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Emission Color Tuning of Green Emitting ZnS-Based CRT Phosphors

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ZnS : Cu,Au,Al; ZnS : Cu,Al and (Zn,Cd)S : Cu,Al are the most important green emitting phosphors for cathode ray tube applications. The latter one contains (toxic) cadmium and therefore tends to be eliminated from tube production whenever possible. Alloying with CdS is applied to control the emission color over a very large range. This work shows how the emission color of the Cd-free phosphors can be tuned as well, at least over the region of interest for the green primary of color TV. Tuning mechanisms control the stoichiometry in the case of ZnS : Cu,Au,Al and proper adjustment of the doping levels in the case of ZnS : Cu,Al. Relations for the emission color are given; possible microscopic mechanisms are discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Emission color tunable green cathode ray tube (CRT) phosphors are needed in order to accommodate varying specifications and consumer demands. Basic material for green phosphors in direct view CRTs is ZnS : Cu,Al, showing intense (blue-) green broadband emission of unsurpassed brightness. The color coordinates (C.I.E. system) under low excitation density are around $x = 0.28$ and $y = 0.62$ for commercially available standard material. For high quality TV sets, this emission color is not acceptable. It lies just on the edge of the EBU (European Broadcasting Union) tolerance quadrilateral [(0.320;0.605), (0.286;0.542), (0.280;0.610), (0.298;0.627) in (x;y) coordinates] and tends to leave it during screen processing by, e.g., unavoidable contamination with the blue and red emitting phosphors. (Zn,Cd)S : Cu,Al usually is set to $x = 0.320$ by alloying with the necessary amount of CdS (some 7 mol%); a practical threshold for alternatives is $x = 0.300$ for the bare phosphor powder. The tuning mechanism in (Zn,Cd)S : Cu,Al is to decrease the band gap, thus readjusting the emitting levels and shifting the emission to yellow-green. Some loss in efficiency seems to be unavoidable.

The need for alternative emission control (without the necessity of employing CdS) can be matched by codoping ZnS : Cu,Al with Au (solely Au,Al-doped ZnS emits yellow). Phosphors with the desired emission color ($x \geq 0.3$) can be prepared this way, once again at the expense of some brightness. Unfortunately, ZnS : Cu,Au,Al tends to be very sensitive to details of the manufacturing process, thus generating some difficulty in preparing a constant emission quality (1).

The luminescence mechanism in all these phosphors is of the donor/acceptor type. In a point charge model, the emission energy $E(r)$ of the zero phonon line is

$$E(r) = E_G - (E_A + E_D) + e^2/(4\pi\varepsilon_0 \cdot r). \qquad [1]$$

E_G, forbidden energy gap; E_A, ionization energy of acceptor; E_D, ionization energy of donor; e, electron charge; ε_0, static dielectric constant; r, distance between donor and acceptor.

Because of the somewhat smaller band gap energy (higher energy efficiency and red-shifted emission) the sphalerite modification of ZnS is used if possible. However, alloys with CdS always crystallize in the wurtzite type. One characteristic of the donor/acceptor mechanism is a gradual blue shift of the emission with increasing excitation density, caused by gradual saturation of the (slower decaying) very distant pairs (2, 3). The amount of this shift on a real screen is a dynamic property and depends on the average green brightness. However, CRTs for consumer application are operated in a region where this shift is not expected to be perceptible.

This paper will first discuss the mechanism behind the sensitivity of ZnS : Cu,Au,Al during preparation and subsequently possible alternatives through redesign of the doping levels in ZnS : Cu,Al.

THEORY

Cu- or Au-doping of ZnS results in two distinct room temperature cathodoluminescence phenomena, their relative amount depending on the dopant concentration and the presence of coactivators. In Cu-doped ZnS, high Cu concentrations and/or the absence of (compensating) coactivators (Cl^-,Al^{3+}, . . .) favor so-called Cu blue emission, which is thought to be caused by Cu_{Zn}–Cu_i pairs.

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Coactivation on moderate doping levels favors Cu green emission, caused by coactivator donors and Cu acceptors. For Au-doped ZnS, in principle both phenomena occur as well, but the "Au green" emission (yellow in this case) can effectively be coactivated only by Al, not by halogens.

