TABLE II

DATA FROM X-RAY DIFFRACTION PATTERNS

$(NH_4)_2(HMoO_3N)$		$K_3(MoO_3N)$		$Ag_3(MoO_3N)$	
d	I/I_0	d	I/I_0	d	I/I_0
1.678	0.28	0.875	0.04	1.260	0.19
1.798	.85	0.941	.06	1.312	.21
1.891	.12	0.965	.07	1.665	.22
2.070	.09	1.001	.08	1.795	.31
2.167	.18	1.240	.09	1.920	.21
2.236	.20	1.453	.08	2.240	.49
2.458	.30	1.550	.08	2.615	.62
2.648	.10	1.711	.11	3.030	.19
3.218	.87	1.750	.13	3.340	1.00
3.319	.95	1.920	.19	4.320	0.76
3.594	.90	2.200	.10		
4.901	.52	2.220	.21		
6.315	.98	2.615	.16		
7.145	1.00	2.453	1.00		
		3.001	0.42		
		3.156	.48		
		3.251	.91		
		3.501	.62		
		5.011	.18		

The same result was obtained using a sample of the lead salt that had been maintained for three hours at 300° (without change in composition) in an atmosphere of dry oxygen-free nitrogen.

Summary

1. The existence of a compound of molybdenum(VI) oxide and ammonia in a 1:3 mole ratio has been confirmed and the compound has been interpreted as the diammonium salt of an aquoammonomolybdic acid.

2. This salt has been shown to be unaffected by treatment with liquid ammonia solutions of ammonium chloride or ammonium nitrate at 25 and 100°.

3. By the use of excess potassium amide in liquid ammonia solution and long time of reaction, the diammonium acid salt has been converted to a yellow tripotassium salt.

4. By metathesis with solutions of silver(I) nitrate and lead(II) iodide in liquid ammonia, the tripotassium salt has been converted to the corresponding silver(I) and lead(II) salts.

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

X-Ray Diffraction Studies of Systems Involved in the Preparation of Alkaline Earth Sulfide and Selenide Phosphors[1]

BY WILLIAM PRIMAK[2a] HERMAN KAUFMAN AND ROLAND WARD

The methods of preparation and some of the properties of the alkaline earth sulfide and selenide infrared phosphors have recently been described.[2,3] It has been shown[4] that in most cases their formation involves a complex interaction between solid phases and a fused salt, or flux, during which the composition of the phases alters. It is important to know the solubility limits of the different base materials which are used in the preparation of phosphors. A knowledge of the ways in which solid solutions may be formed is also useful. This paper presents the results of a study of the intersolubility of some alkaline earth sulfides, selenides and oxides by means of X-ray analysis. The excellent back-reflection powder pictures given by the alkaline earth sulfides, selenides and oxides, all of which have the sodium chloride lattice, have permitted the determination of the lattice constant of these phases with high precision. Our results indicate that the simple Vegard law is applicable over a wide range of composition of mixed sulfides and selenides so that changes in composition of the base material can be determined from the lattice constant measurement.

Experimental

Procedure.—A symmetrical back-reflection focussing powder camera of 6 cm. radius was used for most of the pictures. Several were taken with a Philip's Straumanis type powder camera of 5.72 cm. radius, and these are indicated in footnotes. To obtain a precision lattice constant, the lattice constants computed from the back-reflection lines were plotted against the square of the sine of the Bragg angle and extrapolated to Bragg angle 90°.[5] The error in extrapolation was about $^1/_{10,000}$, but the reproducibility in different samples of supposedly pure material was not better than $^1/_{3000}$. Some of the chemical work did not warrant obtaining lattice constants of such precision. In these cases, lattice constants were computed from a single back-reflection line spacing. They were probably good to $^1/_{500}$.

Preparation of Materials.—All chemicals used were purified as for the preparation of phosphors.[6] Strontium and calcium sulfide were prepared by reducing the sulfates with ammonia, hydrogen or hydrogen sulfide at 850–1050°. They were then treated with hydrogen sulfide at a temperature of 1000°. Strontium selenide was prepared by the reduction of the selenite with ammonia at about 850°. Several preparations of sulfides and selenides were made by the reaction of sulfur or selenium on

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[2] Reports of B. O'Brien, F. Urbach and R. Ward, *J. Optical Soc. Am.*, **36**, 351 (1946).

[3] R. T. Ellickson, *ibid.*, **36**, 261 (1946); R. T. Ellickson and W. L. Parker, *Phys. Rev.*, **69**, 534 (1946).

[4] W. Primak, R. K. Osterheld and R. Ward, THIS JOURNAL, **69**, 1283 (1947).

[5] M. J. Buerger, "X-Ray Crystallography." John Wiley and Sons, Inc., New York, N. Y., 1942, p. 393.

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

the carbonates. These are specifically referred to. Magnesium sulfide was prepared by the action of hydrogen sulfide on magnesium chloride.[7] Strontium and calcium oxides were prepared by treating the carbonates with hydrogen at about 1000° and then with oxygen at the same temperature.

Fluxing Procedures.—Samples were prepared in two ways: (1) 10 to 15 g. of material was molded under a force of 10 tons to form a $^7/_8$ inch diameter cylindrical block, which was then fired on a molded plate of magnesium oxide placed in a platinum boat; (2) 2 to 5 g. of material was placed into a small platinum boat and fired. In both cases the firing was performed by placing the boat into a quartz tube in which a purified nitrogen atmosphere was maintained, and the quartz tube was inserted for the desired length of time into the furnace maintained at a temperature of 1000–1100°.

