the surface, in agreement with Beacom and Riley (1) whose results were obtained on a much larger scale of surface roughness. The layering of incorporated sulfur in regions of the plating where the micrograph shows a laminar structure supports the suggestion by Vanderkooi (3) that layering of the deposit may be associated with the incorporation of additive or compounds derived from it.

Acknowledgments

The authors wish to thank Dr. G. B. Cook and Mr. U. F. Marx for their help and encouragement, and Messrs. Wilmot-Breeden for the provision of experimental facilities and permission to publish this paper.

Manuscript received Aug. 31, 1959.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1961 JOURNAL.

REFERENCES

1. S. E. Beacom and B. J. Riley, *This Journal*, **106**, 309 (1959).
2. E. Bleuler and G. J. Goldsmith, "Experimental Nucleonics," p. 84, Rinehart Publishing Co. (1952).
3. N. Vanderkooi, Doctoral Dissertation, Wayne State University (1958).

(Zn,Hg)S and (Zn,Cd,Hg)S Electroluminescent Phosphors

A. Wachtel

Research Department, Westinghouse Electric Corporation, Bloomfield, New Jersey

ABSTRACT

Solid solutions of (Zn,Hg)S prepared by firing in sealed silica tubes are cubic in structure. With suitable additions of Cu and a coactivator, photoluminescence and electroluminescence are obtained. The coactivators used were halides, Ga, or In. The electroluminescence in the red consists of two emission bands which do not appear to be analogous to the blue and green emission bands of Cu, Cl in ZnS. The quantum efficiency is of the same order of magnitude as that of ZnS:Cu, Cl, but the emission bandwidth is about twice as large and the red electroluminescence consists of emission located to a large extent in the infrared. HgS tends to retain the cubic structure of ternary (Zn, Cd, Hg)S systems provided that the Cd/Hg ratio does not exceed certain limits; until this is so, the introduction of Cd causes increased electroluminescence.

Efforts to prepare EL[1] phosphors emitting at longer wave lengths are usually based on substitution of lattice constituents so as to effect lattice expansion. In ZnS:Cu EL phosphors of Se for S has been investigated by Prener (1) and by Hegyi, Larach, and Shrader (2). Zn(S, Se) and ZnSe constitute good EL phosphors, although the frequency dependence of ZnSe:Cu is large compared to that of ZnS:Cu, so that the low-frequency response is unusually poor.

On the other hand, substitution of Cd for Zn has been shown to result in hexagonal systems with exceptionally poor EL response (3). It is therefore obvious that the effect of substitution of Zn by the next heavier member of the group IIB elements, namely Hg, was of interest. Due to the low sublimation temperature of HgS, its retention in ordinary firing at atmospheric pressure is known to be impossible at temperatures sufficient to cause activator incorporation. Wesch (4) has described a high-pressure furnace by means of which the preparation of pure HgS phosphors was mentioned. Kremheller and Levine (5) prepared (Zn, Hg)S and (Cd, Hg)S solid solutions by aqueous recrystallization under pressure and at temperatures well above the normal boiling point of water, and in a recent publication Kremheller, Levine, and Gashurov (6) describe some of the photoluminescent properties of activated (Zn, Hg)S and (Cd, Hg)S prepared by this method. In the present investigation, the mixed sulfides were prepared by firing in evacuated and sealed silica tubes. Although the pressure developed in the tubes is unknown, the application of hydrostatic pressure from the outside was not found to be necessary.

[1] Electroluminescence or electroluminescent is hereafter abbreviated EL.

Experimental Technique

In addition to the raw materials already described (3), HgS, Ga_2S_3, and In_2S_3 were used. HgS was prepared by reaction of the elements. Ga_2S_3 was prepared by slurrying ZnS with $Ga(NO_3)_3$ solution, drying, and firing in an atmosphere of H_2S. In_2S_3 was precipitated from aqueous solution in the presence of a ZnS carrier, filtered, and dried.

In order to avoid the development of excessive pressure in the sealed tubes, as well as to avoid the influence of gases not normally retained in firings at atmospheric pressure, it was necessary to accomplish complete thermal degassing and decomposition of volatile matter (NH_4-salts, acetate radical) prior to sealing the final mixture into the tubes. All firings were therefore conducted in two stages:

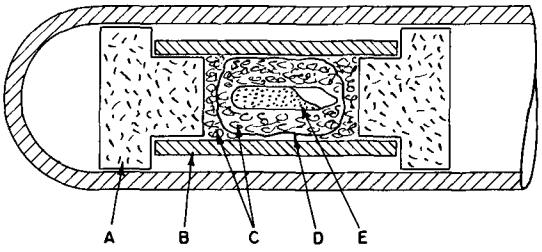

Fig. 1. Technique for firing phosphors with HgS. A, Fire brick; B, mullite tube; C, silica wool; D, silica cloth; E, firing tube.