Kynev and Kuk (4) were the first to explicitly investigate the influence of nonstoichiometry on the luminescence of ZnS : Au, but unfortunately they made use of Cl coactivation. Nevertheless, they found a pronounced effect by varying the S_2 pressure over the phosphor powder during firing. In (1), the effect on ZnS : Au,Al was checked qualitatively. The S_2 equilibrium pressure is connected with the nonstoichiometry of the ZnS host:

$$\begin{aligned} \tfrac{1}{2}\mathrm{S_2\,(g)} &\leftrightarrow \mathrm{S_S} + \mathrm{V''_{Zn}} + 2\mathrm{h^{\bullet}} \\ \mathrm{Zn\,(g)} &\leftrightarrow \mathrm{Zn_{Zn}} + \mathrm{V^{\bullet\bullet}_S} + 2\mathrm{e'} \\ \varnothing &\leftrightarrow \mathrm{V^{\bullet\bullet}_S} + \mathrm{V''_{Zn}}. \end{aligned} \qquad [2]$$

Under equilibrium conditions, ZnS has never been prepared as *p*-type material, because of self-compensation. Only under nonequilibrium condition (e.g., low-temperature MOCVD), *p*-type material has successfully been prepared (5). This behavior clearly shows the prevailance of sulfur vacancies over Zn vacancies at all practical equilibrium conditions.

Sulfur vacancies with their positive effective charge are suspected to interact with (oppositely charged) Cu or Au acceptors. Au^+ is a very large ion compared to Zn^{2+}; the need for local relaxation therefore favors correlation between Au acceptors and S vacancies. For self-activated emission (involving, e.g., $[V_{Zn}Al_{Zn}]'$ acceptors), found for instance in unintentionally doped "pure" ZnS, the influence of nonstoichiometry has been demonstrated (6).

In the present paper, quantitative description of the influence on nonstoichiometry in terms of experimentally controllable parameters will be made. Nonstoichiometry at a fixed temperature is controlled by the partial pressures of S and Zn over the material. The maximum deviation from stoichiometry is given by the (temperature dependent) solubility of Zn or S in ZnS. These solubilities are not known exactly, but are known to be very small. Nevertheless, small deviations from stoichiometry also change the intrinsic defect chemistry dramatically. Dopant concentrations, on the other hand, are commonly quite low (on the 50–500 ppm level).

The experiments concerning the defect chemistry investigated the influence of equilibrium temperature as well as of equilibrium partial pressures. They were conducted on ZnS : Cu,Au,Al phosphor in order to check the technically feasible region for this material, which is used in color CRT tubes. On a qualitative scale, the effect has been demonstrated in (1).

As indicated above, the total amounts of dopants and their ratios control the amount of interstitials and therefore the amount of shortwave emission (Cu blue) (7). Under constant coactivator/activator ratio, at least the mean distance between the impurities is concentration-dependent and for this reason should shift the emission energy. On the other hand, at a certain level concentration quenching will occur, which is thought to be caused by (unwanted) energy transfer between activator or coactivator states and eventually to killer centers.

Influence of excitation density on the emission characteristics was first described in the work of Shionoya (2, 3). The main point is the distribution of distances of the donor/acceptor pairs. The transition probability scales with the overlap of the wavefunctions of these states. Under the assumption of constant effective radii, the overlap is simply determined by the spatial separation. Therefore, the distant pairs with their low transition probability will saturate first upon increasing excitation density, whereas the closer, fast decaying pairs then dominate the emission spectrum. Since Coulomb interaction increases with decreasing distance, the result is a spectral blue shift. The presence of this blue shift depends on a distribution of donor/acceptor distances and thus directly proves the existence of localized states. The high carrier mobility and high density of states in bands rule out such a shift in the case of band/band emission. The same arguments apply for spectral shifts during decay; in this case, a red shift is expected during decay, because the close pairs decay faster. Direct evidence is given by the luminescence decay curves themselves; with increasing load, the decay then seems to become faster.

Saturation behavior, on the other hand, is dominated by the doping level applied. Typically, the sum of activator and coactivator concentration is below 1000 mol-ppm. At higher levels, concentration quenching occurs (see above). Saturation means a decrease in efficiency with increasing excitation density, that is, a sublinear relation between light output and excitation energy input. One simple cause might be ground state depletion; higher doping levels are then a simple remedy. On the other hand, higher order processes such as three center Auger processes are discussed in the literature (8), indicating the presence of more than one mechanism, even with inverse concentration dependence.

