over Drierite. After removal of the ether at atmospheric pressure, 10 ml. of nitrobenzene was added and the solution was refluxed twenty minutes. After removal of the nitrobenzene by distillation at reduced pressure the residue was taken up in dilute ethanol. This solution deposited dark red crystals after standing three days in a refrigerator. After six crystallizations from 95% ethanol 0.5 g. (4%) of pale yellow needles melting at 97.5–98° was obtained. A mixed melting point with the product obtained from Method A was not depressed.

5-Trimethylsilyl-2-furylglyoxal Monohydrate.—Seven grams (0.064 mole) of freshly sublimed selenium dioxide[9] and 9 g. (0.064 mole) of 2-acetyl-5-trimethylsilylfuran[7] in aqueous dioxane were stirred at reflux for two hours. The mixture was worked up in a manner similar to that described for the thienylglyoxal. The yield of yellow oil boiling at 71° (0.6 mm.) was 5.0 g. (40%). This compound quickly darkens and solidifies on standing at room temperature under nitrogen.

A portion of the glyoxal was boiled with ten times its volume of water and the resulting solution was decolorized with Norit. The filtrate deposited white gelatinous flocs of the hydrate on cooling which melted at 108–114°[10] after crystallization from dilute ethanol.

Anal. Calcd. for $C_9H_{12}O_3Si \cdot H_2O$: C, 50.5; H, 6.5. Found: C, 50.6; H, 6.05.

2-(5-Trimethylsilyl-2-furyl)-quinoxaline.—This was prepared by Method A described for the corresponding thiophene derivative. It melted at 63–64°.

Anal. Calcd. for $C_{15}H_{16}ON_2Si$: C, 67.1; H, 6.0; N, 10.45. Found: C, 67.1; H, 6.2; N, 10.42, 10.68.

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Summary

2-Acetyl-5-trimethylsilylthiophene and 2-acetyl-5-trimethylsilylfuran have been oxidized to the corresponding glyoxal by selenium dioxide. It is noteworthy that the silicon–carbon bond in these compounds was essentially unaffected by the oxidizing agent.

The glyoxals formed hydrates and quinoxaline derivatives. 2 - (5 - Trimethylsilyl - 2 - thienyl)-quinoxaline was also prepared in low yield by the addition of 5-trimethylsilyl-2-thienyllithium to the anil linkage of quinoxaline.

LAFAYETTE, INDIANA RECEIVED FEBRUARY 14, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Effect of Activator Concentration on the Infrared-sensitive Phosphor, Strontium Selenide–Samarium, Europium[1,2]

BY HILDA TEXIN, HARRY WILLIAMS[3] AND ROLAND WARD

The brightness of the excited strontium sulfide–samarium, europium phosphor under constant infrared stimulation has been shown to be dependent upon the activator concentrations. Definite and reproducible maxima were observed in the curves relating the brightness with increasing concentrations of one activator, the concentration of the other activator being held constant.[4] Attempts to achieve similar results with the analogous strontium selenide phosphor were not immediately successful and for some time it was thought that there was an inherent difference in the selenide and sulfide phosphors. This paper describes some of the factors which influence the luminescent properties of the selenide phosphor and also gives an empirical method by which the brightness–activator concentration relationship can be established.

The preparation of strontium selenide for use as a phosphor material has been described.[5] In the experimental work reported here, strontium chloride was used as the flux in the conversion of the selenide to the phosphor. It was found that constant brightness values were obtained when the phosphor mixtures were heated at 1050° for one hour or longer. Some modifications were made in the procedure for the preparation of strontium selenide and, perhaps as a result of these improvements, it was no longer found necessary to add any sulfide to produce a sensitive phosphor.

Experimental

In all of this work we have had to depend upon making reproducible samples of the phosphor from a specific sample of strontium selenide. The solid ingredients of the phosphors were weighed and mixed in a dry-box but were exposed to the atmosphere of the laboratory for a short time during the molding of the sample. The reproducibility was usually within about 5%.