1. A normal blue or green emitting ZnS:Cu EL phosphor is prepared at atmospheric pressure by known methods (3). The Cu-acetate and NH_4-halides (if any) decompose, and activator incorporation takes place. Traces of H_2O and air are expelled and particle growth of the ZnS facilitates subsequent degassing. The fired phosphor is, however, not washed in NaCN solution since the total amount of Cu added (now partially present as free Cu_2S) is required for the final synthesis of the mixed (Zn, Hg)S EL system.

2. The above product, hereafter referred to as the singly fired phosphor, is mixed with HgS as well as a small amount of S calculated to produce only a few atmospheres of pressure at the subsequent firing. This sulfur addition is necessary since traces of residual air would cause oxidation of S^{2-} and give rise to S-vacancies[2] and poor EL performance of the finished product. The mixture is transferred to a silica tube of 7 mm ID, 9 mm OD, and 40 mm length, closed at one end and provided with a constricted neck at the other end. The tube is evacuated by means of a mechanical oil pump for about 30 min and then sealed at the constriction. The sealed tube is fired at 900°C as shown in Fig. 1.

The thermal insulation afforded by the silica wool packing, as shown in the figure, is necessary to prevent separation of part of the HgS during cooling. The presence of CdS greatly diminishes this effect, and still more homogeneous products may be obtained by allowing the entire assembly to cool in the furnace, although this was rarely done because of obvious considerations of time limitation. Refiring times of 2 hr were found to be sufficient.

The washing procedure in NaCN solution is the same as used for normal green-emitting ZnS:Cu EL phosphors. Because of the small samples (about 2 g) usually prepared, simple grinding in a mortar and pestle was preferred. All figures for Cu and halide in phosphors specifically refer to amounts added before firing, and not to final compositions.

Measurements were performed with a Spectra Brightness Spot Meter,[3] using a demountable castor oil cell. In order to meet the contract requirements as to color, additional measurements were also taken with a red (NBS #3215) filter inserted in the optical path. The ratio between the respective readings served as a sensitive indication of emission color, and it was noted that small differences in this ratio caused large differences in brightness. To enable a valid interpretation of the relative performance of phosphors emitting with different colors, it was therefore necessary to compensate for this effect. The method used consisted of preparing phosphors that differed only in base lattice composition and plotting their relative brightness (based on 100% for the specified color) as a function of the filter ratio. Data on experimental phosphors could then be corrected to yield values hereafter referred to as "normalized brightness."

[2] In the presence of HgS, such reducing conditions result in the formation of metallic Hg, visible as a separate phase.

[3] Photo Research Corp., Hollywood, Calif.

Table I. Unit cell dimensions of cubic (Zn,Hg)S:Cu,NaCl phosphors

Mole % HgS	a (Å)
0	5.406
5	5.429
10	5.443
15	5.469
20	5.486
25	5.516
30	5.532
40	5.569
60	5.665
80	5.745

Results

Photoluminescence of (Zn:Hg)S phosphors.—Some basic information was obtained by firing photoluminescent ZnS:Cu (0.01%):NaCl phosphors with increasing additions of HgS at 750°C. Table 1 shows the unit cell dimensions obtained by x-ray powder diffraction. All phosphors (up to 80% HgS) were cubic, although the HgS used was hexagonal. HgS alone similarly fired was also hexagonal. The values can be plotted to give a reasonably good fit to a straight line. Figure 2 shows the emission spectra (3650Å excitation) as obtained on a Perkin-Elmer Universal Spectrometer. Figure 3 shows the diffuse reflection spectra in the near ultraviolet and visible regions obtained by illuminating through a Farrand monochromator and measuring the reflected radiation with a Bausch and Lomb monochromator adjusted to the same wave lengths. It may be noted that the regular manner in which the spectra shift to longer wave lengths is very similar to the effect of Cd substitution. The shift in emission caused by Hg is about four times greater than that caused by similar concentrations (in mole %) of Cd. It was noted that at low Hg concentration (5 mole %) the fluorescence was unusually weak.

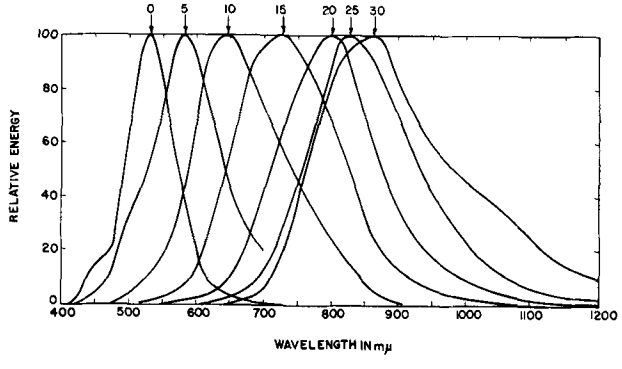

Fig. 2. Emission spectra of (Zn, Hg)S:Cu, NaCl phosphors. Numbers denote mole % HgS in phosphors. Excitation = 3650Å.

