In general, the uncertainties of the calculated total ionic strengths of these solutions, due to the probable errors in the stability constants of the chloro-complexes of copper(I) and copper(II) are estimated to be 5% or less.

Acknowledgments.—This research has been supported by the Office of Naval Research. We are indebted to Professor Dan H. Campbell for many kindnesses in connection with the use of the spectrophotometer. Professor W. H. Stockmayer, as a referee, contributed a valuable suggestion concerning the presentation of equation (4).

Summary

The non-additive light absorption in the 400–600 mμ wave length range of solutions maintained at unit ionic strength with perchloric acid and which contain copper(I), copper(II), and low concentrations of chloride ion, has been interpreted in terms of an "interaction" complex, Cu_2Cl_3. The symmetry of the structure Cl–Cu–Cl–Cu–Cl may be important for the large contribution of this complex to the interaction absorption. At higher chloride ion concentrations of the same ionic strength, interaction complexes of higher chloride coördination (but still containing only one copper(I) and one copper(II) in each complex) are important.

PASADENA 4, CAL. RECEIVED OCTOBER 20, 1949

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

The Preparation of Pure Magnesium Sulfide and its Use as a Base Material for Infrared Phosphors[1]

BY E. BANKS, V. J. RUSSO AND R. WARD

Phosphors having the property of storage of energy and energy release under infrared stimulation have been described by Urbach,[2] Ward[3,4,5] and others. Earlier work by Tiede[6] and co-workers, had shown that magnesium sulfide yields efficient phosphors when singly activated, exhibiting normal fluorescence and phosphorescence when excited with ultraviolet light. Urbach and his co-workers[7] prepared infrared sensitive phosphors with magnesium sulfide using the activator pairs Ce–Sm and Eu–Sm. The stimulation peaks for these phosphors were identical, confirming Urbach's opinion that the trapping centers are associated with the samarium ions. The magnesium sulfide was prepared by passing a stream of dry nitrogen saturated with carbon disulfide over magnesium sulfate.[8] The phosphors were not nearly so sensitive as the corresponding strontium sulfide phosphors and it was suspected that this may be due to the presence of impurities such as magnesium oxide.

The present work was initiated in order to determine whether brighter phosphors could be prepared using a highly-purified oxide-free base material. Phosphors prepared from this material were used in an investigation into the factors involved in the dependence of brightness on activator concentration.

Experimental

I. Preparation of Pure Magnesium Sulfide.—Pure magnesium sulfate was obtained by heating purified magnesium ammonium chloride in a stream of hydrogen sulfide according to the method of Sarge.[9] It was found necessary to keep the temperature below the melting point of magnesium chloride for about an hour and to raise the temperature gradually to 1000° over a period of an hour and one-half. The product was a white to cream-colored powder containing 43.32% magnesium, 57.35% sulfur, and a trace of chloride.

II. Magnesium Sulfide Phosphors.—The activator ions were incorporated mainly by the addition of solutions containing small amounts of the chloride or nitrate to a supposedly inactive flux and evaporating to dryness. The flux and activator mixture was then mixed with an appropriate proportion of magnesium sulfide and the mixture was heated above the melting point of the flux. Several fluxes such as LiF, $MgCl_2$, KCl, NaCl, and mixtures $MgCl_2$ + NaCl, MgF_2 + NaCl, were used. The most effective appeared to be sodium chloride, which could be used in proportions up to 50 mole per cent.

The elements tried as activators were Pb, Ag, Mn, Sb, Ce, Sm and Eu. The infrared response was very poor with all except the rare earth pairs Eu–Sm and Ce–Sm. The latter gave the brightest phosphors, having a green emission similar to the corresponding strontium sulfide phosphor (Standard VII). Under the best conditions found, however, the brightness of this phosphor was less than one-tenth that of Standard VII.

