is expressed in the following positions:

	Perovskite (large) cell	"Anti-perovskite" cell (Zachariasen)	Present structure cell
4Na	$\frac{1}{2}00$ (12 neighbors)	$\frac{1}{2}00$ (6 neighbors)	$\frac{1}{2}00$ (6 neighbors)
4I	$00\frac{1}{4}$ (6 neighbors)	$00\frac{1}{4}$ (12 neighbors)	0.01, 0.01 $\frac{1}{4}$ (3 + 2 + 1 neighbors)
4O	000	$\frac{1}{2}0\frac{1}{4}$	0.656, 0.08, $\frac{1}{4}$
8O	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$	$\frac{1}{4}\frac{1}{4}0$	0.122, 0.165, 0.043

It is interesting to compare the dimensions of XO_3 groups in chlorates, bromates and sodium iodate

	Halogen-oxygen, Å.	Oxygen-oxygen, Å.	Regular tetrahedral radical, Å.
$KClO_3$	1.42	2.33 2.48	2.33
$KBrO_3$	1.68	2.73	2.73
$NaIO_3$	2.05 2.08	3.35 3.55	3.35

Summary

Sodium iodate, $NaIO_3$, has an orthorhombic lattice with space group V_h^{16}—Pbnm, $a = 5.75$ Å., $b = 6.37$ Å., $c = 8.10$ Å., $z = 4$. The structure has been completely determined by the aid of oscillation diagrams. It contains distinct IO_3 radicals with iodine-oxygen distance 2.05 and 2.08 Å., respectively. For parameter values see the text.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Function of Fluxes in the Preparation of Infrared Sensitive Phosphors of the Alkaline Earth Sulfides and Selenides[1,2]

BY WILLIAM PRIMAK,[3] R. KEITH OSTERHELD AND ROLAND WARD

The development of infrared-sensitive phosphors with remarkable capacities for energy storage has been described in a cursory manner elsewhere.[4] A more detailed description of the properties of these phosphors has been given by Urbach[5] who shows the relationship of the infrared-sensitive phosphors to the Lenard phosphors.

The empirical methods used by Lenard and adapted by Urbach to the preparation of infrared sensitive phosphors lead to products of rather uncertain composition.[5,6] The alkaline earth sulfides were prepared in this process by the reaction of the carbonate with sulfur at 1000 to 1100°. A mixture of sulfide with about 30% sul-

$$4MCO_3 + S \longrightarrow 3MS + MSO_4 + 4CO_2$$

fate and smaller amounts of carbonate and oxide was obtained. To this about 6% of a fluxing agent such as calcium fluoride or lithium fluoride containing activators was added along with additional quantities of sulfur. This mixture was again heated at 900 to 1000°. The luminescent properties of materials prepared in this way were subject to wide variations which apparently depended upon the heating cycles and upon the atmosphere to which the samples were exposed at high temperatures.

Strontium sulfide was prepared by the method of Tiede[7] or by heating the carbonate or sulfate in hydrogen sulfide so that it was substantially free from sulfate. The activators, samarium and europium, and the flux, calcium fluoride, were added to this preparation and the mixture was heated at 1000° in nitrogen saturated with carbon disulfide. The product had rather low infrared sensitivity. Subsequent addition of about 6 weight per cent. of strontium sulfate and reheating, however, increased the sensitivity.[5]

To arrive at a better understanding of the fluxing process so that more reproducible phosphors could be obtained, the composition of the flux and its interaction with the base material were studied in some detail. While this investigation was going on, another phosphor, SrSe(Sm,Eu) was developed,[4] the properties of which will be given in a subsequent article.[8] The fluxing of the selenide phosphor was also studied. In this paper attention is directed mainly to the physical and chemical action of the fluxes. The luminescent characteristics of the products are described only to show their dependence on the changes in base material.

Experimental

Pure strontium sulfide was prepared by complete reduction of strontium sulfate with hydrogen. Mixtures of this with either strontium sulfate or calcium fluoride when heated at 1000° showed no evidence of fusion but a mixture of all three substances, when similarly treated, appeared to have been partly fused. It seems obvious, therefore, that the mixture of calcium fluoride and strontium sulfate was acting as a flux.