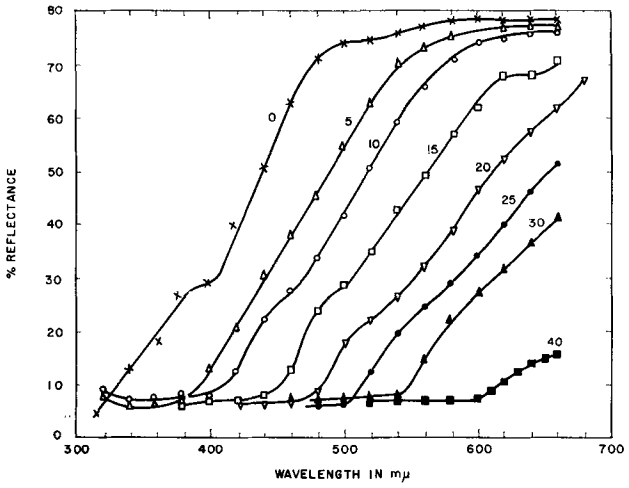

Fig. 3. Diffuse reflection spectra of (Zn, Hg)S:Cu, NaCl phosphors. Numbers denote mole % HgS in phosphors.

The decreasing concentrations of Cu and Cl resulting from increasing additions of HgS were not considered to appreciably influence the shape of the emission and reflection spectra, because Cl was present in excess and only the long wave-length emission band was developed.

Electroluminescent phosphors.—The activator requirements for EL are known to be greater than for photoluminescence. For the systems under investigation, they were also noted to vary with the type of coactivator used. In the case of Cl, additions of the order such as to produce optimum green-emitting singly fired ZnS:Cu, Cl phosphors proved to be too high not only for Cl, but also for Cu. Figure 4 shows the emission spectra of a series of (Zn, Hg)S:Cu(0.2%), Cl(0.075%) phosphors excited at 10,000 cps. The activator additions are such that the ZnS:Cu, Cl phosphor emits predominantly the blue Cu band and are optimum with respect to the orange or red emitting compositions. The emission band gradually shifts to longer wave lengths and broadens until above about 20 mole % Hg, a long wave length emission band increases quite suddenly in relative intensity. It will be shown that this cannot necessarily be identified with the "Cu-green" band emitted in more highly coactivate ZnS-Cu phosphors.

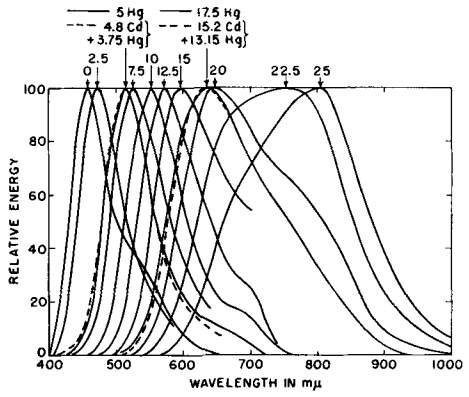

Fig. 4. Emission spectra of (Zn, Hg)S:Cu (0.2%): Cl(0.075%) and two (Zn, Cd, Hg)S:Cu (0.2%:Cl (0.075%) EL phosphors. Numbers denote mole % HgS in samples. Excitation = 10,000 cps.

The effect of Cd on the emission color was determined empirically for orange to deep red emitting (Zn, Hg)S. It was noted that the emission color of [(1 − x)Zn, xHg] S:Cu may be duplicated approximately by firing [(1 − 4n)Zn, 4nCd] S:Cu and refiring this with (x − n)HgS. However, substitutions of more than half of the original concentration of Hg by Cd result in a shift to longer wave lengths. Table II shows the effect on EL brightness of a series of orange-red emitting phosphors based on the original composition (0.8Zn, 0.2Hg)S:Cu (0.2%):Cl(0.075%). The table includes brightness readings of NaCN-washed aliquots of the singly fired (Zn, Cd)S:Cu, Cl phosphors. It also shows measurements by x-ray powder diffraction, so as to illustrate how in both cases the breakpoint in brightness coincides with the appearance of an appreciable percentage of hexagonal phase. These measurements also include values of interlattice spacings (d/n) of the 311 plane. Very similar results are shown in Fig. 5 on deep red emitting phosphors coactivated with Br + I or Ga and excited at 400 cps. This is in agreement with the observation made by Zalm (7), than in ZnS:Cu EL phosphors the cubic phase is preferable.