Attempts to obtain some rational explanation for the poor performance of this phosphor by investigating the MgS–NaCl system have not been successful. There is no solid solution of sodium chloride in magnesium sulfide that could be detected by precision lattice constant measurements.[10] The solubility of magnesium sulfide in molten sodium chloride at 1000° is about 1 mole per cent.[11]

The low solubility of magnesium sulfide in sodium chloride at about 800° is also indicated by the small freezing

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(1) This work was carried out under Contracts Nobs-28370 and Nobsr-39045 between the Polytechnic Institute of Brooklyn and the Bureau of Ships.

(2) F. Urbach, D. Pearlman and H. Hemmendinger, *J. Opt. Soc. Am.*, **36**, 372 (1946).

(3) A. L. Smith, R. D. Rosenstein and R. Ward, THIS JOURNAL, **69**, 1725 (1947).

(4) K. F. Stripp and R. Ward, *ibid.*, **70**, 401 (1948).

(5) "Preparation and Characteristics of Solid Luminescent Materials," John Wiley and Sons, Inc., New York, N. Y., 1948.

(6) (a) E. Tiede and A. Schleede, *Centr. Mineral. Geol.*, 154–158 (1921); (b) E. Tiede and A. Schleede, *Ann. d. Physik*, **67**, 573–580 (1922); (c) E. Tiede and W. Schikore, *Ber.*, **75B**, 586–590 (1932).

(7) University of Rochester Report No. 16.5-125 on Contract OEMsr-81, dated September 24, 1945.

(8) E. Tiede and F. Richter, *Ber.*, **55**, 69 (1922).

(9) T. W. Sarge, U. S. Patent 2,358,661, Sept. 19, 1944.

(10) W. Primak, H. Kaufman and R. Ward, THIS JOURNAL, **70**, 2043 (1948).

(11) R. W. Mason, Dissertation, Polytechnic Institute of Brooklyn, 1948.

point depression (about 5°) for a mixture containing 5 mole per cent. magnesium sulfide.

It was found that reproducible phosphors could be prepared directly without the use of a flux by incorporating the activators as chlorides in the magnesium ammonium chloride and converting the mixtures to phosphors by heating in hydrogen sulfide as previously described. The products were fine powders, the optical properties of which were not altered by grinding in a mortar. This may indicate that the crystallite size was very small and it is conceivable that some increase in brightness might be obtained if the crystal size could be increased. This evidence and the low solubility of magnesium sulfide in the flux seem to indicate that a major function of the flux is to effect crystal growth in the activated base material.

III. **The Effect of Activator Concentrations on Optical Properties.**—Samples of these active powders were prepared for optical measurements by packing them into cells made from microscope slides and cover slips sealed with picein. The brightness measured on such samples were not comparable to those measured on molded samples because of reflections at the glass surfaces and scattering by the loosely-packed powders. For comparisons among powder samples, however, these specimens were satisfactory.

Brightness measurements were made by the method described by Stripp and Ward.[4] Maxima indicating an optimum composition, are the rule in plots of phosphor brightness *vs.* activator concentration.[4,12] A few of the curves obtained with magnesium sulfide phosphors are given in Figs. 1 and 2.