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[1] This paper is based on work done for the Office of Scientific Research and Development under contract No. OEMsr 982 with the Polytechnic Institute of Brooklyn.

[2] Abstracted from part of a thesis submitted by William Primak in partial fulfilment of the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn, 1946.

[3] Present address: Argonne National Laboratory, P. O. Box 5207, Chicago, Illinois.

[4] Proceedings Winter Meeting of Optical Society, session on infrared sensitive phosphors, *J. Optical Soc. Am.*, **36**, 351 (1946).

[5] F. Urbach, D. Pearlman and H. Hemmendinger, *J. Optical Soc. Am.*, **36**, 372 (1946).

[6] N. Riehl, "Physik und technische Anwendung der Lumineszenz," J. Springer, Berlin, 1941.

[7] E. Tiede and F. Richter, *Ber.*, **55B**, 69 (1922).

[8] A. L. Smith, R. D. Rosenstein and R. Ward, paper in preparation.

Consequently the liquidus of the reciprocal salt system strontium sulfate–calcium fluoride was investigated.

The mixtures were placed in a platinum crucible and heated well above the melting temperature in a Fletcher gas furnace. A Pt–10% Rh–Pt calibrated couple was used, the bare junction being placed in the melt. Cooling curves were obtained on a "Micromax Recorder." To slow the rate of cooling, it was found convenient to place the platinum crucible containing the mixture within two concentric rose crucibles each fitted with a cover.

Freezing points could be determined within 5 to 10°, which was adequate for this system since melting occurs over such a wide range of temperatures. The points close to the line of two-fold saturation were determined using a platinum stirrer which rotated around the couple. The liquidus for the strontium sulfate–calcium fluoride system[8a] is plotted in Figs. 1 and 2.

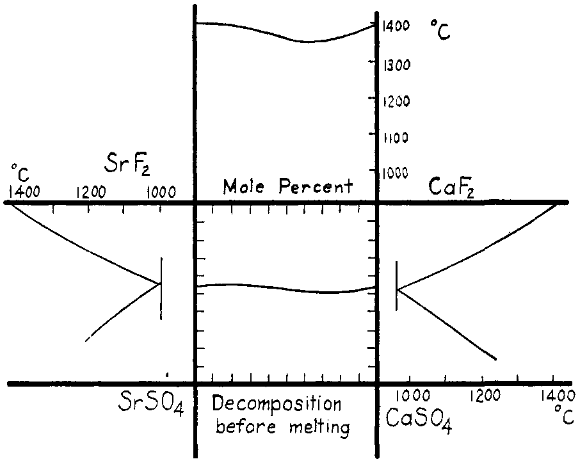

Fig. 1.—The reciprocal salt system: CaF_2–$SrSO_4$.

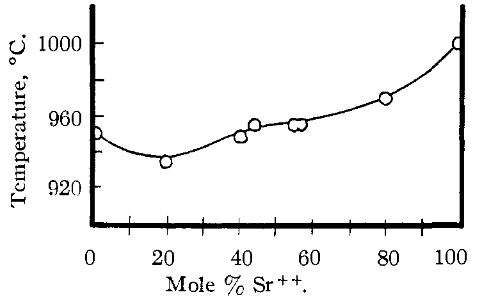

Fig. 2.—Line of 2-fold saturation in CaF_2–$SrSO_4$.

In another phosphor, SrS(Ce,Sm),[5] lithium fluoride was used instead of calcium fluoride. The phase diagram of the lithium fluoride–strontium sulfate reciprocal salt pair was therefore investigated in a similar manner. The liquidus for this system is shown in Fig. 3. The data are listed in Table I.

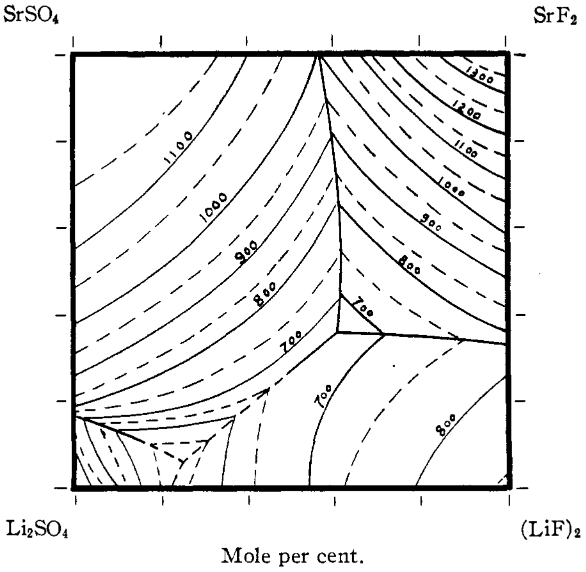

Fig. 3.—The reciprocal salt system: LiF–$SrSO_4$.

