly charged cations for Zn^{2+}. The only suitable isovalent cation available for this substitution is Be^{2+}. Because of the hazards in working with Be, we elected to examine substitutions with more highly charged ions. Al^{3+} and Ga^{3+} are suitable for this purpose, and they provide some potential, additional advantages. Substitution of Al^{3+} or Ga^{3+} for Zn^{2+} in ZnS produces cation vacancies. To maintain charge compensation on substitution, Zn defects will be formed according to the representative formula $Zn_{1-3x/2}\square_{x/2}Ga_xS$:Mn, thereby lowering the coordination number of some S atoms. Such S atoms will bond more strongly to Mn in comparison to those not associated with a Zn vacancy, producing a stronger crystal field and a red shift in the emission. In addition, greater relaxation is expected for the Mn−complex excited state, also leading to a red shift in the emission.

As shown in Figure 1, the emission color[7] of the ZnS:Mn phosphor can be specifically controlled in the system $Zn_{1-3x/2}Ga_xS$:Mn, i.e., a systematic wavelength shift occurs with increasing Ga concentration. For samples prepared at 1123 K, increasing Ga concentrations lead to a decrease in the volume of the hexagonal cell of ZnS from 79.5 Å^3 at $x = 0$ to 77.0 Å^3 at $x = 0.35$, the approximate solubility limit. Luminescent decay times[8] and chromaticity values[9] are summarized in Table 1. The decay curves are readily fit by single-exponential

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[7] Luminescence spectra were recorded with a right-angle spectrometer. The excitation wavelength was selected with a Cary model 15 prism monochromator, and the sample emission was passed through an Oriel 22500 $^1/_8$-m monochromator prior to detection with a Hamamatsu R636 photomultiplier tube (PMT). Current from the PMT was measured with a Keithley 486 picoammeter that was interfaced to a computer.

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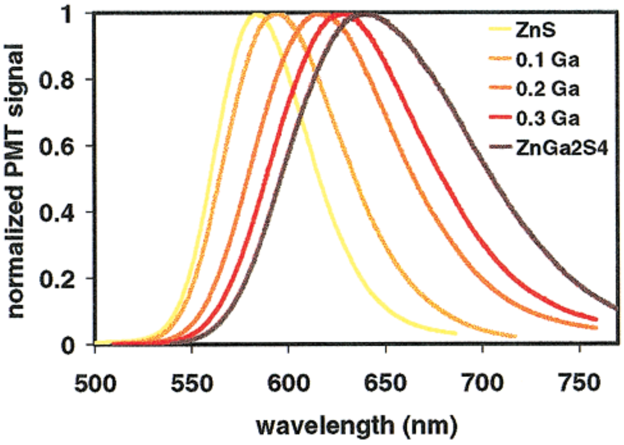

Figure 1. Photoemission spectra for the series $\mathrm{Zn}_{1-3x/2}\mathrm{Ga}_x\mathrm{S}$: 1 atom % Mn ($0 \leq x \leq 0.5$).

Table 1. Luminescent Lifetimes and Chromaticity Values for $\mathrm{Zn}_{1-3x/2}\mathrm{Ga}_x\mathrm{S}$:1 Atom % Mn

	x	lifetime, ms	chromaticity (x,y)
ZnS	0	0.85	0.54, 0.46
$\mathrm{Zn}_{0.85}\mathrm{Ga}_{0.1}\mathrm{S}$	0.1	0.75	0.58, 0.43
$\mathrm{Zn}_{0.7}\mathrm{Ga}_{0.2}\mathrm{S}$	0.2	0.83	0.62, 0.38
$\mathrm{Zn}_{0.55}\mathrm{Ga}_{0.3}\mathrm{S}$	0.3	0.75	0.64, 0.36

functions, and the resulting lifetimes are consistent with direct emission from the Mn center, rather than a donor–acceptor recombination. As seen from the chromaticity values $x = 0.64$ and $y = 0.36$ for the composition $\mathrm{Zn}_{0.55}\mathrm{Ga}_{0.3}\mathrm{S}$:Mn, a true red phosphor can be produced in this series.[10] A red shift in the luminescence of ZnS:Mn has also been observed by substitution of Zn with Al.