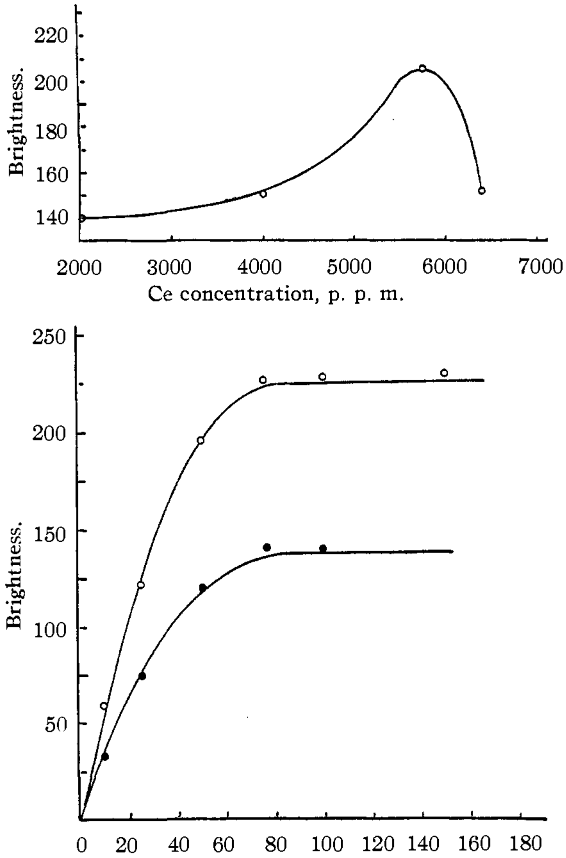

Fig. 1.—Brightness *vs.* activator concentration (NaCl flux): top constant Sm; bottom, constant Ce; ○, 1000 p. p. m. Ce; ●, 150 p. p. m. Ce.

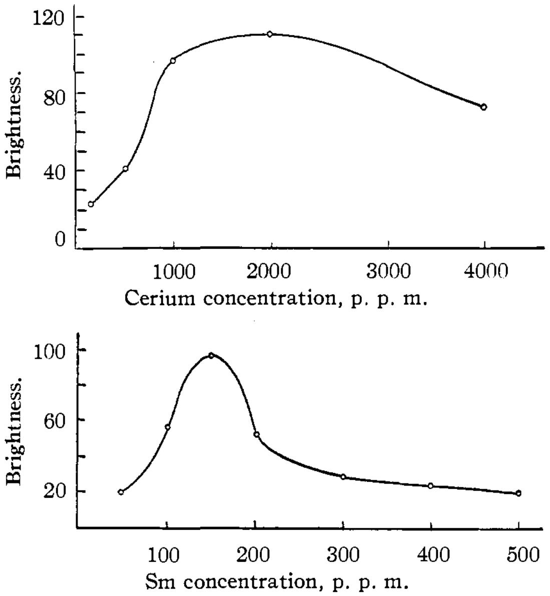

Fig. 2.—Brightness *vs.* activator concentration (no flux): top, constant Sm (150 p. p. m.); bottom, constant Ce (1000 p. p. m.).

Figure 1 shows two curves for the phosphor prepared by fluxing with sodium chloride. The lower set of curves gives the variation of brightness with samarium concentration at constant cerium concentrations. The upper curve represents brightness *vs.* cerium concentration at constant samarium concentrations. Similar plots for the active powders are shown in Fig. 2. The samarium concentrations in the fluxed samples were carried up to only 150 p. p. m., while active powders were prepared up to much higher concentrations. The curves for the active powders show a pronounced maximum at 150 parts samarium per million, while the fluxed samples attain a constant brightness value between 80 and 150 parts per million. In the constant samarium series, the fluxed samples show a maximum at 5500 parts cerium per million, while the active powders show a broad maximum at about 2000 p. p. m. These differences are undoubtedly due to activator distribution effects in the fluxed samples. No detailed explanation can be given, since we have been unable to determine the activator distribution using the method of Mason.[13] It is noteworthy that the optimum concentration of the activators in the samples prepared without a flux is about 10 times that found for the Standard VII phosphor.

IV. Spectroscopic Study of MgS Phosphors

(1) **Stimulation Spectra.**—The stimulation peaks for fluxed samples and active powders, both activated with cerium and samarium, were measured, using a Beckman spectrophotometer as monochromator and the blue-sensitive photocell as detector. Both types showed the same stimulation curve, peaking at 1.05 μ, as shown in Fig. 3. This is a longer wave length than the peak for Standard VII (SrS:Ce,Sm), which occurs at about 1.02 μ.

(2) **The Study of Brightness-Composition Maxima by Spectroscopic Methods.**—The maxima in the brightness-composition curves are typical of all infrared phosphor systems known. Magnesium sulfide phosphors, where high activator concentrations are the rule, seemed to be a particularly suitable system for an investigation of these

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[12] H. Texin, H. Williams and R. Ward, This Journal, **71**, 2494 (1949).

[13] R. W. Mason, C. F. Hiskey and R. Ward, *ibid.*, **71**, 509 (1949).