EXPERIMENTAL

Phosphor materials were initially prepared from luminescence grade ZnS (Philips Lighting) by slurrying it with the proper amounts of $AlCl_3 \cdot 6H_2O$, $HAuCl_4 \cdot 4H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$. After adding approximately 5 wt% of sulfur, the resulting mixture was evaporated to dryness and finally dried for several hours at 120°C in air. For

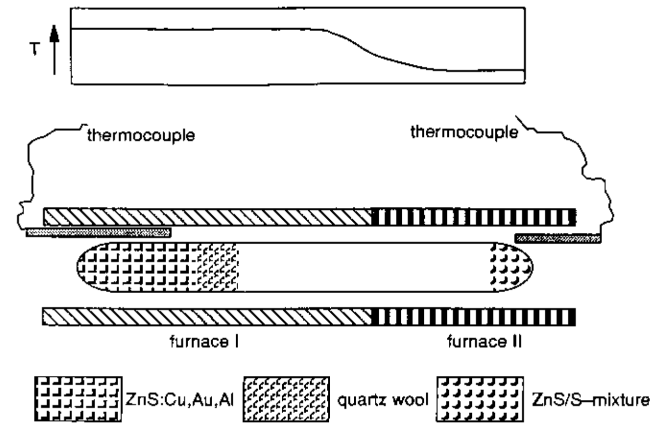

FIG. 1. Arrangement with two-temperature furnace. The diagram at the top gives the temperature profile over the ampoule.

firing,the raw material was placed in a quartz tube (sealed on one side) and covered with activated charcoal. The loaded tube was placed horizontally in an electric furnace and heated slowly to the end temperature of 980°C, soaked for 2 hr at this temperature, and subsequently quenched in ice water. The cooled phosphor was then separated from the charcoal, gently crushed in a mortar, washed with doubly distilled water, and dried at 120°C for several hours in air.

Experiments with varying sulfur pressure were performed in a two-zone furnace (Fig. 1). An evacuated quartz ampoule, containing on one end the phosphor sample to be equilibrated and on the other end elemental S or Zn, was inserted into the furnace so that the phosphor powder was located inside the hot region of the furnace. Upon heating, the S or Zn distilled into the cooler zone; the temperature in this zone dictated the vapor pressure of the liquid element and thus the partial pressure of this element over the phosphor powder. In this way the elemental partial pressure was controlled by the temperature of the cool zone and the equilibration temperature of the phosphor itself was equal to the temperature of the hot zone. Experiments with varying equilibration temperatures were performed; the equilibration times were then chosen according to the tracer diffusion data of Blount *et al.* (9) for S in ZnS.

Emission spectra of phosphor powders were recorded at room temperature under cathode ray excitation (12 keV, 5 nA) using an OMA system; outputs are the emission spectra as well as the color coordinates according to the C.I.E. chromaticity diagram. The emission properties as a function of excitation density were measured at 30 keV on thin phosphor layers on glass, covered with a 200-nm Al layer to exclude charging. Measurement of luminescence decay was performed with electron beam pulsing (30 keV, 20-μm spot size, 30 μsec). Light detection was accomplished with a photomultiplier tube and a two-channel gated photon counter, operated in boxcar mode.

RESULTS AND DISCUSSION

The results show that variations of the intrinsic defect chemistry of ZnS (equivalent to deviation from stoichiometry) have a large impact on the emission color of Au-doped ZnS. Table 1 gives examples of runs with various

TABLE 1
Selected Results of Diffusion and Doping Experiments

Sample	Diffusion at (°C)	*c*(Cu) [ppm]	*c*(Au) [ppm]	*c*(Al) [ppm]	Pressure (bar)	*x*	*y*
Standard	—	150	70	500	—	0.314	0.606
MB165	700	150	70	500	0.25 (S_2)	0.283	0.623
MB166	700	150	70	500	0.85 (S_2)	0.281	0.623
MB167	700	150	70	500	2.7 (S_2)	0.284	0.623
MB168	800	150	70	500	2.7 (S_2)	0.320	0.607
MB169	900	150	70	500	2.7 (S_2)	0.315	0.608
MB173	900	150	70	500	4.2 (S_2)	0.327	0.604
MB175	980	150	70	500	6.5 (S_2)	0.331	0.602
MB176	980	150	70	500	0.015 (Zn)	0.271	0.612
MB177	800	150	70	500	0.015 (Zn)	0.278	0.610
MB126	—	885	—	3099	—	0.309	0.601
MB131	—	778	—	7039	—	0.294	0.600
MB142	—	366	—	931	—	0.300	0.615
JM23	—	50	—	150	—	0.277	0.618
MI167	—	150	—	700	—	0.282	0.622

Note. ZnS:Cu,Au,Al samples were all made from the starting material denoted as "standard" (standard preparation procedure). Samples with different doping were prepared individually.