It has already been pointed out[5] that samples of strontium selenide prepared at different times frequently showed differences in brightness, time lag[5a] and phosphorescence. While it was suspected that most of these differences were due to the presence of varying amounts of oxide in the final phosphor, a search was made for other con-

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[1] This work was performed under Contract NObsr 39045 of the Bureau of Ships with the Polytechnic Institute of Brooklyn.

[2] Abstracted in part from a thesis submitted to the Graduate School of the Polytechnic Institute of Brooklyn by H. Williams in partial fulfillment of the requirements for the degree of Master of Science, 1948.

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[4] K. F. Stripp and R. Ward, THIS JOURNAL, **70**, 401 (1948).

[5] A. L. Smith, R. D. Rosenstein and R. Ward, *ibid.*, **69**, 1725 (1947).

[5a] "Time Lag" is an expression for the number of seconds that elapse between the time that the stimulating infrared light is turned on the phosphor until the brightness of the phosphor reaches maximum intensity. It decreases with increasing intensity of the infrared radiation.

taminants. Qualitative spectrographic analysis revealed the presence of calcium, magnesium and silicon.

The most obvious source of the latter is the silica boat in which the strontium selenite is reduced. Examination of the sintered block of strontium selenide under ultraviolet radiation showed that the areas which had been in contact with the silica boat were fluorescent. When the fluorescent regions were removed by scraping, the remaining selenide gave a phosphor which showed much shorter time lag on stimulation.

To corroborate this, a series of phosphors of composition expressed as parts by weight 100 SrSe (0.005 Eu, 0.015 Sm) 10 $SrCl_2 + xSr_2SiO_4$ were prepared as previously described.[4] The data in Table I, show that the presence of silicate in the mixture not only increases the time lag but also lowers the brightness of the phosphor.

TABLE I

THE EFFECT OF STRONTIUM SILICATE ON THE PROPERTIES OF THE MIXTURES 100SrSe(0.005 Eu, 0.015 Sm)10 $SrCl_2$ + x Sr_2SiO_4

Selenide sample	x	Brightness	Time lag, sec.
Silicate film not removed	0	2200	55
	0.5	1680	90
	1.0	1390	120
	2.0	1000	150
	6.0	~500	...
Silicate film removed	0	2645	35
	0.5	2215	80
	1.0	1860	105

It is quite obvious that contamination with silica should be avoided but no suitable container in which to reduce the strontium selenite has been available to us. Spectroscopically pure graphite was tried but was found to give a very poor selenide. The present procedure is to use silica boats and to remove all fluorescent particles by scraping with a porcelain spatula. Lest any silica be introduced by the use of ammonia solutions which had been stored in glass bottles, all the ammonium hydroxide used in the purification process is now freshly prepared.

The reduction of strontium selenite to selenide with ammonia at 830° gives close to theoretical weight loss. It was found, however, that an additional loss of about 0.12% was usually obtained on heating the selenide so obtained at 1000° in dry hydrogen. Somewhat more uniform phosphors were obtained by this treatment which apparently results in the reduction of some residual strontium selenite. The effect of addition of strontium selenite to the phosphor mixture was therefore tested with the results shown in Table II. Selenide samples 1 and 2 were prepared from different batches of strontium selenite. They were both given the additional heating in hydrogen at 1000°. Sample 3 was from the same strontium selenide preparation as 2 but had not been further treated with hydrogen. When strontium selenide samples 2 and 3 were tested by addition of silicate as previously described they each showed about the same increase in time lag and decrease in brightness. The reproducibility of phosphors prepared from the same and from different strontium selenite batches was tested using the procedures just described to avoid contamination of the samples with silicate or selenite. The phosphor samples were all heated for one hour at 1050°.