It can be seen that in all cases Cd increases the emittance of the system until interference by formation of hexagonal material occurs. It can also be

Table II. Effect of Cd/Hg ratio on structure and electroluminescence

First firing					Second firing					
Mole % Cd used	Brightness 10,000 cps	Emission color	% Hex. phase	d/n, (311)	Mole % HgS added	Mole % Cd in phosphor	Brightness 400 cps	Brightness 10,000 cps	% Hex. phase	d/n, (311)
0	6.2	Blue	0	1.630	20	0	0.77	2.4	0	1.653
2	6.8	White-blue	0	1.633	19.5	1.7	0.68	3.5	0	1.653
4	3.5	Green-blue	4	1.634	19	3.2	0.89	3.95	0	1.656
8	1.8	Blue-green	27	1.638	18	6.6	1.10	3.8	0	1.660
16	0.055	Green-blue	100	1.649	16	13.4	1.49	4.9	0	1.665
20	0.024	Green-blue	100	1.654	15	17.0	2.01	5.55	7	1.668
24	0.014	Green-blue	100	1.660	14	20.6	1.16	3.3	43	1.671
28	0.008	Blue-green	100	1.664	13	24.4	0.22	0.17	100	1.677
32	0.006	Green	100	1.668	11*	28.8	0.12	0.25	100	1.679
64	—	—	100	1.707	0	64	—	0.15	100	1.710
72	Faint	Red	100	1.719						
80	Very faint	Red	100	1.728						

* Relationship of 1 Hg = 4 Cd begins to break down. Therefore, only 11 instead of 12 mole % HgS used.

seen that in the presence of HgS a much higher concentration of Cd is permissible before this occurs. The optimum substitution of Hg by Cd appears to be in the neighborhood of 20-25% of the original Hg concentration. Most of the ensuing investigations were therefore performed on such (Zn, Cd, Hg)S:Cu phosphors. The two dashed curves in Fig. 4 represent the emission spectra of (Zn, Cd, Hg)S:Cu, Cl phosphors in which 25% of the Hg was replaced by Cd in the manner outlined above. The compositions are based on original Hg concentrations of 5 mole % (green emission) and 15 mole % (orange emission) and are seen to coincide closely with the emission spectra of the respective (Zn, Hg)S:Cu, Cl phosphors, but the brightness was appreciably higher.

It has been mentioned that optimum additions of Cu and Cl were smaller than those found useful in green-emitting ZnS:Cu, Cl phosphors(3). It was therefore interesting to note that the optimum addition of Br + I [4] was higher, namely similar to that for ZnS:Cu phosphors, although the estimated excess Cu_2S concentration still had to remain smaller than about 0.2 mole %. Such Br + I coactivated phosphors were about two to three times brighter than Cl-coactivated phosphors. In the case of Ga or In coactivation, phosphors were prepared with additions of Cu equal to 0.6 mole % more than the concentration of Ga or In added. Their normalized brightness, excited at 400 cps, increased linearly with coactivator concentration up to 0.125 mole % and then decreased. On the other hand, phosphors coactivated with 0.125 mole % Ga or In showed two brightness maxima with respect to Cu addition, as shown in Fig. 6. It can be seen that the first maximum is very sharp and more pronounced in the case of In coactivation. Prefiring at 1100°C [5] decreases the low Cu maximum. Ga-coactivated phosphors prefired at 1100°C show only a gradual increase in brightness, leveling off at about 1 mole % Cu.

Figure 7 shows the brightness of Br + I and of Ga coactivated (Zn, Cd, Hg)S:Cu phosphors as a function of Cd + Hg concentration. The activator concentrations are not optimized for either system but chosen so that the total Cu addition as well as the green emission color of the ZnS:Cu phosphors are the same. It is interesting to note that in the case of Br + I coactivation there occurs the same initial drop in output at low Hg concentrations as has been observed in the photoluminescent as well as the Cl-coactivated EL phosphors, while, on the other hand, the Ga-coactivated ZnS:Cu is characterized by comparatively poor output, presumably because of the greater trap depth caused by Ga (8, 9). Introduction of Cd + Hg [6] causes an increase in brightness well beyond the point of maximum luminosity (yellow green). This means that, except for the initial drop noted with halide coactivation, the radiant output of the phosphors increases at least up to the point of maximum observed brightness and possibly beyond that. In the case of Ga-coactivation, this might be explained by decreasing trap depth due to lowering of the conduction band, assuming that a similar effect occurs as noted by Klasens for Cd substitution (10). Unfortunately, the

[4] Equimolar mixtures of NH_4Br and NH_4I yielded slightly better results than NH_4Br alone. However, only a very small fraction of the added I^- is retained, so that additions were based on Br^- alone.

[5] To compensate for decreased particle growth in the absence of halides.

[6] The same relationship was noted in the absence of Cd.