TABLE I

IMPORTANT POINTS IN LiF–$SrSO_4$ SYSTEM

Point	Composition, mole per cent. Li₂	F₂	Sr	SO₄	Temp., °C.
Unary freezing point	50	50			855 (840, 870[a])
Unary freezing point	50			50	875 (856[a])
Unary freezing point		50	50		1400 (1400[a])
Binary eutectic	35	50	15		775
Binary eutectic	50	12		38	525
Binary eutectic	8		42	50	735 (746[a])
Binary eutectic		28	50	22	1000
Liquidus composition at 2:2 transformation (approx.)	32	30	18	20	690
Liquidus composition at 3:1 transformation (approx.)	47	13	3	37	520

[a] "International Critical Tables."

These phase diagrams indicate the range of composition of the sulfate–fluoride mixtures which may furnish a liquid medium in the phosphor samples when they are heated at 1000°.

The addition of strontium sulfide and strontium oxide do not greatly lower the melting point of the fluxes. This is shown by the data in Table II in which some freezing points of pure fluxes are compared with those of fluxes to which strontium sulfide and strontium oxide had been added.

Several phosphors were prepared by fluxing at 1000° activated base material with mixtures containing a wide range of composition in the Ca^{++}–Sr^{++}–F^-–$SO_4^=$ system. It was found in general that sensitive phosphors were formed quickly with flux mixtures which gave a substantial amount of liquid phase at 1000°. These mixtures lie close

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(8a) The m. p. of SrF_2, 1400°, is taken from "I. C. T.," Vol. 4, p. 64, which appeared to fit our data better than the value 1190 which is given in some handbooks.

TABLE II

EFFECT OF ADDITION OF SrS AND SrO ON THE FREEZING POINTS OF THE CaF_2–$SrSO_4$ MIXTURE AND OF LiF

Constituents added, wt. per cent.	CaF_2 35 wt. % $SrSO_4$ 65 wt. % F. p., °C. (uncor.)	F. p. depression, °C.	LiF F. p., °C. (uncor.)	F. p. depression, °C.
None	922	..	825	..
10 SrS	907	15	790	35
3 SrO	922	0	803	22
3 SrO 10 SrS	892	20	790	35

to the line of two-fold saturation shown in Figs. 1 and 2. The period of heating required to produce a sensitive phosphor was about fifteen to twenty minutes which is not much more than is required to bring the sample to the furnace temperature. These results were obtained with strontium sulfide or selenide activated with samarium and europium. With strontium sulfide activated with cerium and samarium bright phosphors are also obtained using lithium fluoride (m. p. 855°) alone as flux.

From these results it appears obvious that an important function of sulfate ion is to give a sufficient quantity of liquid phase at a convenient firing temperature. Presumably the liquid serves as a recrystallizing medium for the base material and during the recrystallization the activator ions are incorporated in the lattice of the base material. That this interpretation is essentially correct is supported by the following experimental evidence.

When a flux containing calcium ions was used with a strontium sulfide or selenide phosphor, the color of the emission was found to shift toward that of the corresponding calcium sulfide phosphor.[5] Thus, SrS (Eu,Sm) ($CaSO_4$–CaF_2) and SrSe(Eu,Sm) ($CaSO_4$–CaF_2) showed a shift toward the red in the color of the emitted light when compared with the same phosphors fluxed with ($SrSO_4$–SrF_2) or with lithium fluoride. An anionic effect was also observed. The addition of strontium sulfide was found to shift the emission of SrSe(Eu, Sm) toward the red. Small amounts of strontium oxide on the other hand appeared to change the emission of SrSe(Eu,Sm) to somewhat shorter wave lengths. The characteristic emission colors of the simple phosphors are listed in Table III.

