very low, and it is not impossible that absolutely pure chromous chloride would not react at all.

A solution of mixed phenylchromium halides, prepared according to Hein,[11] failed to yield any detectable carbonyl after treatment with carbon monoxide under pressure. On the basis of this negative result, and our experience with chromous chloride, we venture the opinion that none of the mechanisms proposed in the literature for the formation of chromium carbonyl is correct.

Acknowledgment.—The authors express their gratitude to Mr. J. F. Sweeney of the Struthers

Wells Corporation for the loan of high pressure equipment, and to Drs. P. G. Stevens and E. W. Fager for experimental assistance at the beginning of this work.

Summary

A procedure is described by which a 60% yield of chromium hexacarbonyl may be obtained by the action of carbon monoxide upon phenylmagnesium bromide and chromic chloride. The results obtained by some alternative procedures are discussed.

NEW HAVEN, CONNECTICUT

The Preparation of Strontium Selenide and its Properties as a Base Material for Phosphors Stimulated by Infrared[1,2]

BY ARTHUR L. SMITH,[3] R. D. ROSENSTEIN AND ROLAND WARD

Alkaline earth selenide phosphors have been reported by Pauli,[4] Kittleman,[5] Lenard, Tomaschek and Schmidt.[6] They prepared the selenides by heating a mixture of either the oxide or the carbonate with selenium at a high temperature in a specially constructed furnace. These workers were aware that poor yields of selenide were obtained by this procedure. Lenard[6] drew attention to the harmful effect of the presence of "inactive material" in strontium selenide activated with samarium, although Kittleman[5] stated that it did not affect the quality of the phosphors activated with other ions.

Methods for the preparation of alkaline earth selenides in reasonably pure condition have been known since the time of Berzelius. Fabre[7] and Henglein and Roth[8] obtained the selenides by reducing the corresponding selenates with hydrogen at red heat. The latter authors gave the temperatures at which reaction begins and claimed yields of 95 to 98% of theoretical. Slattery[9] prepared strontium and barium selenides for X-ray studies from the selenites by a similar process.

None of these investigators was concerned with the use of the alkaline earth selenides as phosphors.

This paper describes some further studies on the preparation of strontium selenide from strontium selenite and the preparation of infrared-stimulated phosphors from the pure selenide.

Experimental

A. Preparation of Pure Strontium Selenide.—Since the presence of metallic ions in concentrations less than 1 part per million may have profound effects upon the luminescent properties of phosphors, it is necessary to eliminate these impurities as completely as possible. The following procedure has been found to be adequate.

Reagent grade chemicals were used as source materials and all of the water was twice distilled, the second distillation being carried out in Pyrex stills.

A slurry of 2.2 kilos of strontium carbonate with one liter of distilled water is made in a 12-liter flask and 1825 to 1850 ml. of concentrated nitric acid is introduced slowly. Fifteen ml. of concentrated sulfuric acid is added to precipitate most of the barium and the mixture is boiled. The hot solution (pH about 6) is treated for thirty minutes with tank hydrogen sulfide, which is previously passed through barium hydroxide solution. The precipitate is allowed to settle and the solution is filtered. All of the filtering is accomplished, as illustrated in Fig. 1A, by drawing the solution into an evacuated flask through fritted glass filters which are protected with filter paper pulp. This technique serves to prevent contamination by dust particles.

The filtrate is treated with 100 ml. of saturated ammonium oxalate solution to remove calcium and the pH adjusted to 7 with ammonium hydroxide. The mixture is boiled and while still hot is treated with hydrogen sulfide, allowed to stand overnight, and filtered. The filtrate is acidified with nitric acid to a pH of 3. A slight excess of bromine (about 5 ml.) is added to oxidize any iron or manganese which remains at this point, and the solution is boiled till the excess bromine is removed. Ammonium hydroxide is again added until the pH is 8 when the solution is further treated with hydrogen sulfide and filtered after standing for several hours. The filtrate is again acidified to a pH of 3 with nitric acid, boiled and filtered. This solution of strontium nitrate is sufficiently free from heavy metal impurities to be used for the preparation of the phosphors.