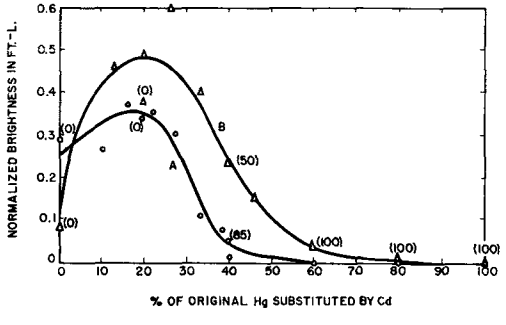

Fig. 5. Normalized brightness of (Zn, Cd, Hg)S:Cu phosphors as a function of Cd/Hg ratio. A, Compositions based on (0.81 Zn, 0.19 Hg)S:Cu(0.4%), (Br + I)(0.46%); B, compositions based on (0.85 Zn, 0.15 Hg)S:Cu(0.9%), Ga(0.13%) Numbers in parentheses denote % hexagonal phase present. Excitation = 400 cps. Groups A and B approximately match in emission color.

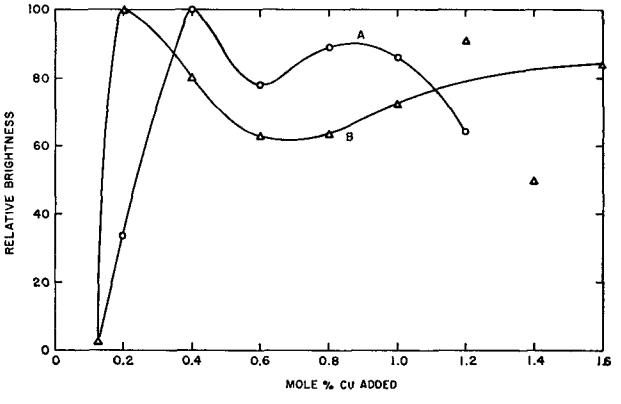

Fig. 6. Normalized relative brightness of red-emitting A:(Zn, Cd, Hg)S: x Cu: 0.125 mole % Ga and B: (Zn, Cd, Hg)S x Cu: 0.125% In phosphors as a function of Cu addition. Excitation = 400 cps.

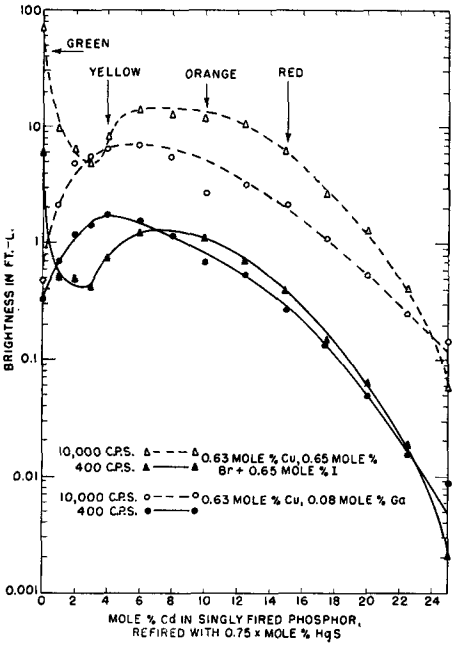

Fig. 7. Brightness and emission colors of (Zn, Cd, Hg)S:Cu phosphors as a function of base lattice composition.

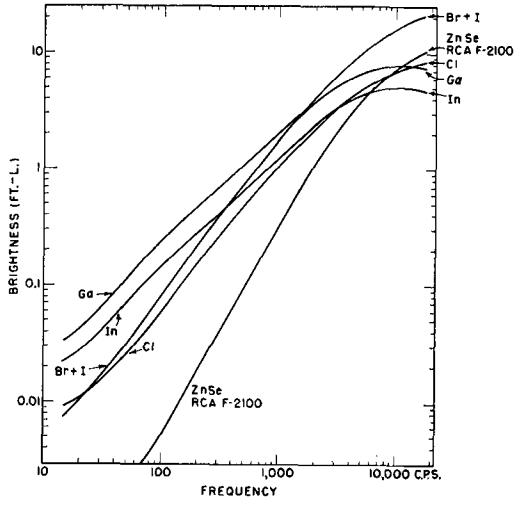

Fig. 8. Brightness of orange-red emitting (Zn, Cd, Hg)S:Cu phosphors with different coactivators and of ZnSe:Cu as a function of frequency.

scope of the present investigation did not permit independent measurements of radiance (such as by thermopile) or glow curves for these samples.

An indication of decreasing trap depth with increasing Cd + Hg concentration was noted, however, by visual observation of thermoluminescence. Similarly, a comparison of the frequency dependence of typical red-emitting phosphors as shown in Fig. 8 indicates decreased output of Ga and In coactivated phosphors at frequencies where no such decrease is evident with halide coactivated phosphors. It should be mentioned that at the red end of the spectrum, the usual variation in emission color with frequency represents variations in brightness which may be more pronounced than in the case of green-emitting phosphors, and that this effect therefore increases the slope of the frequency dependence curves. The phosphors were selected so that at intermediate frequencies their emission color approximately matches that of the ZnSe:Cu phosphor also shown in Fig. 8 for comparison. Therefore they do not necessarily represent specimens suitable for comparison of brightness as a result of optimum conditions of preparation.