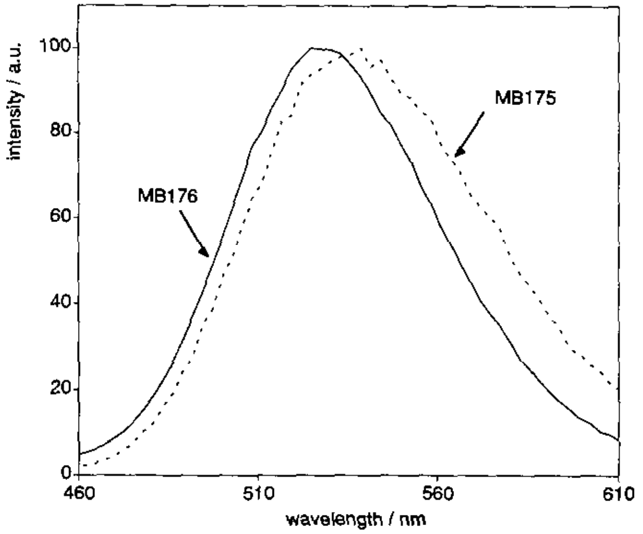

FIG. 2. Emission spectra of phosphors annealed under Zn vapor (MB176) and under S vapor (MB175). Spectra are normalized to peak intensity 100. For further details, see Table 1.

equilibration temperatures and vapor pressures. The effect is controlled by the equilibration temperature as well as by the partial pressures over the phosphor; increasing S pressure as well as increasing temperature shifts the emission to the desired yellow-green. As a rule, the emission efficiency is not systematically correlated with the measures described. The spectral shift represented by x values of the emission chromaticity is shown explicitly in Fig. 2. It shows the emission spectra of the two extreme members of the runs of Table 1. The spectra show a real shift of the emission and not a simple broadening. The spectral shift clearly depends on the diffusion temperature as well as on the vapor pressure. As an example, Fig. 3 gives the variation of chromaticity value x with equilibration temperature.

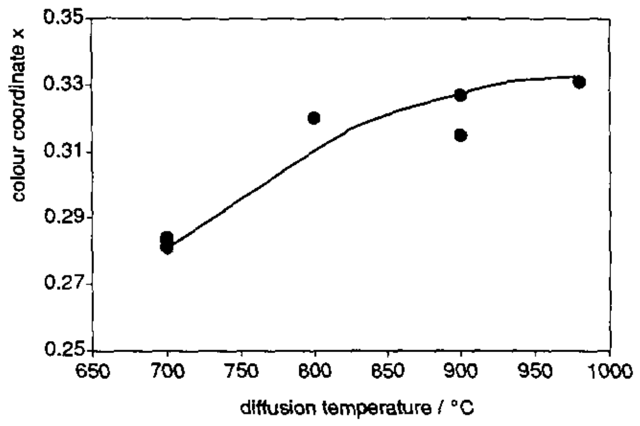

FIG. 3. x value of the chromaticity versus diffusion temperature. The line is a guideline for the eye.

Since diffusion temperature as well as vapor composition affects the emission, deviation from stoichiometry seems to be the determining factor. High sulfur pressure as well as high temperature is expected to cause high solubility for S in ZnS. High S content or even surplus is (in equilibrium) synonymous with low concentration of S vacancies. Zn vacancies, on the other hand, are present as charge compensators for the surplus of Al coactivator independently of defect chemistry and will not change their concentration by small shifts of the stoichiometry. The most probable mechanism for the blue shift observed with decreasing S content is direct interaction between positively charged S vacancies and the negatively charged acceptor states, decreasing the ionization energy of the acceptor. This is most effective for the Au states (*1*) and might be driven by local relaxation (Au^+ is very large).