TABLE II

THE EFFECT OF STRONTIUM SELENITE ON THE BRIGHTNESS OF THE PHOSPHOR 100 SrSe(0.005 Eu, 0.015 Sm)10 $SrCl_2$ x $SrSeO_3$

Selenide sample	x	Brightness
1	0	2390
	0.3	1720
	0.45	1415
2	0	2820
	0.25	1340
	0.50	825
3	0	2645
	0.25	1330

The results shown in Table III are typical. They indicate that an occasional wide deviation in brightness is likely to be obtained due to faulty preparation of the phosphor sample. These values marked with an asterisk indicate such samples and if they are discarded, the deviation of the other values from the average of their group is, in all cases but one, less than 10%. Upon this basis it can be seen that quite close agreement can be obtained in results from two different selenide preparations. (The average brightness values of phosphors from samples 1 and 2 agree within 2.5% and those from 3 and 4 within 7%). The average brightness values of the phosphors from 3 and 4, however, are about 40% higher than those from 2 and 3.

TABLE III

TEST OF REPRODUCIBILITY OF PHOSPHORS 100 SrSe (0.005 Eu, 0.015 Sm)10 $SrCl_2$ MADE FROM DIFFERENT STRONTIUM SELENITE PREPARATIONS

Selenite	Brightness	Average	% Deviation from average
1	2280		− 6
	2410		− 0.6
	2685*		+11
	2320	2424	− 4
2	2370		− 3
	2220		− 9
	1785*		−27
	2320		− 5
	2640		+ 8
	3285*	2437	+30
3	3175		
	3380	3278	+ 3
4	3775		+13
	3310		− 0.5
	3630		+ 9
	3320		− 0.2
	2600*	3327	−22

A quantitative spectrographic analysis of the strontium nitrate used for the precipitation indicated the presence of about 20 to 50 parts per million of calcium ion. By three recrystallizations of the nitrate, the calcium content was lowered to about 10 parts per million. Further recrystallization did not improve the product.

The recrystallization of the strontium nitrate was effected by evaporation of the purified strontium nitrate solution to incipient crystallization and by distilling into this solution nitric acid from a glass-still fitted with a silica condenser. Two lots of strontium selenite which had been precipitated from thrice recrystallized strontium nitrate were converted to selenide. From each of these selenide preparations a series of phosphors was prepared with increasing quantities of calcium ions incorporated in the flux as calcium chloride. The brightness values of these phosphors are given in Table IV.

TABLE IV

THE EFFECT OF CALCIUM IONS ON THE BRIGHTNESS OF THE PHOSPHORS 100 SrSe(0.005 Eu, 0.015 Sm)10 $SrCl_2$ x Ca^{2+}

Concentration of Ca^{2+} (parts per million)		0	10	100	1000	10000
Brightness	Series 1	1785	1960	1785	1660	1540
	Series 2	2640	2870	2100	2100	1990

It can be seen that the addition of 0.1 to 1% of calcium unquestionably lowers the brightness of these phosphors but that quantities of the order of 10 parts per million cause an apparent increase in brightness which, however, is within experimental error.

The density of the magnesium lines in the spectrum from the recrystallized strontium nitrate was not sufficient to give precise information as to the concentration of magnesium except that it is less than 0.01%. Series of phosphors containing magnesium, prepared in the manner described for the calcium tests, did not give satisfactory results due apparently to some interaction of magnesium chloride and strontium selenide. Some of the results indicated that the effect of magnesium was similar to that of calcium.

We infer from these results that the presence of calcium and magnesium in the small amounts found in our strontium selenite could not cause the large differences among the phosphors and are forced to conclude that the disparity is due to small differences in the amount of oxide introduced during the reduction of the selenite or by hydrolysis of the selenide at a later stage. It is conceivable that the physical character of the strontium selenite determines the extent of hydrolysis.

During the course of an attempt to study the effect of changes of activator concentration on the brightness of the selenide phosphor, it was found that one series of samples gave unexpected results. These results were, moreover, analogous to those found for the sulfide phosphor[4] where the addition of a small amount of strontium oxide to the phosphor mixtures gave rise to an increase in brightness. The data are given in Table V.