It was of obvious interest to determine the actual quantum yield and efficiency of the red phosphor in comparison to a standard green-emitting ZnS:Cu, Cl EL phosphor. The following samples were selected for this purpose:

1. (0.754Zn, 0.133Cd, 0.113Hg)S:Cu, Ga prepared from (0.85Zn, 0.15Cd)S:Cu(0.9%), Ga (0.13%) by refiring with 11.25% HgS. Emission color, red.
2. (0.6945Zn, 0.163Cd, 0.1425Hg)S:Cu, Ga prepared from (0.81Zn, 0.19Cd)S:Cu(0.9%), Ga (0.13%) by refiring with 14.25% HgS. Emission color, deep red.
3. A normal ZnS:Cu, Cl green emitting phosphor.

Each phosphor was operated at 400 cps in the same castor oil cell and the brightness and power consumption measured as a function of applied voltage. In addition, each phosphor while in the same cell was operated at 400 cps and 600 v and the spectral distribution determined, using the same slit width and amplification of the spectrometer. The absolute heights of the resultant curves were therefore comparable. These were corrected for energy, quanta, and luminosity, but not normalized to equal peak heights. Table III gives the integrated values. It is apparent that under similar conditions of excitation the output in energy or quanta for the red phosphors is considerably smaller than for the green phosphor. Nevertheless, the differences in luminosity are much greater and are the main reason for the low brightness presently obtainable with the red-emitting phosphor.

The actual quantum yield was determined according to[7]

$$K = \frac{B\,A\,Q \times 10^{17}}{1.26L}$$

where K is the number of quanta emitted per second, A is the area of the cell in cm², Q is the integrated quantum output, L is the luminosity factor of the spectrum, and B is the brightness in foot-lamberts. Table IV shows the data calculated for each phosphor operating at the voltage where maximum luminous efficiency was observed. It can be seen that the quantum efficiency of the red-emitting phosphor is comparable to that of ZnS:Cu, Cl.

Efforts to increase the brightness without change in emission color appeared to require a narrowing of the spectral distribution with particular emphasis on increasing its slope on the short wave length side. It is well known that in ZnS:Cu phosphors either the blue or the green emission band can be

[7] Let the number of quanta emitted/cm²-sec $= K = \int \frac{C}{h\nu} \cdot \frac{dE}{d\lambda}\, d\lambda$, where C is a constant introduced to correct the arbitrary units in which the spectrum is measured to watts/cm². Then,

$$K = \frac{C}{hc} \int \lambda \frac{dE}{d\lambda}\, d\lambda = \frac{C\,Q}{hc}$$

The constant C may be determined from the measured brightness B (in foot-lamberts) and the spectral distribution as follows:

$$B(\text{ft-L}) = \frac{680\ \text{lpw}}{A\ (\text{ft}^2)} \int C y \frac{dE}{d\lambda}\, d\lambda = \frac{680 \times 929C}{A\ (\text{cm}^2)} \int y \frac{dE}{d\lambda}\, d\lambda = \frac{680 \times 929CL}{A}$$

Therefore,

$$C = \frac{AB}{680 \times 929L}$$

Since $hc = 1.99 \times 10^{-16}$ erg $= 1.99 \times 10^{-23}$ watt-sec,

$$\frac{Q}{1.99 \times 10^{-23}} \cdot \frac{AB}{680 \times 929L} = \frac{B\,A\,Q \times 10^{17}}{1.26L}$$

Table III. Integrated emission spectra of three phosphors excited in 60μ castor oil cell at 400 cps and 400 v

	Energy $E = \int \frac{dE}{d\lambda} d\lambda$	Quanta $Q = \int \lambda \frac{dE}{d\lambda} d\lambda$	Luminosity $L = \int y \frac{dE}{d\lambda} d\lambda$
Sample No. 1 (red emission)	102.9	77.6	1.36
Sample No. 2 (deep red emission)	166.6	134.8	0.28
ZnS:Cu, Cl (green emission)	472.1	257.0	290.7

Table IV. Output and efficiency of three phosphors excited in 60μ castor oil cell at 400 cps and optimum voltage. Area of cell = 10.8 cm²