Considering the emission color with respect to the EBU recommendation, the values of Table 1 cross the whole tolerance quadrilateral. The important conclusion is that controlling the defect chemistry or stoichiometry allows for control of the emission color at the (brightness optimized) doping level usually applied over a sufficiently large range. On the other hand, the necessity of reproducing the stoichiometry exactly during phosphor manufacture demands thorough process control during firing, cooling procedures included.

Contrary to ZnS : Cu,Au,Al as described above, ZnS : Cu,Al shows only a minor influence of the defect chemistry on the luminescence. On the other hand, increasing the doping level with Cu (under constant Cu/Al ratio) causes a red shift of the emission, which also can yield (chromaticity) x values over 0,3. Figure 4 shows the results plotted as a function of the Cu content at different Al doping levels. All curves start well down in the blue; low Cu content leads to self-activated (light blue) emission

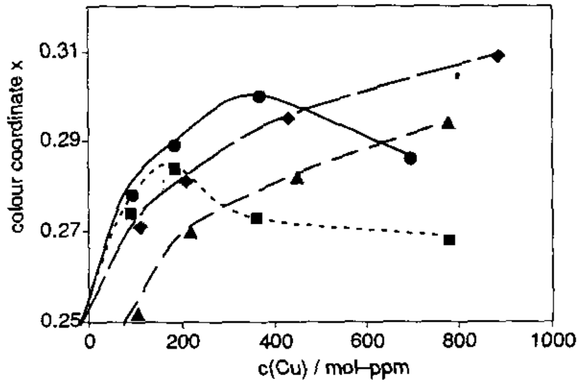

FIG. 4. x value of the chromaticity for ZnS : Cu,Al phosphors of various doping levels. The concentration of Al is the parameter of the curves. Squares: c(Al) = 490 ppm. Circles: c(Al) = 931 ppm. Diamonds: c(Al) = 3099 ppm. Triangles: c(Al) = 7034 ppm. The lines are guidelines for the eye.

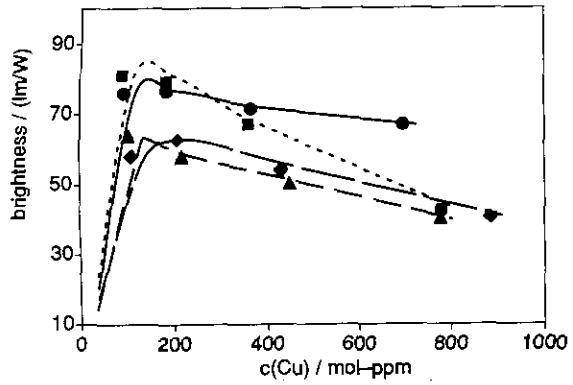

FIG. 5. Lumen efficiency of ZnS : Cu,Al phosphors of various doping levels. The concentration of Al is the parameter of the curves. *Squares*: $c(\mathrm{Al}) = 490$ *ppm*. *Circles*: $c(\mathrm{Al}) = 931$ *ppm*. *Diamonds*: $c(\mathrm{Al}) =$ 3099 ppm. Triangles: $c(\mathrm{Al}) = 7034$ ppm. The lines are guidelines for the eye.

typical for ZnS : Al. With increasing Cu content, the emission color gradually turns green. With the Cu/Al concentration ratio becoming greater than the optimum of $\frac{1}{3}$, the color coordinate x decreases again. Now the reason is Cu blue emission. From Fig. 4 alone, the desired red shift in the emission color could be obtained by high Cu doping with a threefold surplus of Al coactivator. However, increasing concentration quenching lowers the brightness considerably (Fig. 5). A compromise can be found on doping with ca. 360 ppm Cu and ca. 930 ppm Al; while the x value is 0.3, the brightness is lowered only by some 15%, compared to standard (Zn,Cd)S : Cu,Al.

The red shift of the emission with increasing doping level at constant Cu/Al ratio is in contradiction to the naive picture of donor/acceptor luminescence. Increasing doping level will decrease the average separation of donors and acceptors and therefore is expected to cause a blue shift instead of a red shift. In order to check if the heavily doped materials still show D/A characteristics, the emission and decay under increasing excitation density were measured. Figures 6 and 7 show examples of the measurements. Qualitatively speaking, the blue shift with excitation density is the same for all samples, regardless of their doping level. This is reflected in a similar decrease in decay time (Fig. 7) with increasing excitation density for all samples. Additionally, some decrease in decay time with increasing doping level is observed from the figure, in accordance with the expected decrease of D/A pair distances. Together, emission and decay behavior indicate that the D/A character does not change with increasing dopant concentration.