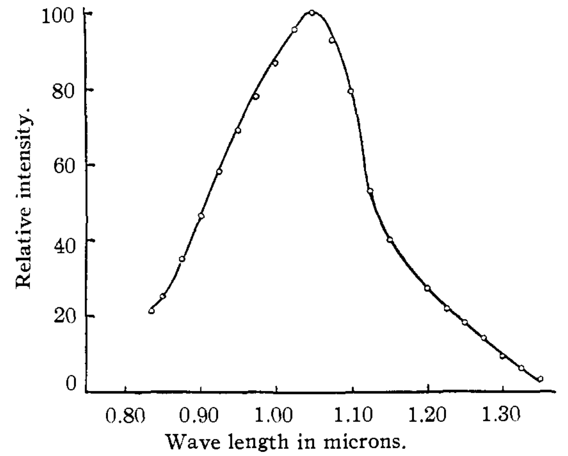

Fig. 3.—Stimulation spectrum of MgS(Ce,Sm) phosphor.

effects. The active powders were used for this work, since at the time it was thought that the presence of the flux might modify the optical properties. Samples were prepared containing constant quantities of samarium and varying quantities of cerium (as $CeCl_3$) up to 10% cerium by weight. The conversion of the mixed chlorides to sulfide was carried out as described above. Debye–Scherrer photographs of a sample containing 10% Ce showed no new lines, but this is believed to be due to poor crystallinity of any excess phase that may have been present. A sample of cerium(III) sulfide was prepared by hydrogen sulfide treatment of the anhydrous chloride, as described by Klemm, *et al.*[14] The product was a deep red powder, with a very complex X-ray pattern, as reported by these authors.

Absorption measurements were made on the sample of cerium sulfide and on samples of active powder containing 2000, 4000, and 50,000 parts cerium per million. The values of $(1 - R^2)/2R$, where R = % reflectance, are plotted against wave length in Figs. 4 and 5. Figure 4 shows the absorption spectra for the three active powders, while Fig. 5 compares the curve for Ce_2S_3 with that of the active powder containing 5% cerium. The curves in Fig. 4 show an absorption peak at 475 mμ, which increases in intensity as the cerium concentration increases. The curve for the sample containing 5% cerium has an appreciable absorption at wave lengths from 500–600 mμ. Figure 5 shows that the absorption of Ce_2S_3 is practically 100% at wave lengths below 600 mμ.

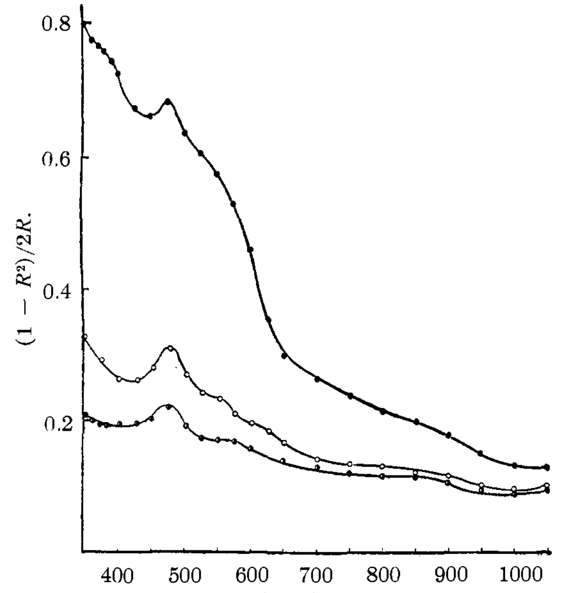

Fig. 4.—Absorption spectra of active MgS powders: ●, MgS (5% Ce, 150 p. p. m. Sm); ○, MgS (0.4% Ce, 150 p. p. m. Sm); ◑, MgS (0.2% Ce, 150 p. p. m. Sm).