TABLE III

EMISSION COLORS OF INDIVIDUAL SULFIDE AND SELENIDE PHOSPHORS

Base material	Activators		Exciting light	Emission
SrS	Eu	Sm	Blue-green	Orange-red
SrS	Ce	Sm	Ultraviolet, or radium emission	Green: (background, green or orange)
SrSe	Eu	Sm	Blue-green or ultraviolet or radium emission	Yellow
CaS	Eu	Sm		Red
CaSe	Eu	Sm		Orange-red

Samples of strontium selenide to which small amounts of strontium sulfide had been added were fluxed with strontium fluoride–strontium sulfate mixtures. Lattice constants of the products obtained by the back reflection method are given in Table IV. The data show that a solid solution of strontium sulfide in strontium selenide has occurred. Rumpf[9] gives some similar evidence for mixtures of calcium sulfide and strontium sulfide. Evidence for the formation of solid solutions of calcium and strontium selenides upon fluxing is given in Table V.

TABLE IV

LATTICE CONSTANTS OF SrSe–SrS MIXTURES FLUXED WITH SrF_2–$SrSO_4$

Composition Wt. %	a, Å.	Δa obs., Å.	Δa calcd.,[a] Å.
SrSe 100%	6.232		
SrSe + 2% SrS	6.224	0.008	0.007
SrSe + 4% SrS	6.217	.015	.013
SrS 100%	6.008	.224	

[a] Calculated from Vegard's law, assuming complete solid solution.

TABLE V

X-RAY EVIDENCE FOR THE FORMATION OF SOLID SOLUTIONS UPON FLUXING

Composition, parts by wt.	Reduced product a, Å.	After fluxing with LiF a (obs.)	Δa (obs.)	Δa calcd.[a]
$SrSeO_3$	6.232	6.228	0.004	
$100SrSeO_3 + 10SrSO_4$	6.230	6.206	.026	0.025
$100SrSeO_3 + 10CaSO_4$	6.200	6.181	.051	.075
$100SrSeO_3 + 5CaSeO_3$	6.213	6.219	.013	.020
$100SrSeO_3 + 10CaSeO_3$	6.224	6.213	.019	.037
CaS from $CaSO_4$		5.684		.548
CaSe (calcd.)[a]		5.908[a]		.324

[a] Calculated by Vegard's law assuming complete solid solution.

The sulfate ion, however, may perform in certain instances an additional function which may be either beneficial or detrimental to the infrared sensitivity of the phosphor.

It was found that strontium selenide containing less than 1 per cent. oxide[8] when fluxed with 15 weight per cent. of a mixture of equal weights of calcium fluoride and strontium sulfate gave a phosphor which was active on the surface, but not in the interior. Small samples (1–2 g.) heated in nitrogen flowing at 200 ml. per minute became extremely bright throughout in half an hour. The phosphorescence of the surface became very pronounced. A loss in weight of the sample and an evolution of selenium accompanied the gain in activity. The selenium was collected in glass wool and weighed. Some of the results obtained are given in Table VI.

(9) E. Rumpf, *Ann. Physik*, **84**, 313 (1927).

TABLE VI

WEIGHT LOSSES AND SELENIUM EVOLVED UPON SUCCESSIVE HEATINGS OF SrSe(Eu,Sm)(CaF$_2$–SrSO$_4$)

Weight of sample, g.	Rate of flow of nitrogen, ml./min.	Time of heating, min.	Temp., °C.	Weight loss, mg.	Selenium collected, mg.
1.643	50		1050	30.5	24
1.840	50	20	1050	30.3	22.3
	50	20	1050	8.6	6.9
1.951	50	20	800	18.2	13.8
	100	20	1050	23.8	17.8
	50	20	1050	6.2	5.7
1.716	50	15	800	12.6	8.4
	50	15	1050	16.6	15.0

The nitrogen probably contained less than 10^{-5} mm. of oxygen and less than 10^{-4} mm. of water vapor since it had been passed through two long columns containing freshly prepared copper heated to 350° and through phosphorus pentoxide. Thus, the formation of oxide in the phosphor by its reaction with the impurities in the nitrogen could not account for the large weight losses observed. These weight losses and the weight of selenium collected could be accounted for by the following reactions taking place approximately in the ratio of 1 to 3.

$$SrSO_4 + 4SrSe \longrightarrow 4SrO + SrS + 4Se$$
$$SrSO_4 + SrSe \longrightarrow 2SrO + SO_2 + Se$$

Similar reactions between sulfides and sulfates have been reported by other investigators.[10]

If the reactions are not reversible, they at least can be prevented, for samples heated in a small quartz bomb at 1050° for several hours showed neither appreciable changes in weight nor increase in luminescence.