TABLE V

THE EFFECT OF ACTIVATOR CONCENTRATION AND OXIDE UPON THE BRIGHTNESS OF THE PHOSPHOR 100 SrSe (xEu ySm)10 $SrCl_2 \cdot zSrO$

Activator concentration Eu	Sm	Brightness No oxide	0.5 oxide
0.005	0.015	1200	3600
.010	.030	750	3500
.020	.060	600	2100
.040	.120	200	. .

The difference between this series and the others was traced to the presence of ammonium chloride in the strontium chloride. It was apparent that the ammonium chloride was reacting with the strontium oxide according to the equation $2NH_4Cl + SrO \longrightarrow 2NH_3 + H_2O + SrCl_2$. To test this, several mixtures of strontium oxide, ammonium chloride and strontium chloride were heated to-

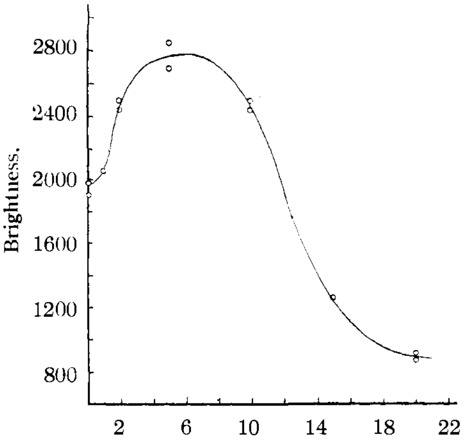

Fig. 1.—Brightness of the phosphor 100 SrSe (0.005 Eu, 0.015 Sm) 10 $SrCl_2$ with the addition of varying amounts of NH_4Cl.

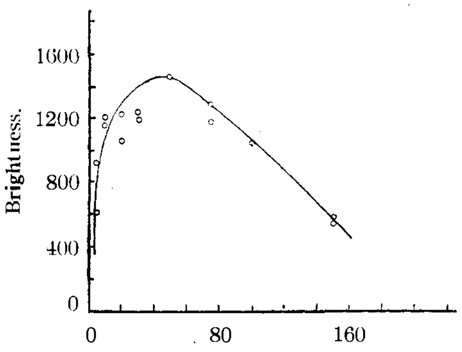

Fig. 2.—Brightness of the phosphor 100 SrSe 10 $SrCl_2$ [0.5 NH_4Cl] with constant concentration of Eu (0.001) and varying concentrations of Sm.

gether below red heat and then at a higher temperature to remove the excess ammonium chloride. The residual oxide was determined by titration with standard acid. The results are given in Table VI, and they show that the reaction occurs to a greater extent in the presence of strontium chloride. It was also found that ammonium chloride is not completely removed from strontium chloride upon fusion. For two different selenide samples, the change in brightness caused by the addition of strontium oxide and by the simultaneous addition of strontium oxide and ammonium chloride is shown in Table VII.

TABLE VI

EXTENT OF REACTION OF SrO WITH NH_4Cl IN PRESENCE OF $SrCl_2$

SrO	Composition of mixture, g. NH_4Cl	$SrCl_2$	Residual SrO, g.	% SrO removed
0.7595	2.5798	....	0.195	74
1.0218	2.6420	2.8007	.121	88
0.8343	2.1504	2.8977	.050	95

TABLE VII

THE EFFECT OF OXIDE AND AMMONIUM CHLORIDE ON THE BRIGHTNESS 100 SrSe(0.005 Eu, 0.015 Sm)10 $SrCl_2$ x SrO [$y$$NH_4Cl$]

x	y	Brightness Series I	Brightness Series II
0	0	3050	850
.5	0	1800	450
.5	.5	2900	1180

It can be seen that the introduction of ammonium chloride essentially counteracts the lowering of brightness caused by the introduction of oxide. These facts along with the knowledge that strontium oxide is much more soluble in strontium chloride than is the selenide[6] establish reasonably well the useful function served by the ammonium chloride in the preparation of strontium selenide phosphors.