Cathodoluminescence in the system SrS:Cu has been described by Lehmann,[11] and results of photoluminescence measurements have been detailed by Yamashita and co-workers.[12] In general, either blue or green luminescence has been observed—blue in lightly doped samples and green in heavily doped samples. On the basis of the concentration dependence, blue emission has been associated with isolated Cu centers and green emission with aggregates of Cu centers.[12]

Our conclusions from interpretation of the available SrS:Cu spectral data are different. Because the Cu atoms enter the matrix in the +1 oxidation state, Cu doping results in the formation of S vacancies. Two types of Cu sites can exist, one without an adjacent S vacancy (six-coordinate Cu) and one with an adjacent S vacancy (likely a five-coordinate Cu). If this is the case, we should be able to control their relative concentrations, hence, the emission color of the phosphor. This result should be achieved by substitution of a trivalent cation in conjunction with Cu to decrease the concentration of S vacancies, and substitution of a monovalent cation in conjunction with Cu to increase S vacancies. In accordance with these ideas, we have prepared SrS:Cu powder phosphors exhibiting controlled emission wavelengths spanning the blue and green regions of the spectrum (Figure 2.) Importantly, these colors are achieved by fixing the Cu concentration at 0.2 atom % and carefully adjusting the concentrations of the codopants Y^{3+} and Na^{+}; a number of other M^{3+} and M^{+} cations can be used to produce the same results. On the basis of optical studies and solid-state NMR data,[13] we believe the emission color arises from distinct surroundings of the Cu centers, i.e., likely a six-coordinate site for the blue-emitting Cu atoms and a five-coordinate site for the green-emitting Cu atoms. Charge compensation of Cu^{+} with an M^{3+} cation in the NaCl-type host of $\mathrm{Sr}^{2+}\mathrm{S}^{2-}$ preserves a six-coordinate environment for the Cu^{+} ion, leading to a predominant blue emission. Incorporation of a sufficient quantity of M^{+} cations, i.e., Na^{+} or other alkali-metal cation, leads to an increased formation of S vacancies. Cu^{+} ions distributed through such a matrix occupy sites associated with these vacancies. A reduced coordination number results for the Cu^{+} ions, and a green emission can be observed. By varying the relative concentrations of the M^{3+} and M^{1+} codopants, the concentrations of the two types of emission centers and the resulting emission color can be controlled. The larger breadth of the emission band peaking near 505 nm (cf., Figure 2) relative to those at shorter and longer wavelengths is likely a reflection of the bimodal distribution of the Cu atoms between the two different types of coordination environments.

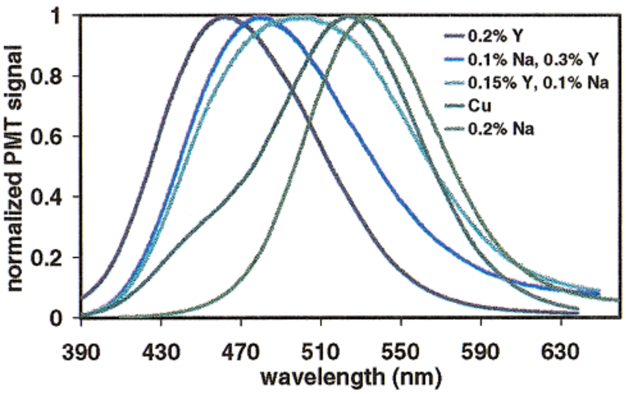

Figure 2. Photoemission spectra for SrS codoped with Na, Y, and 0.2 atom %Cu.