Two mechanisms for the observed red shift with increasing dopant concentration seem to be possible after a glance at Eq. [1]. The first is interaction between the acceptor or donor states, leading to ionization energy splitting and, in the extreme, to dopant subbands. However, established subbands would disturb the D/A character of the emission; the blue shift and decrease of the decay time with increasing excitation density would not be expected. Interaction might be expected first between the donor states, since they are shallow and therefore possess a larger Bohr radius. The second possibility is a decrease of the Coulomb interaction energy. A simple

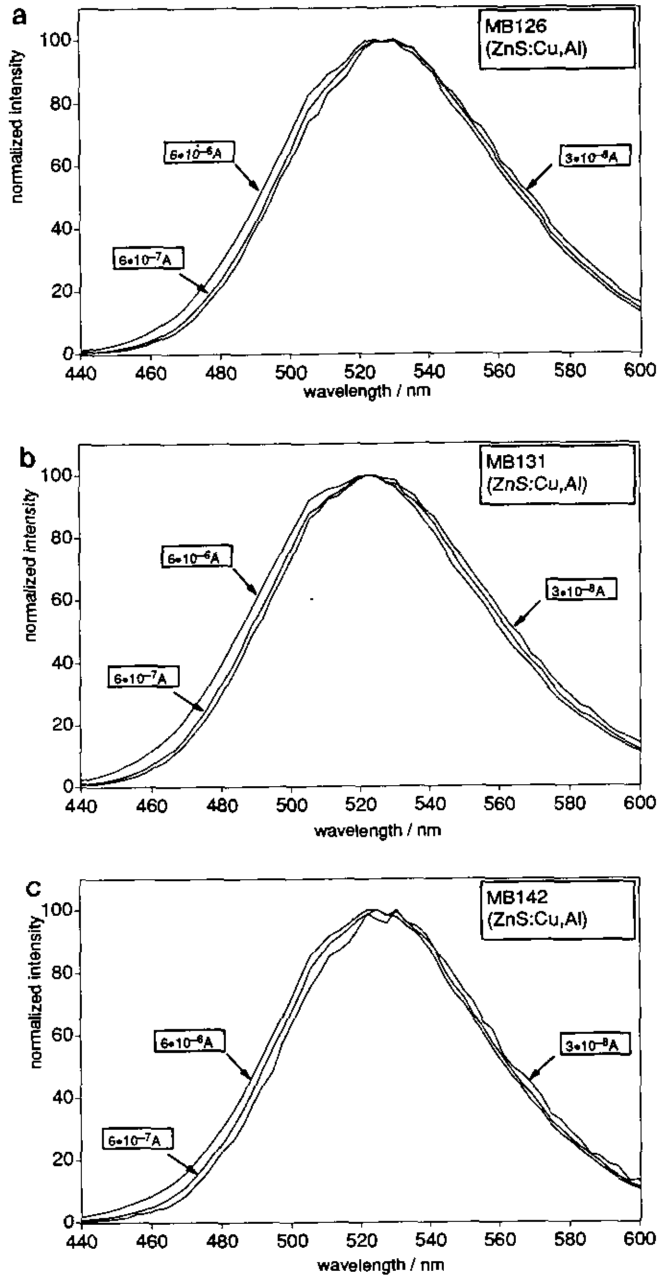

FIG. 6. Emission spectra of ZnS : Cu,Al phosphors of various doping levels (*a–c*) at different excitation densities (normalized to peak intensity). Beam currents are as denoted in the figures. For further details, see Table 1.