The brightness values were determined for a series of phosphors: 100 SrSe (0.005 Eu, 0.015 Sm) 10 $SrCl_2$[$x$$NH_4Cl$] where x varies from 0 to 2 g. The results are shown in Fig. 1 from which it would appear that at least 2 g. of ammonium chloride per 100 g. of strontium selenide would be required to remove most of the oxide. The phosphor samples, however, containing more than 0.5 g. of ammonium chloride per 100 g. of strontium selenide showed a tendency to crack when heated so that the specimens were unsuitable for optical measurement.

Nevertheless, an attempt was made to investigate the dependence of brightness on activator concentration using mixtures 100 SrSe (xEu, ySm) 10 $SrCl_2$ 0.5 NH_4Cl. The results obtained for a series of constant europium contours are given in Figs. 2 to 6 and from these it is possible to construct the rough contour diagram shown in Fig. 7. The latter appears to indicate that the brightest phosphor is obtained with about 30 micrograms of europium per gram of strontium selenide and about three times as much samarium.

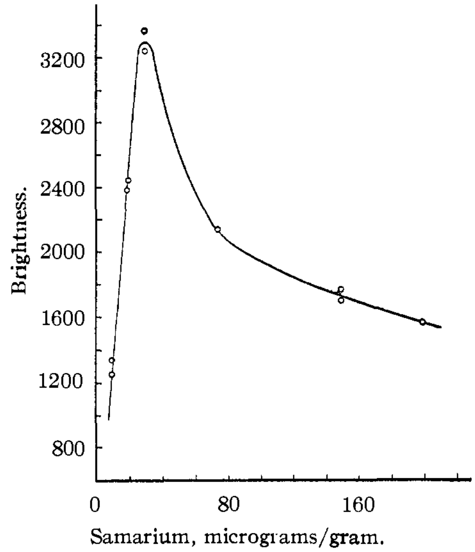

Fig. 3.—Brightness of the phosphor 100 SrSe 10 $SrCl_2$ [0.5 NH_4Cl] with constant concentration of Eu (0.002) and varying concentrations of Sm.

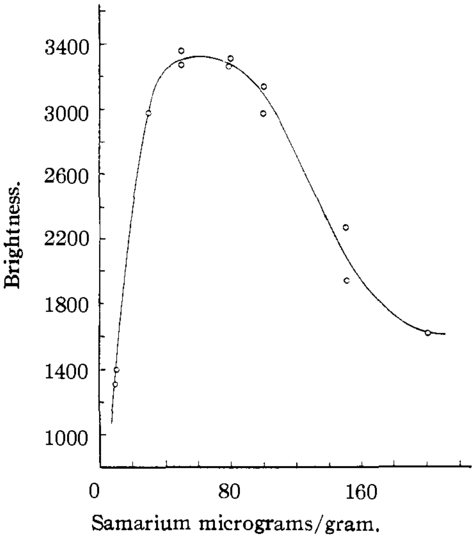

Fig. 4.—Brightness of the phosphor 100 SrSe 10 $SrCl_2$ [0.5 NH_4Cl] with constant concentration of Eu (0.0025) and varying concentrations of Sm.

While these results must be regarded as semiquantitative at the best, they serve to indicate that the optimum concentrations of europium and samarium in the strontium selenide phosphor are about the same as for the strontium sulfide phosphor.[4] The higher concentration of samarium found necessary in these experiments is undoubtedly due to the presence of some residual oxide. It has recently been shown that the distribution

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[6] R. W. Mason, C. F. Hiskey and R. Ward, THIS JOURNAL, **71**, 509 (1949).