Baxter[10] found that four successive crystallizations of strontium nitrate effectively eliminates heavy metal impurities. The supernatant liquid was removed from the crystals by decantation. Fused quartz and Vycor flasks were used rather than platinum, which seemed to introduce copper. This procedure is not so convenient as the method just described for the purification of large amounts of materials.

Selenium dioxide may be purified by a series of sublimations in an apparatus previously described.[11] The selenium dioxide is dissolved without handling by placing the wide end of the sublimate receiver tube in distilled water and drawing the water into the tube by applying suction at the narrow end. The stoichiometric quantity of selenious acid solution is added to the hot purified strontium nitrate solution and the mixture is rendered alkaline with ammonium hydroxide. The strontium selenite precipitate is washed six times using a liter of hot water each time. The wash water is removed through a fritted glass filter stick as shown in Fig. 1B. The selenite so obtained should be free from nitrate. It is dried in a Pyrex beaker for twenty-four hours at 200°.
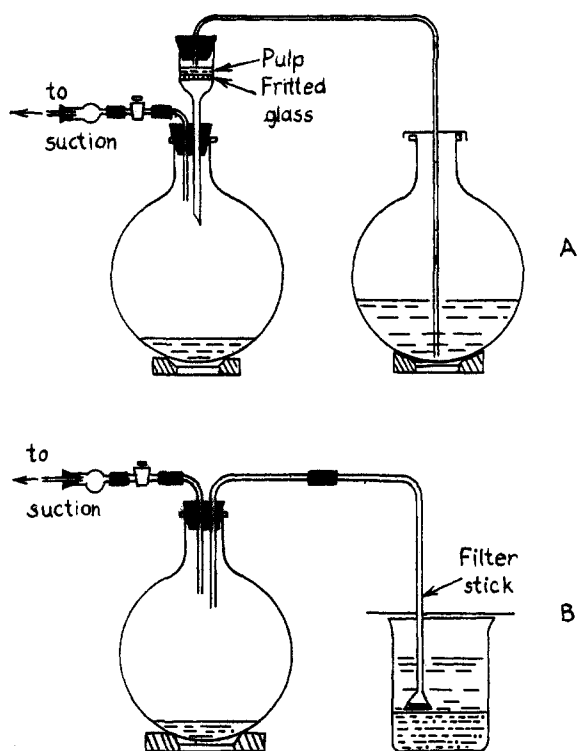

Fig. 1.

The dry strontium selenite is reduced to the selenide by heating in an atmosphere of ammonia at 860°. A Globar type tube furnace with a silica glass combustion tube is convenient for this operation. The selenite is placed in a silica glass boat of about 350 g. capacity and is pushed into the combustion tube through which nitrogen is flowing. Ammonia from a tank is then passed through the tube at 2 to 3 liters per minute. After three hours, the selenite should be completely reduced to selenide. The boat is moved to the end of the tube where it is allowed to cool before removing it from the furnace. The product contains from 98 to 99.7% strontium selenide.

When hydrogen was used for the reduction of the selenite in the manner described by previous investigators,[7,8,9]

(10) G. P. Baxter, private communication, 1943.

(11) J. Pitha, J. Chem. Ed., 23, 403 (1946).

there was in most cases an appreciable amount of selenium evolved. The use of small samples previously dried in nitrogen at 600° and reduced with oxygen-free hydrogen at temperatures below 575 to 650° were found by Baxter[10] to give weight losses of only about 0.09 to 0.17% in excess of 22.37%, the theoretical weight loss for the conversion of anhydrous strontium selenite to strontium selenide.