	Voltage, v	Brightness, ft-L	Watts	Lumens/watt	Quanta/sec	Quanta/sec watt
Sample No. 1 (red emission)	350	1.1×10^{-1}	6.4×10^{-4}	2.0×10^{-2}	4.3×10^{18}	6.7×10^{21}
Sample No. 2 (deep red emission)	300	7.2×10^{-3}	1.51×10^{-4}	5.6×10^{-3}	2.35×10^{18}	1.55×10^{22}
ZnS:Cu, Cl (green emission)	350	3.66	1.63×10^{-4}	2.6	2.3×10^{18}	1.4×10^{22}

isolated by employing very low or sufficiently high ratios of coactivator to activator. If the broad spectral distribution of the red-emitting phosphors is the result of superimposed emission bands shifted to longer wave lengths but arising from the same centers, then similar variations in activator proportions should also influence the spectral distribution of the red-emitting phosphor in the same manner. Figure 9 shows, however, that this was not observed. The phosphors represented in the figure were prepared in an effort to maintain approximately the same emission color as measured by means of the filter ratio discussed above. This was reasonably successful but required that with increasing coactivator addition, the concentration of Cd+Hg had to be lowered. Nevertheless, the short wave-length emission band increases with such decreasing Cd+Hg concentration and is quite pronounced at a high coactivator concentration such as to result in only the green-emission band in ZnS:Cu phosphors. The increased brightness obtained at higher Br+I addition may now be explained at least partially by the increased slope of the short wave-length side of the emission spectrum.

Discussion

Perhaps the most important question concerning this study is why substitution of Zn by Hg results in good EL at emission colors similar to the photoluminescence emission colors of the respective phosphors, while substitution of Zn by Cd does not. For (Zn, Cd, Hg)S phosphors with a sufficiently high ratio of Cd/Hg so as to effect a decrease in EL, no evidence of a separate (Cu, Cd)S phase (3) could be observed. Therefore, the only clue in this direction is offered by the difference in crystal structure of the two systems.

It has been noted that hexagonal and cubic ZnS:Cu, Cl phosphors prepared with low Cu concentration (such as 0.01 mole %) perform about

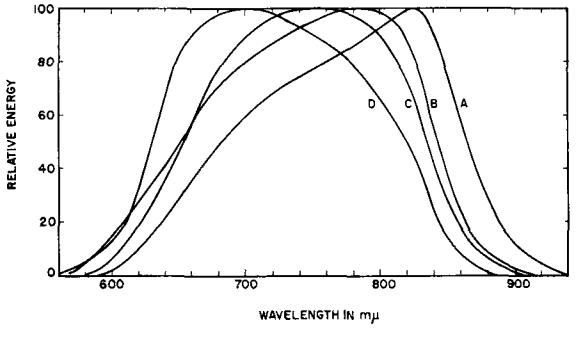

Fig. 9. Emission spectra of (Zn, Cd, Hg)S:Cu phosphors as a function of composition. Excitation = 400 cps. (A), 20.3% Cd, 18.7% Hg, 0.01% Br + 0.01% I; (B), 15.9% Cd, 13.8% Hg, 0.1% Br + 0.1% I; (C), 14.8% Cd, 11.1% Hg, 0.3% Br + 0.3% I; (D), 11.1% Cd, 9.3% Hg, 0.7% Br + 0.7% I.

equally well under artificially induced contact-EL (11). It must therefore be concluded that the better EL performance of cubic (Zn, Hg)S or cubic (Zn, Cd, Hg)S, as compared to the poorer performance of hexagonal (Zn, Cd)S or (Zn, Cd, Hg)S phosphors, results from differences in the means of EL excitation only. In the former case, the field intensifying Cu_2S inclusions are present and active. If in the latter case they are also present, then they are not active, possibly as a result of the different electrical nature of the barrier represented by the nonisomorphic junctions.

The sharp minimum in EL noted at low concentration of Hg is accompanied by a similar minimum of photoluminescence. At present, its appearance can not be explained. Inspection of Fig. 3 shows, however, that the weakly emitting (0.95 Zn, 0.05 Hg)S:Cu, Cl phosphor lacks the secondary hump in reflectivity near the absorption edge. According to an investigation by Froelich (12) the introduction of small amounts of Cu causes just such a hump in the diffuse reflection spectrum of ZnS. This suggests the possibility that at such critically low concentration of Hg, the incorporation of Cu is somehow hindered.

The identity of the long wave-length emission band is questionable since it is favored not by high coactivator concentration (as in ZnS:Cu) but by high Hg concentrations. Bowers and Melamed (13) proposed that the blue emission in ZnS:Cu, Cl may be identified with the "self-activated" blue caused by Zn-vacancies. It now appears that introduction of a sufficient concentration of Hg results in increasing probability that the vacancy becomes a Hg-vacancy. The decreased population of Zn-vacancies would result in the disappearance of the short wave-length band in favor of a different emission band as shown to occur quite abruptly in Fig. 4 and 9. Figure 2 shows that there is also slight evidence that a similar phenomenon occurs with low-Cu photoluminescent phosphors which are sufficiently coactivated so as to give rise to predominantly green (long wave-length band) emission in ZnS.

According to this mechanism, a similar phenomenon should occur on substitution of Zn by Cd. This, however, has not been reported. Instead, Van Gool (14) noted the opposite, namely, a relative increase in the short wave-length emission band of (Zn, Cd)S:Ag phosphors occurring with increasing Cd concentration. These measurements, however, were taken at 77°K while, with increasing temperature, the short wave-length emission band was more rapidly quenched. It is therefore also possible that the increase of relative intensity of the long wave-length emission band with increasing concentration of Hg is caused by increasing thermal quenching of

the short wave-length emission band. The characteristics of the two emission bands in red-emitting (Zn, Hg)S:Cu phosphors are such that at present, no definite conclusions can be drawn as to their origin.