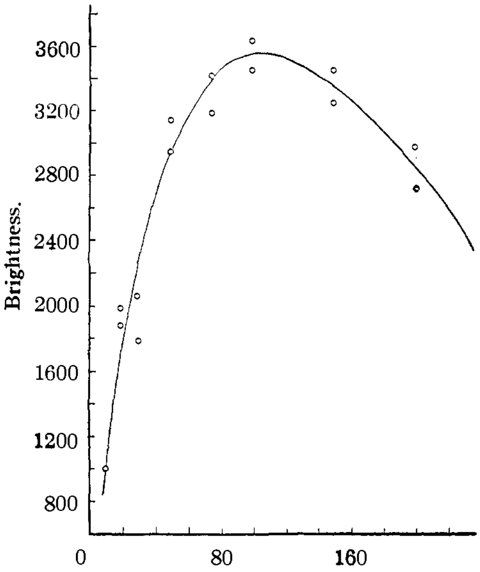

Fig. 5.—Brightness of the phosphor 100 SrSe 10 $SrCl_2$ [0.5 NH_4Cl] with constant concentration of Eu (0.0035) and varying concentrations of Sm.

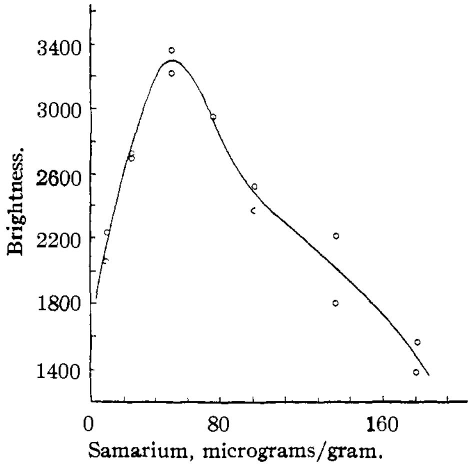

Fig. 6.—Brightness of the phosphor 100 SrSe 10 $SrCl_2$ [0.5 NH_4Cl] with constant concentration of Eu (0.005) and varying concentrations of Sm.

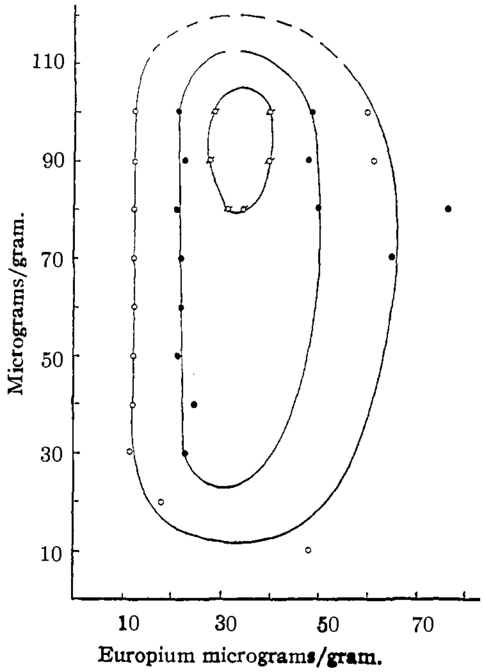

Fig. 7.—Contour diagram relating brightness to variation in composition of activators in the phosphor 100 SrSe (x Eu, y Sm) 10 $SrCl_2$ [0.5 NH_4Cl]; brightness: ○, 2000; ●, 3000; ⌀, 3400.

of samarium between the molten strontium chloride and the solid strontium selenide is extraordinarily sensitive to the presence of oxide while the distribution of europium is changed but little.[7] It may be possible to devise a technique by which satisfactory samples can be prepared using enough ammonium chloride to remove essentially all of the oxide from strontium selenide. As it stands, the procedure is quite empirical.

Summary

Some improvements have been made in the procedure for making pure strontium selenide. It has been shown that the presence of strontium selenite and strontium silicate affect the luminescent properties of strontium selenide–europium, samarium phosphors. Small amounts of silicate cause an increase in the time lag of the phosphors under infrared stimulation.

By using ammonium chloride to remove oxide which invariably is present in the phosphors, it has been possible to study the effect of activator concentrations upon the brightness of the strontium selenide–europium, samarium phosphor. The effect has been shown to be similar to that found in the strontium sulfide–europium, samarium phosphor.

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(7) Prener, Mason and Ward, THIS JOURNAL, 71, 1803 (1949).