With such procedures, however, the rate of reaction is too slow for practical purposes. Experiments were therefore made to ascertain the losses which might result from working at a higher temperature. Samples came to constant weight in undiluted hydrogen in from one to two hours, depending on the amount of selenite. Weight losses were obtained of 23.7 ± 1% at 730° (two experiments); 800°, 22.6% with selenite fused before reduction as compared to 23.0% with ordinary selenite; 23.8 ± 0.1% at 820° (three experiments); 23.6 ± 0.4% at 830° (seven experiments); and at 1000° (one experiment), 25.8%. With hydrogen diluted by nitrogen, a weight loss of 22.4% was obtained at 800° in eleven hours. Using ammonia, constant weight was obtained in two to three hours, giving weight losses of 21.7 ± 0.1% at 730° (two experiments); 22.3 ± 0.2% at 780° (four experiments); 22.3 ± 0.1% at 800° (two experiments); 22.4 ± 0.02% at 860° (one hundred experiments); and 24.4% at 1000°. It will be seen that the reduction with hydrogen, except when the selenite had been fused before reduction or when the hydrogen was diluted with nitrogen, leads to weight losses about 1% in excess of theoretical which corresponds approximately to the formation of about 4% strontium oxide.

Representative samples of strontium selenide prepared by the use of hydrogen and ammonia were analyzed by selenium determination. The results were in substantial agreement with those predicted from the weight loss. Reduction with hydrogen gave products containing 96 to 98% strontium selenide while with ammonia 99 to 99.7% was found.

It was found that carbon monoxide is quite unsuitable for the reduction of strontium selenite at all temperatures between 460 and 860°. Profuse quantities of selenium are liberated.

Even with ammonia as reducing gas some side reactions occur. A small amount of selenium is evolved which may be due to the reaction of some selenide with the water produced in the reaction

$$2NH_3 + SrSeO_3 \longrightarrow SrSe + 3H_2O + N_2$$
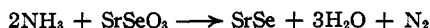
On the cool portion of the reaction tube is deposited a small amount of black material which sometimes detonates when the boat is pulled over it. It seems likely that the deposit contains N_4Se_4.[12,13] The explosion is not hazardous.

Attempts to prepare pure calcium selenide by these procedures were usually quite unsuccessful. The final products contain as little as 60% calcium selenide and seldom more than 80%.

B. Preparation of Strontium Selenide Phosphors.— The procedures for the preparation of phosphors from pure strontium sulfide have been described.[14,15] The "Standard VI" phosphor discovered by Urbach,[14] for example, may be prepared by heating a mixture of pure strontium sulfide at 1000° in nitrogen with about 12% of its weight of a mixture of equal weights of calcium fluoride and strontium sulfate to which samarium and europium salts have been added. The concentration of the samarium and europium which are the activators is of the order of 200 parts per million of the strontium sulfide. The composition of this phosphor may be represented by the notation

$$100SrS(0.020Sm,0.020Eu)(6SrSO_4,6CaF_2)$$
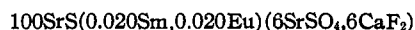
(12) Van Valkenburgh and Bailar, THIS JOURNAL, 47, 2134 (1925).

(13) Strecker and Claus, Ber., 56, 362 (1923).

(14) F. Urbach, D. Pearlman and H. Hemmendinger, J. Optical Soc. Am., 36, 372 (1946).

(15) W. Primak, R. K. Osterheld and R. Ward, THIS JOURNAL, 69, 1283 (1947).

When strontium selenide was substituted for strontium sulfide the phosphor produced by the same treatment had a dim yellow-green emission when excited by blue light and stimulated by infrared. It was found, however, that the mixture 100SrSe(0.20Sm,0.020Eu)(6SrSO₄,6-CaF₂) gave rise to a very sensitive phosphor which had a yellow emission on stimulation with infrared. The introduction of strontium sulfite instead of the sulfate indicated that the increase in sensitivity was due to the presence of a small amount of sulfide in the final product since strontium sulfite decomposes at the firing temperature according to the equation

$$4SrSO_3 \longrightarrow 3SrSO_4 + SrS$$
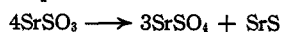
The mixture 100SrSe + 5SrS (0.020Sm,0.020Eu)(6-SrSO₄,6CaF₂) was found to give a product resembling that obtained by use of strontium sulfite. For the sake of brevity, this phosphor is referred to as the strontium selenide phosphor, SrSe(Sm,Eu), even when small amounts of sulfide or other impurities have been added.