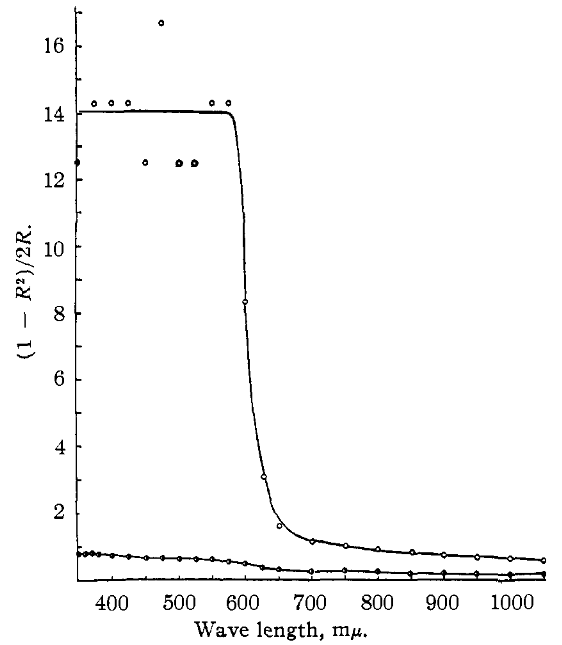

Fig. 5.—Absorption spectra of Ce_2S_3 and MgS(Ce,-Sm) phosphor: ○, Ce_2S_3: ◑, MgS (5% Ce, 150 p. p. m. Sm).

The emission spectrum of one of the active powder samples was measured by alternately exciting and stimulating the phosphor with ultraviolet light from a "contiglo" lamp and infrared from a filtered tungsten source, respectively. The stimulated emission was detected by

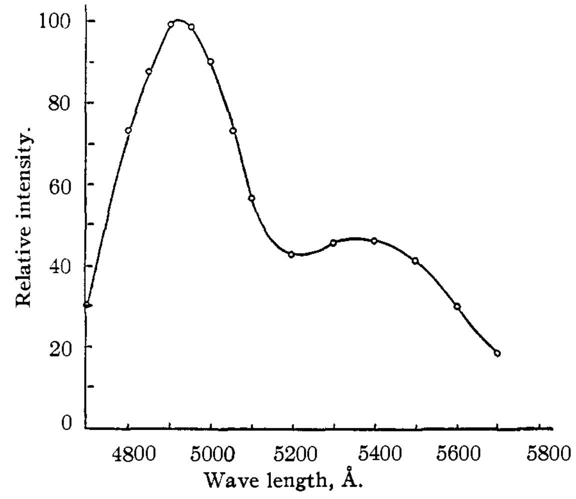

Fig. 6.—Emission spectrum, active MgS powder (2000 p. p. m. Ce, 150 p. p. m. Sm).

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[14] W. Klemm, K. Meisel, H. V. von Vogel, *Z. anorg. allgem. Chem.*, **190**, 123–144 (1930).

means of a 1P22 photomultiplier tube at the exit slit of a constant-deviation spectrometer. The emission spectrum of Fig. 6 shows two peaks, the first at 4925 Å. and the second at 5375 Å. This emission spectrum is similar to that of Standard VII, but is shifted by about 100 Å. in the direction of longer wave lengths.

On comparison of the emission and absorption spectra, it can be seen that the peak of the emission spectrum at 4925 Å. corresponds to a region of strong absorption in the visible absorption spectrum. This may be at least a partial explanation for the decrease in brightness when the activator concentration is increased beyond the optimum value. This self-absorption, while not necessarily the only factor, seems to play an important part in the diminution of brightness after reaching the peak of the brightness–concentration curves.

Summary

1. Pure, oxide-free magnesium sulfide has been prepared and used to prepare infrared-sensitive phosphors by activation with rare-earth pairs, both with and without fluxes.
2. On the basis of indications as to the low solubility of magnesium sulfide in the flux, it is suggested that a major function of the flux is to act as a recrystallizing agent for the base material, incorporating the activators during the process.
3. Measurement of emission and absorption spectra indicate that self-absorption, due to the overlap of the absorption and emission bands, accounts in part for the maxima observed in brightness–activator concentration curves.