The overall effects of manipulating codopant concentrations in the systems (Zn,Ga)S:Mn and (Sr,Y,Na)S:Cu are illustrated by the photoluminescence of samples shown in Figure 3. Yellow to red emission is observed in the ZnS system and blue to green in the SrS system.

A series of luminescent materials has been developed on the basis of the two important EL hosts ZnS and SrS.

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(8) Luminescence decay curves were measured by using a Nd:YAG laser (pulse width = 10 ns) equipped with a frequency mixing crystal to provide excitation at 355 nm. The emission was passed through a filter to remove the excitation light and detected with a PMT connected to a Tektronix digital oscilloscope (model TDS 350); 50 waveforms were averaged for each sample.

(9) Chromaticity values are derived on the basis of CIE conventions derived from human color perception. The values x, y, and z ($x + y + z = 1$) are the relative contributions of the tristimulus values in a three-component color system. They provide a quantitative description of a color. In simplified terms, the values x, y, and z can be considered to be the percentages of red, green, and blue stimuli, respectively, that are mixed to produce a specific color; hence for white light $x = y = z = 0.333$. Of course, the stimuli are not represented as delta functions since color perception varies among the population.

(10) The chromaticity values are identical to those that we obtain for a sample of the commercial red phosphor $\mathrm{Y_2O_3}$:Eu provided by Osram-Sylvania.

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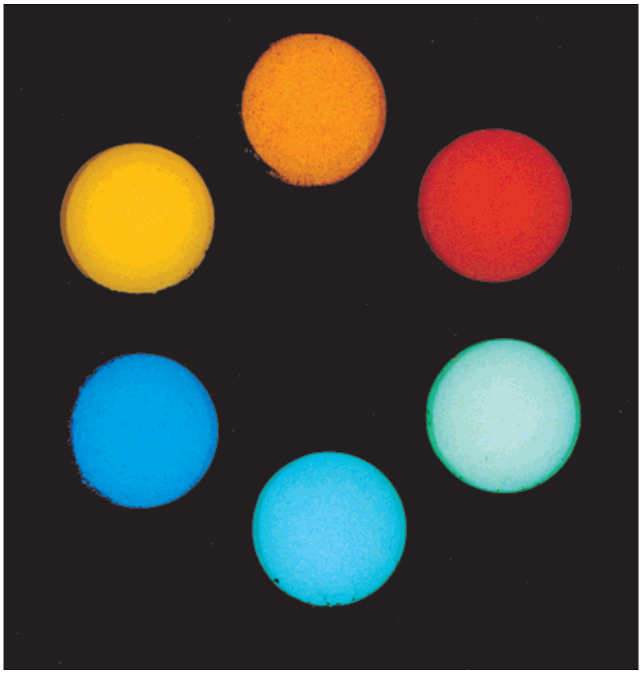

Figure 3. Luminescence of (Zn,Ga)S:Mn and (Sr,Y,Na)S:Cu phosphors under UV excitation.

For the first time, full range emission color control has been achieved in phosphor hosts having demonstrated utility in EL displays. While the optical results presented above were obtained by photoexcitation of powders, we have observed the same emission characteristics in thin-film EL devices that have been fabricated by evaporation, electron-beam, and sputtering methods of deposition. Very thin (~500 nm thick,) deep-red emitting films of (Zn,Ga)S:Mn ($x = 0.62$, $y = 0.37$) exhibit thresholds near 47 V with levels of luminance near 1 cd/m^2.[14] The exceptionally small threshold voltage may provide a new approach to low-voltage light generation. For devices containing thin-film SrS codoped with Cu and K, performance is characterized by a luminance of 53 cd/m^2 and a luminous efficiency of 0.97 lm/W (40 V above threshold and a frequency of 60 Hz.)[15] Color coordinates are $x = 0.289$ and $y = 0.596$, indicating the attainment of a saturated green color. Insofar as we know, the efficiency is unsurpassed by any other EL device operating in a saturated green mode under commercially realistic conditions.

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