The stimulation spectrum, given in Fig. 2, represents the sensitivity of the 100SrSe + 5SrS(0.02Sm,0.02-Eu)(6CaF₂,6SrSO₄) phosphor to the infrared spectrum in terms of its brightness response, measured with a Beckman quartz spectrophotometer. Figure 3 shows the emission spectrum of the stimulated phosphor, obtained by photographing the spectrum with a Hilger Constant Deviation spectrometer and analyzing the spectrograms with a Leeds and Northrup recording microphotometer. The peaks of the stimulation and emission bands lie at
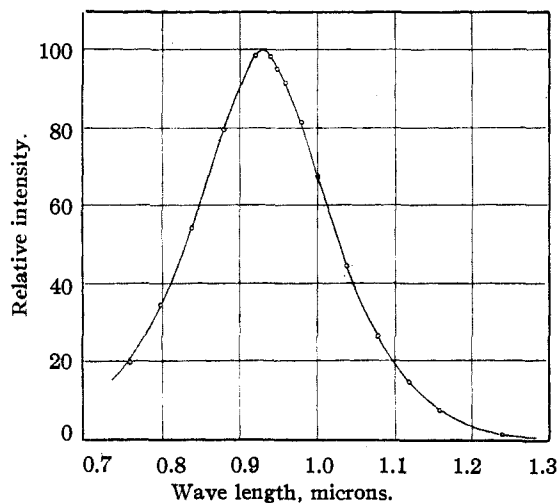
0.93 and 0.59 micron, while those for the Standard VI appear at 1.02 and 0.63 microns.[14] The shift of the emission spectrum to the yellow afforded about 10-fold advantage over the Standard VI phosphor in observation with scotopic vision.

The Standard VI phosphor when excited by ultraviolet radiation has an orange phosphorescence or background, part of which is due to a line emission attributed to the samarium. The same lines are obtained with the SrS(Ce,-Sm) phosphor. The SrSe(Sm,Eu) phosphor on the contrary does not show this line emission, the phosphorescence spectrum being the same as the emission spectrum.

Many activator pairs were tried with the strontium selenide base material. These were prepared by heating mixtures, SrSe(A+B)(SrSO₃,CaF₂) at 1000° in nitrogen. A and B represent the two activators. The pairs which were found to yield infrared-stimulated phosphors are listed in Table I. Of these activators only the europium

TABLE I

ACTIVATORS WHICH PRODUCE INFRARED-SENSITIVE PHOSPHORS WITH SrSe

Activator pair	Fluorescence	Phosphorescence	Infrared activity	Color of emission
Bi–Mn	Yellow	Yellow	Very weak	....
Bi–Pb	Orange	Orange	Very weak	....
Cu–Bi	Yellow-green	Orange-yellow	Weak	Green
Cu–Pb	Blue-green	Green ·	Weak	Green
Eu–Pb	Orange	Blue	Weak	Orange
Eu–Bi	Yellow	Yellow	Strong	Yellow ·
Sm–Bi	None	None	Weak	Green
Sm–Ce	Blue	None	Weak	Green

and bismuth pair was noteworthy. The stimulation spectrum for this phosphor is shown in Fig. 4. It shows the overlapping double band which seems to be characteristic of bismuth.[14]
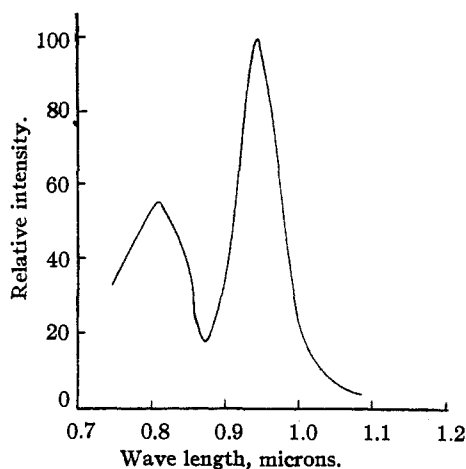

Fig. 2.—Stimulation spectrum of 100SrSe + 5SrS-(0.020Sm,0.020Eu)(6SrSO₄,6CaF₂).