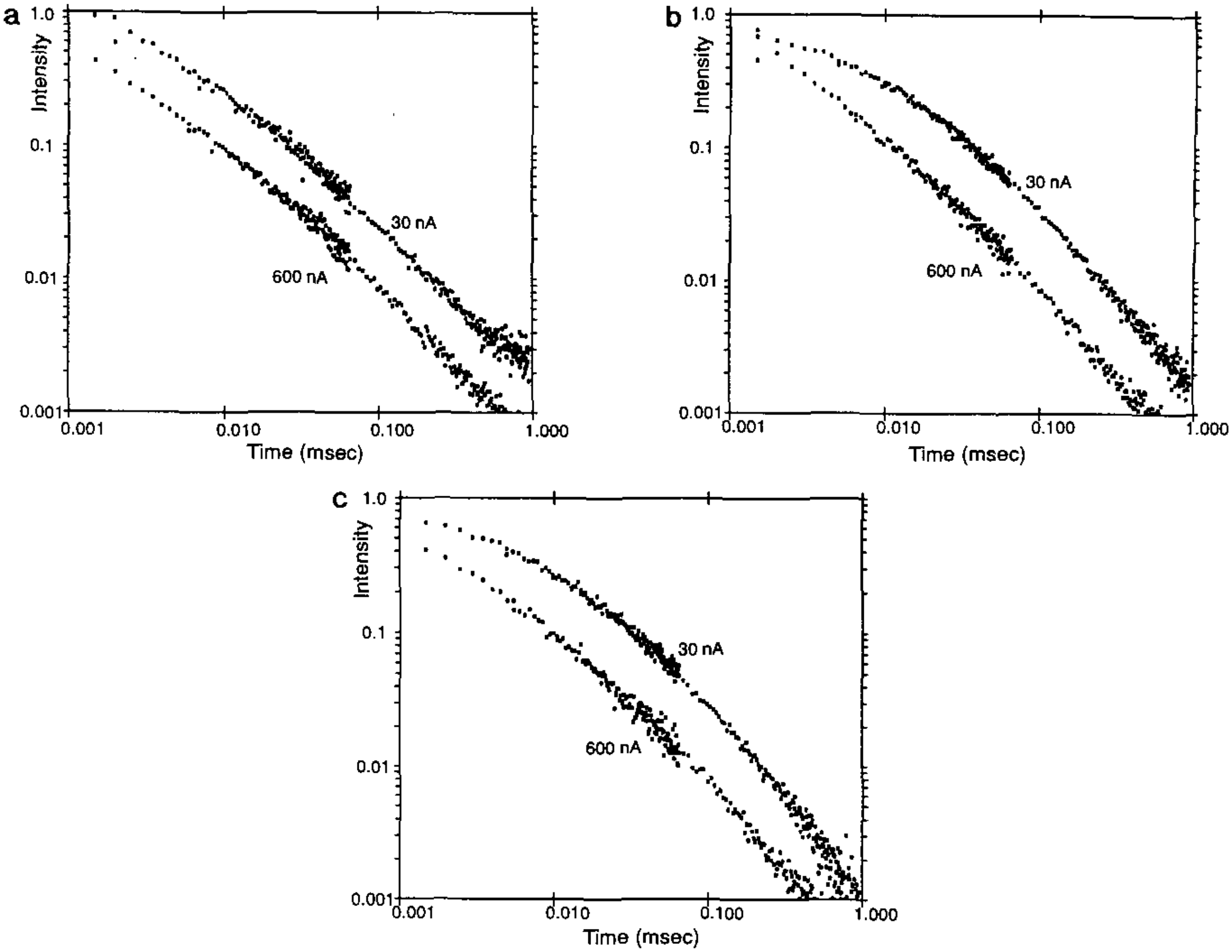

FIG. 7. Luminescence decay at various doping levels (*a–c*) and two different excitation densities. Beam currents are as denoted in the figures. Conditions: (a) JM23: 50 ppm Cu, 150 ppm Al; (b) MI167: 150 ppm Cu, 500 ppm Al; (c) MB131: 780 ppm Cu, 7030 ppm Al. For further details, see Table 1.

cause might be a more diffuse charge distribution, for instance, of the donors, once again caused by interaction between the localized states. The simple point charge model then is no longer valid; on the whole, more diffuse charge clouds lead to decreased Coulomb interaction.

SUMMARY

For ZnS : Cu,Au,Al phosphor, relations between emission color and equilibration temperature and equilibrium vapor composition have been established. Shifts in emission color have been correlated to the stoichiometry of the ZnS host.

For ZnS : Cu,Al phosphor, the desired red shift of the emission has been found for increasing doping level. Since the luminescence still has donor/acceptor characteristics, this must be caused by interaction between the donor or acceptor states, giving rise to increased ionization energy or reduction of the Coulomb interaction via increase of the effective radius.

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