Summary

Introduction of Hg into ZnS:Cu phosphors causes a shift in emission to longer wave lengths which, for moderate substitutions, is about four times as high as that caused by similar molar concentrations of Cd. At sufficient activator concentrations, EL is observed. For compositions emitting in the red end of the spectrum, the quantum efficiency of the EL was found to be of the same order of magnitude as that of green-emitting ZnS:Cu, Cl. This is attributed to the cubic modification of the system, as favored by the presence of HgS, even in ternary (Zn, Cd, Hg)S composition whose concentration of Cd would, in the absence of Hg, result in hexagonal and non-EL systems.

Procedures for the preparation of (Zn, Hg)S and (Zn, Cd, Hg)S EL phosphors have been described. All procedures involve firings with HgS in sealed tubes, using only prefired raw materials. Especially for low-frequency excitation, the substitution of Hg for Zn enables the use of Ga or In as coactivators, presumably due to a decrease in trap depth caused by lowering of the conduction band. For phosphors emitting in the red end of the spectrum, the relative heights of the two emission bands are primarily dependent on Hg concentration. Their identity cannot necessarily be assumed in terms of an analogy with the blue- and green-emission bands in ZnS:Cu phosphors.

From a practical point of view, the (Zn, Hg)S:Cu and (Zn Cd, Hg)S:Cu EL phosphors are preferable to the ZnSe:Cu EL phosphors, mainly because of their better response at low frequencies of excitation, the extent of which can be estimated roughly from Fig. 8. At higher HgS concentrations, EL emission occurring entirely in the infrared has been obtained; the writer does not know to what extent this can be accomplished with (Zn, Cd)Se:Cu EL phosphors. A serious disadvantage is, however, the high volatility of HgS which necessitates special techniques of phosphor preparation.

Acknowledgments

The writer wishes to thank Miss I. Walinski for preparation and brightness measurements of the phosphors, Mr. I. Meister for determinations of spectral distributions, Dr. C. K. Lui-Wei for x-ray diffraction measurements, and Dr. W. Lehmann for determinations of luminous efficiencies. Thanks are also due to Dr. H. F. Ivey for reading and suggesting improvements of the original manuscript.

Manuscript received March 11, 1960. This paper was prepared for delivery before the Chicago Meeting, May 1-5, 1960. This work was supported by Contract AF33(616)-5811 from the Wright Air Development Center.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1961 JOURNAL.

REFERENCES

1. J. S. Prener, U. S. Pat. 2,731,423, Jan. 17, 1956.
2. I. J. Hegyi, S. Larach, and R. E. Shrader, *This Journal*, **104**, 717 (1957).
3. A. Wachtel, *ibid.*, **107**, 602 (1960).
4. L. Wesch, Reichsamt Wirtschaftsausbau Chem. Ber. Investigation No. 15 (PB 52016) pp 487-501 (1942).
5. A. Kremheller and A. K. Levine, *Sylvania Technologist*, **10**, No. 3 (1957).
6. A. Kremheller, A. K. Levine, and G. Gashurov, *This Journal*, **107**, 12 (1960).
7. P. Zalm, *Philips Research Repts.*, **11**, 353 (1956).
8. W. Hoogenstraaten, *This Journal*, **100**, 356 (1953).
9. C. Haake, *J. Opt. Soc. Am.*, **47**, 881 (1953).
10. H. A. Klasens, *This Journal*, **100**, 72 (1953).
11. W. Lehmann, *ibid.*, **104**, 45 (1957).
12. H. C. Froelich, *ibid.*, **100**, 496 (1953).
13. R. Bowers and N. T. Melamed, *Phys. Rev.*, **99**, 1781 (1958).
14. W. Van Gool, *Philips Research Repts.*, **13**, 157 (1958).

Crater Resistance of Submerged Arc Smelting Furnaces Simulated by a Simple Model

Oluf Chr. Bockman

Elektrokemisk A/S, Oslo, Norway

ABSTRACT

An electrolytic trough technique has been used to study the effect of size and shape of the smelting crater on the ohmic resistance of the crater of submerged arc smelting furnaces. The ohm-inch rule is demonstrated, and the correct use of this rule is discussed.

In designing submerged arc smelting furnaces, the anticipated ohmic crater resistance of the projected furnace is the key to the specification of the electrical circuit. Naturally, many workers have devoted themselves to the study of this problem. In 1933, Andrea pointed (1) out that the product of electrode diameter D and crater resistance R of electric smelting furnaces is fairly independent of furnace size. He defined a "peripheral ohm inch factor" r by

$$r = \pi DR \qquad [1]$$