Fig. 3.—Emission spectrum of 100SrSe + 5SrS(0.020 Sm,0.020Eu)(6SrSO₄,6CaF₂).

Fig. 4.—Stimulation spectrum of 100SrSe(Bi,Eu)(6SrSO₃,-6CaF₂).

In the strontium sulfide system, the most sensitive phosphor so far discovered is Urbach's Standard VII.[14] It contains the activator pair cerium and samarium. These activators in strontium selenide give a phosphor of very low infrared sensitivity.

C. The Influence of Small Changes in Composition of SrSe(Sm, Eu) Phosphor Upon Its Sensitivity to Infrared.—The preparation of samples for an investigation of this kind calls for the exercise of some care since contamination from the container during the fluxing operation can readily occur. A fairly satisfactory procedure is to mold the intimate mixture of activated flux and base material in the form of a disc in a hydraulic press. This disc is placed on a pressed magnesium oxide slab in a platinum or

fused silica boat and is fluxed in a stream of oxygen-free nitrogen in a fused silica tube at 1000° for about fifteen to thirty minutes. The sample is allowed to cool in the nitrogen.

An apparatus described by Ellickson and Parker[16] was used to measure the light emitted by the fully excited phosphor under constant infrared radiation. The light from the phosphor is focused by means of a spherical mirror on an R. C. A. 931A electron multiplier tube. The anode current in the multiplier tube is measured directly on a galvanometer. The relative brightness of different phosphor samples under the same infrared intensity is taken as proportional to the galvanometer deflection.

A standard procedure[16] was adopted in measuring different preparations. The phosphor sample was placed in the holder and fully excited by five minutes exposure to light from a tungsten lamp. The red and infrared radiation was eliminated from the exciting light by means of Corning 3962 and 4308 filters. The intensity of illumination was greater than 210 foot-candles without filters. Upon removal of the exciting light, the aperture of the photocell was opened and the galvanometer deflection due to the phosphorescence of the sample was observed until it fell to a negligible value. This usually occurred within two or three minutes. The infrared source was turned on five minutes after excitation and the maximum galvanometer deflection was taken as a measure of the brightness. The intensity of the infrared radiation was maintained constant for all readings. The intensity of the source was such as to give an illumination of about 4×10^{-4} lumens/sq. cm. at the sample without filter.

In most samples of the SrSe(Sm,Eu) phosphor, the brightness does not reach its maximum value until some time after the stimulating light has been turned on. Typical runs on two samples are shown in Fig. 5. The stimulating intensity was about 0.1 foot candle filtered through one thickness of XR7X25. In these cases, it took about one minute for the brightness to reach a maximum. The time lag increases as the intensity of stimulation is decreased and is hardly noticeable when the samples are examined under a high intensity of stimulation. The relative brightness values given in the table refer to the maximum intensity.
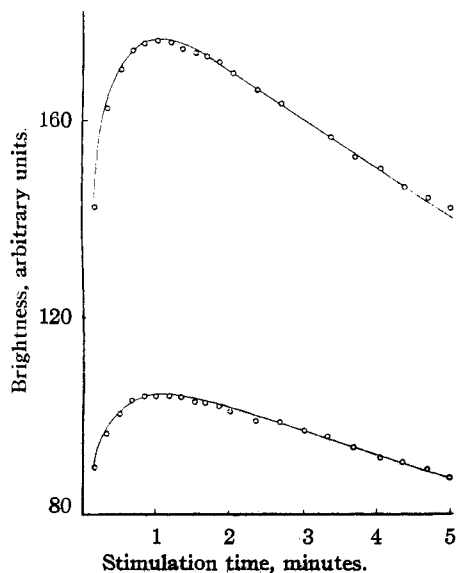

Fig. 5.—Time lag of stimulated emission of 100SrSe (0.020Sm,0.020Eu)(6SrSO₄,6CaF₂).