Strontium selenide was fluxed with several fluorides. The weight losses observed upon firing without sulfate present were compared with those obtained when a little strontium sulfate was added. About 1-g. samples consisting of 100 parts of strontium selenide with the proportion of flux materials listed in Table VII were used.

TABLE VII

COMPARISON OF WEIGHT LOSSES OBTAINED ON FLUXING STRONTIUM SELENIDE WITH REACTIVE AND NON-REACTIVE FLUXES

Composition of flux Parts					Weight losses on successive heatings, mg.					
					850°		1050°		1150°	Total wt. loss
MgF$_2$	CaF$_2$	SrF$_2$	SrSO$_4$	LiF	20 min.	30 min.	30 min.	30 min.	45 min.	
7.5	7.5				1.9		3.6			5.5
7.5	7.5					−3.9	8.5	0.6		5.2
7.5	7.5		1.75			28.0	11.5	0.0	0.3	39.8
7.5		7.5			0.8		3.2			4.0
7.5		7.5				2.2	1.3	0.5		4.0
7.5		7.5	1.75			28.1	9.9	0.6	1.0	39.6
15					1.1		4.3			5.4
15						2.7	1.6	1.6		5.9
15			1.75			28.6	16.6	0.0	0.2	45.4
				15	0.7		0.4			1.1

Oxygen-free nitrogen was allowed to flow over the samples at 100 ml. per minute. The successive weight losses on heating at various temperatures for the periods indicated show that in presence of sulfate ion the weight loss is about 40 mg., while in absence of sulfate ion it is less than 6 mg. The latter may be due to the absorption of moisture which is difficult to avoid in the preparation of the sample.

The sulfate ion may be desirable as a component of a flux if the introduction of small quantities of oxide is advantageous. The sensitivity of the selenide phosphor is apparently increased substantially by such a process. It is interesting to note that the addition of a few per cent. of sulfide ion to the SrSe(Sm,Eu) phosphor likewise increases its sensitivity.[8]

The substitution of cerium for europium in the SrS(Sm,Eu) phosphor necessitates the use of somewhat different fluxing conditions. When pure strontium sulfide is heated in nitrogen at 1000° with about 6 to 12 weight per cent. of lithium fluoride to which appropriate quantities of samarium and europium have been added, the product has extremely low infrared sensitivity. The samarium–cerium phosphor prepared in the same way, on the other hand, is an excellent infrared-sensitive phosphor. Urbach[5] has indicated that less oxidation is permissible with the cerium than with the europium. It may be rather that the samarium–europium phosphor requires oxidation or the presence of oxide while the samarium–cerium phosphor does not.

Some attempts were made to prepare these phosphors without the addition of a flux. The activators were added to the sulfate or selenite which were then reduced, without melting, to the sulfide or selenide, respectively. The reduction was carried out under conditions previously established as satisfactory and was followed by determining the weight losses of the samples.

Samples of strontium sulfate activated with samarium and europium when reduced with hydrogen, ammonia, or hydrogen sulfide gave infrared-sensitive powders which were nearly as active as those prepared by use of a flux. The spontaneous phosphorescence of the preparations differed according to the reducing gas used. It was greatest with hydrogen, less with ammonia and least with hydrogen sulfide. When samples prepared with hydrogen or ammonia were heated in hydrogen sulfide, the phosphorescence diminished but no weight change could be detected within 1 part in 1000. The infrared sensitivity was not noticeably changed by this treatment. Samples of SrS(Sm,Eu) prepared by reaction of strontium carbonate with hydrogen sulfide at 1000° were also infrared-sensitive phosphors but were less sensitive than those prepared from the sulfate.

In contrast to these results it is found that strontium sulfate, activated with cerium and sa-

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[10] Zwadski, *et al.*, *Z. anorg. allgem. Chem.*, **205**, 180 (1932), and also previous articles; R. Schenck and F. Hammerschmidt, *ibid.*, **210**, 305 (1933).

marium, when similarly treated gave products of very low sensitivity. Likewise strontium selenite activated with samarium and europium and reduced with ammonia at 850° showed very little stimulation with infrared.