BROOKLYN 2, N. Y. RECEIVED NOVEMBER 29, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

An Equilibrium Study of the Thermal Dissociation of Ferric Bromide

BY N. W. GREGORY AND BETTY A. THACKREY

The anhydrous ferric halides may be thermally decomposed into free halogen and the corresponding ferrous compounds. The ease of decomposition increases markedly in the order expected from a consideration of the size and electron affinity of the halogen concerned. Ferric fluoride does not decompose appreciably until the temperature is above 1000°[1]; ferric chloride begins to decompose materially at its normal boiling point (319°)[2]; ferric bromide cannot be sublimed unless a pressure of bromine in excess of one atmosphere is maintained in the system; and solid ferric iodide has not been prepared as yet.

In connection with a general program of study of the thermodynamic properties and structures of iron halides, we have investigated the equilibrium $FeBr_3(s) = FeBr_2(s) + 1/2Br_2(g)$ in the temperature interval 65–140°.

Experimental Part

(a) **Reaction of Iron and Bromine.**—Crystalline ferric bromide was prepared by the bromination of iron powder. The reaction vessel consisted of a pyrex tube bent in the shape of an inverted "V." Iron was introduced into one arm of the tube, and the other connected to a vacuum line and a supply of anhydrous bromine. After thorough outgassing, bromine was sublimed into the evacuated reaction vessel and condensed there by means of a liquid-air-bath. The tube was then sealed off and the bromine transferred to the arm opposite the iron. The temperature of the iron was increased to 175–200° and that of the bromine to 120° by means of separate furnaces which came into contact at the apex of the tube. At 120° the vapor pressure of bromine is approximately five atmospheres.[3] Under these conditions ferric bromide can be sublimed away from the iron and will collect in the form of beautiful black shiny plates just beyond the 200° furnace. A small amount of yellow crystalline ferrous bromide will be observed at the end of the furnace if the bromine pressure is not maintained sufficiently high, or if the furnace heating the iron is kept at higher temperatures. The rate of sublimation can be materially increased under the latter condition.

Iron will react quite readily with bromine at lower temperatures. A mixture of liquid bromine and iron powder react very noticeably at room temperature, causing vigorous boiling of the bromine. Ferric bromide forms under these conditions, yielding a black crystalline product which is very hygroscopic. However, it was found almost impossible to get complete conversion of the iron particles into ferric bromide unless the latter is sublimed away from the reaction zone. If this is not done, the ferric bromide forms a protective coating about the iron particles which prevents further attack by bromine. In one instance a mixture of iron and bromine was allowed to stand for several weeks at room temperature. At the end of this period the iron appeared to have reacted completely; however, upon dissolving the sample it was found that nearly one-half of the iron powder remained trapped inside the crystallne product.

The samples of ferric bromide used for the equilibrium study were prepared independently and analyzed by standard methods. They were found to possess Fe/Br ratios between 1:2.97 and 1:3. Measurements were not made beyond 122° for sample 1 as an insufficient quantity of material was introduced into the apparatus to establish an equilibrium pressure of bromine beyond this temperature. A relatively large excess of ferric bromide was used in the second series of measurements.

(b) **Equilibrium Measurements.**—The solid ferric bromide was transferred in a dry box into a glass membrane manometer.[4] The manometer consisted of a very thin walled pyrex bulb, flattened on one side, with a slender glass rod (10 cm. long) sealed on to the flat surface to act as a pointer to detect motion of the membrane. The thin walled bulb was inserted by means of a ring seal into a pyrex tube and connected to the vacuum line and manometer in the usual manner. The sensitivity of the gage was such that pressure measurements could be made with an uncertainty of not more than ±1 mm. The position of the pointer at the null point was found to be independent of temperature and pressure over the range of interest.

After introduction of the sample, the apparatus was

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(1) K. Jellinek and A. Rudat, *Z. anorg. allgem. Chem.*, **175**, 281 (1928).

(2) C. G. Maier, U. S. Bureau of Mines Bulletin, T. P. 360 (1925).

(3) "Int. Crit. Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1938, p. 201.

(4) F. Daniels, THIS JOURNAL, **50**, 1115 (1928).