Samples of the selenide phosphor 100SrSe + XSrS (0.023Sm,0.020Eu)(7.5SrSO₄,7.5CaF₂) and 100SrSe +

(16) R. T. Ellickson and W. L. Parker, *Phys. Rev.*, **70**, 290 (1946).

YSrS(0.023Sm,0.020Eu)(7.5SrSO₄,7.5CaF₂) were prepared in which X varied from 0 to 5 and Y varied from 0 to 8. The relative brightness values are given in Table II. The maximum brightness is obtained at 3 parts strontium sulfide and at 2 parts strontium oxide to 100 parts strontium selenide. It should be noted that the decrease in intensity of emission obtained upon further addition of strontium oxide is real. The decrease in intensity of emission with more than 3 parts strontium sulfide, on the other hand, may be due in part to the shift in color of emission toward the red. The photocell used in these observations (R. C. A. 931A) is less sensitive in this region of the spectrum.

TABLE II

INFLUENCE OF OXIDE AND SULFIDE IONS UPON THE BRIGHTNESS OF STRONTIUM SELENIDE PHOSPHORS

(a) SrS	0	1	2	3	4	5	6	8
Rel. brightness	70	78	102	140	100	70	75	67
(b) SrO	0	1	2	3	5			
Rel. brightness	60	84	112	94	42			

A series of phosphors 100SrSe + XSrO + YSrS(0.023-Sm,0.020Eu)(7.5SrSO₄,7.5CaF₂) were prepared in which X = 0, 1 and 2 and Y = 0 to 4. The results listed in Table III appear to indicate that, with increasing amounts of oxide, less sulfide is required to give the phosphor its maximum efficiency.

TABLE III

INFLUENCE OF SIMULTANEOUS ADDITION OF SULFIDE AND OXIDE IONS UPON THE RELATIVE BRIGHTNESS OF STRONTIUM SELENIDE PHOSPHORS

SrS		0	1	2	3	4
SrO	0	70	78	114	140	117.
	1	120	125	128	120	
	2	123	136	130		

The reproducibility of the brightness values for any one sample was within about 5%. A reasonable correlation among samples in a particular series usually was obtained, but wide variations were frequently found from one series to another. These discrepancies may be attributed to: (a) different strontium selenide preparations, (b) different atmospheric conditions during the mixing of samples, (c) slight variations in firing conditions, (d) the oxidation of strontium selenide by sulfate ion at the surface of the samples which has been previously reported.[15]

It seemed reasonable to suppose that better control of the final composition of the phosphors would result from the use of non-oxidizing fluxes. A mixture 100SrSe + 4SrS + 3SrO(0.023Sm,0.020Eu)(5LiF,6CaF₂) was heated at 1050° in a stream of oxygen-free nitrogen for periods of time varying from fifteen minutes to two hours. The results are given in Table IV. They show that the

TABLE IV

EFFECT OF DURATION OF HEATING ON LUMINESCENT PROPERTIES USING A NON-OXIDIZING FLUX

Time, min.	Phosphorescence at 30 sec. after excitation	Relative brightness under I. R. stimulation
15	210	10600
30	420	14200
60	420	13900
120	460	12400

brightness and phosphorescence change very little after thirty minutes of heating. (It should be noted that the measuring device was altered in the interim between these and the previous measurements so that the new readings

are probably about 100 times greater for the same brightness value.) While the elimination of sulfate ion from the flux makes the heating time less critical, erratic results were still obtained when different strontium selenide preparations were used. An example of this is given in Table V where results are given for two series of mixtures 100SrSe + XSrO(0.023Sm,0.020Eu)(5LiF) prepared from different batches of strontium selenide. The results are very different in some respects but both series show a maximum in brightness at about 3 parts strontium oxide.