Since it had been found that the brightness of the selenide phosphor was increased remarkably with the addition of small proportions of oxide or sulfide ions, an attempt was made to synthesize such mixtures without fluxing. Three mixtures were prepared by melting strontium selenite activated with samarium–europium with small amounts of strontium sulfate, strontium carbonate, calcium sulfate, respectively. These mixtures were heated in ammonia at 850° to constant weight. The products had only a slightly greater sensitivity than the SrSe(Eu,Sm). Heating the samples to 1150° did not yield more sensitive phosphors. When they were fluxed with lithium fluoride, however, a marked increase was observed. Lattice constants for the samples before and after fluxing are given in Table V. These show that very little solid solution occurred during the reduction of the mixtures. Upon fluxing, however, solid solutions were obtained, the concentrations approaching in most cases the theoretical values.

It is not entirely clear why such differences in behavior should be observed in the substitution of cerium for europium or in the substitution of strontium selenide for strontium sulfide. It is perhaps significant that no procedure has yet been found to make a good infrared-sensitive phosphor using the cerium–samarium activator pair with either calcium sulfide or strontium selenide as base materials. The following observations may have some bearing on this matter.

When heated in a reducing atmosphere, both samarium and europium are reduced to the divalent state. In this state of oxidation they may enter the strontium sulfide lattice more readily than the cerium ion which would probably be trivalent under the same conditions. The oxidation state of the activators, however, in the phosphors is not known with certainty. It should be noted that the sulfate ion may behave as an oxidizing agent toward Eu^{2+}, Sm^{2+} and Ce^{3+} as well as toward S^{2-} and Se^{2-} and that Se^{2-} and S^{2-} may behave as reducing agents toward Eu^{3+} and Ce^{4+} at high temperatures. These systems should be studied separately.

With the SrSe(Sm,Eu) phosphor it is possible that anionic impurities such as sulfide or oxide play a more important part than in the SrS(Sm,Eu) phosphor. These impurities may be required in a higher concentration in the selenide than in the sulfide. It may not be possible to secure a sufficiently homogeneous solution of these anionic impurities without the use of a flux since strontium oxide, sulfide and selenide are all highly refractory substances.

We may conclude that the sulfate ion in these phosphors is a useful constituent of the flux when such high melting salts as calcium or strontium fluoride are used. It serves in these instances to give a sufficient quantity of liquid phase at the usual furnace temperatures so that recrystallization of the base material and consequent distribution therein of activator ions may readily occur. The liquid phase also permits the speedy formation of solid solutions of one base in another and cationic exchange between base material and flux. In addition to this function the sulfate ion can behave as an oxidizing agent producing oxide and sulfide ions which apparently play an important part in the SrS(Eu,Sm) and SrSe(Eu,Sm) phosphors.

The authors wish to express their appreciation to Ira Friedman for his assistance in determining cooling curves in the lithium fluoride–strontium sulfate system.

Summary

The preparation of infrared phosphors of the alkaline earth sulfides and selenides by the Lenard method is shown to involve a complicated interaction of the base material and the flux. Some of the phenomena found to occur are the following:

1. Reciprocal salt systems are formed. The liquidus of two of these, calcium fluoride–strontium sulfate and lithium fluoride–strontium sulfate are given.
2. Reactions may occur between the flux and the base material. The reaction between strontium selenide and strontium sulfate to give strontium oxide and strontium sulfide was studied.
3. Cationic and anionic exchange between flux and base material is shown to occur. The introduction of calcium ion into a strontium sulfide or selenide phosphor, oxide and sulfide ion into a selenide phosphor, and oxide ions into a sulfide phosphor are cited as examples.

That fluxes may not be essential to the formation of all alkaline earth sulfide, infrared-sensitive phosphors is indicated by the preparation of a bright phosphor, SrS(Sm,Eu), without the addition of a flux.

BROOKLYN, NEW YORK RECEIVED[11] DECEMBER 31, 1946

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[11] An earlier version of this manuscript was received by *Industrial and Engineering Chemistry* on April 25, 1946.