TABLE V

EFFECT OF ADDED OXIDE UPON BRIGHTNESS AND PHOS-
PHORESCENCE OF SrSe+SrO(0.023Sm,0.020Eu)(5LiF)

Series	X(SrO)	Phosphorescence at 30 seconds after excitation	Relative brightness under I. R. stimulation
1	0	Not detectable	470
	1	72	600
	2	560	4470
	3	2490	6510
	4	5300	3420
2	0	500	6000
	1	200	5400
	2	300	7600
	3	400	11400
	4	500	5900

Although most samples of calcium selenide which have been prepared in this Laboratory contain large amounts of oxide, it was found that good infrared-sensitive phosphors could be prepared from them. The only one which has received more than casual attention is 100(CaSe,CaO)(0.020Sm,0.020Eu)(6CaSO₄,6CaF₂). The stimulation band for this phosphor is shown in Fig. 6. The emission color is yellow-orange, the peak of the emission band being approximately 0.585 micron. From some X-ray studies of selenide phosphors containing calcium we might infer that the calcium ion tends to form a separate phase with oxide.[15]

Acknowledgment.—The authors wish to thank Dr. W. L. Parker for his determination of the stimulation and emission spectra.
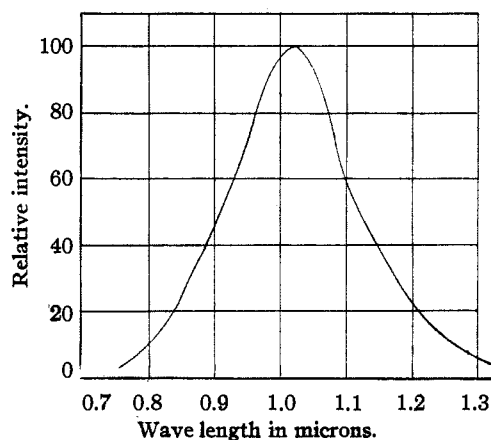

Fig. 6.—Stimulation spectrum of 100(CaSe,CaO)(0.020Sm, 0.020Eu)(6CaSO₄,6CaF₂).

Summary

A procedure is described for the preparation of strontium selenide suitable for the preparation of infrared-stimulated phosphors.

Several activator pairs are listed which give infrared-stimulated phosphors with strontium selenide. The presence of a small proportion of sulfide or oxide is shown to increase the sensitivity of the SrSe(Sm,Eu) phosphor. Increasing proportions of sulfide cause a shift of the emission color of the phosphor to the red while the oxide in concentrations above 3% causes a rapid decrease in sensitivity.

The emission and stimulation spectra for the 100SrSe + 5SrS(Sm,Eu)(6SrSO₄,6CaF₂) phosphor and the stimulation spectra for the SrSe(Eu,Bi)(SrSO₃,CaF₂) and the (CaSe,CaO)(Sm,Eu)(CaSO₄,CaF₂) phosphors are given.

Organic Compounds of Germanium. The Direct Synthesis from Elementary Germanium

BY EUGENE G. ROCHOW[1]

The first organic compound of germanium was prepared by the discoverer of that element, Clemens Winkler,[2] who employed the reaction between zinc diethyl and germanium tetrachloride to make germanium tetraethyl. In the intervening sixty years, many compounds having germanium–carbon linkages have been prepared by further use of zinc alkyls,[3] by the action of sodium on a mixture of germanium tetrahalide and organic halide,[4,5] and by application of the Grignard re-

action.[6,7,8] Such methods require the preliminary preparation of an organometallic compound as reagent or rely upon its formation in situ; one exception is found in the preparation of ethylgermanium triiodide by the addition of ethyl iodide to germanium diiodide.[9,10]

This paper describes a general method for the preparation of organogermanium halides by the

(1) Research Laboratory, General Electric Company.

(2) J. prakt. Chem., 144 (N. F. 36) 177 (1887).

(3) Dennis and Hance, THIS JOURNAL, 47, 370 (1935).

(4) Tabern, Orndorff and Dennis, ibid., 47, 2039 (1925).

(5) Kraus and Nutting, ibid., 54, 1622 (1932).

(6) Dennis and Hance, J. Phys. Chem., 30, 1055 (1926).

(7) Dennis and Patnode, THIS JOURNAL, 52, 2779 (1930).

(8) Orndorff, Tabern and Dennis, ibid., 49, 2512 (1927).

(9) Flood, ibid., 54, 1663 (1932).

(10) For a more complete bibliography, see Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937, pp. 295–310.