Lattice Constants for Base Materials.—Precision lattice constants were determined for several different preparations of a number of alkaline earth oxides, sulfides, and selenides. They are given in Table I.

TABLE I

PRECISION LATTICE CONSTANTS

Base	Parts base	Flux	Parts flux	Minutes fluxed	Lattice constant "a" in Å.
SrS		None			6.0079
SrS	20	LiF	3	120	6.0080
SrS	100	LiF	9	90	6.0063
SrS	25	$SrCl_2$	3	90	6.0063
SrSe		None			6.2320
SrSe	10	LiF	1	30	6.228
SrSe	20	$SrSO_4$-SrF_2 (1:1 wt.)	3	30[a]	6.2309
CaS		None			5.6836
CaS	20	LiF	3	120	5.6835
CaSe		(Calculated)[b]			5.908
MgS		None			5.1913
MgS		None			5.1913
MgS	5	LiF	1	180	1.1900
MgS	5	NaCl	2	180	5.191
SrO	10	LiF[c]	1	120	5.1396
CaO		None			4.7990
CaO	10	LiF	1	30	4.799

[a] Phillip's Straumanis camera was used. [b] Calculated from the lattice constants given for strontium sulfide, strontium selenide and calcium sulfide, using Vegard's law. [c] Strontium oxide, unfluxed, gave diffuse lines which were attributed to poor crystallinity. When fluxed with sodium chloride or strontium chloride, a slight improvement was observed, but with lithium fluoride, rather sharp lines were obtained.

It is seen from these results that the flux does not affect the lattice constant within the limits of experimental error.

Solid Solutions of Strontium and Calcium Sulfides.—This system was previously investigated by Rumpf and Travnicek.[8] They used mixtures of strontium and calcium sulfides and sulfates prepared by the reaction of sulfur with a mixture of carbonates at high temperatures and observed large apparent deviations from Vegard's law, which they could not explain satisfactorily. For the work described here, practically pure sulfides were used. Two mixtures of strontium sulfide and calcium sulfide were prepared by grinding the constituents together in a ball mill. The one contained 75 mole per cent. strontium sulfide, the other 50 mole per cent. strontium sulfide. Several fluxes were used: (a) lithium fluoride; (b) mixtures of lithium fluoride, calcium fluoride, and strontium fluoride with the molar ratio of strontium to calcium ions the same as that of the respective sulfide mixtures. Lithium fluoride constituted one-third the weight of the mixture to give a mixture that was completely molten at the temperature of fluxing. (c) Mixtures of strontium fluoride, calcium fluoride and strontium sulfate with the molar ratio of strontium to calcium ions the same as that of the respective sulfide mixtures. The composition chosen was close to the line of two-fold saturation in the liquidus of the reciprocal salt system.[4]

The results obtained with these mixtures are given in Table II.

TABLE II

LATTICE CONSTANTS FOR FLUXED MIXTURES OF CALCIUM SULFIDE AND STRONTIUM SULFIDE

Base composition (mole% SrS)	Flux composition (Grams of flux for 10 g. sulfide)				Lattice constant ("a" in Å.)
	LiF	CaF_2	SrF_2	$SrSO_4$	
75	1.5				5.9375
75	0.5	0.172	0.828		5.936
75		.205	.330	0.965	9.535
75	Calculated from the lattice constants given in Table I for SrS and CaS, using Vegard's law				5.927
50	1.5				5.853
50	0.5	0.384	0.616		5.854
50		.447		1.053	5.868
50	Calculated from the lattice constants given in Table I for SrS and CaS, using Vegard's law				5.846

These results show that complete solid solution of the two sulfides results on fluxing; and also that using a flux containing calcium and strontium ions in the same molar ratio as in the sulfide does not change the composition of such solid solutions. One would not expect any better agreement than is found above, because of the difficulty experienced in compounding solids quantitatively.

If having the same molar cation ratio in base and flux is the equilibrium condition for ion exchange between base and flux, it should be possible to reach this condition starting with a base containing the one cation and a flux containing the other. Accordingly, calcium sulfide was fluxed with a flux containing strontium fluoride; and strontium sulfide was fluxed with a flux containing calcium fluoride. The lattice constants given by these samples are given in Table III.

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(7) V. Russo, M.S. Thesis, Polytechnic Institute of Brooklyn, 1947.

(8) Rumpf and Travnicek, *Ann. Physik*, [5] **4**. 725 (1930).

TABLE III

ION EXCHANGE BETWEEN BASE AND FLUX

Original base (10 g.)	Original flux (g.) LiF	SrF_2	CaF_2	"a," Å.	Mole per cent. SrS Found[a]	Calculated[b]
SrS	0.50		1.00	5.974	89.6	86.8
CaS	0.50	1.00		5.699	4.6	5.4

[a] Calculated from the lattice constant using Vegard's law. [b] Calculated from the composition, assuming ion exchange continues until the cation ratio is the same in flux and base.

Although complete transposition apparently did not occur in the time of fluxing, it is clearly established that cation exchange does take place. In applying this information to the study of phosphors, it could be assumed that cation exchange results in equal concentrations of these ions in base and flux.

The lattice constants obtained for calcium sulfide, strontium sulfide, and their solid solutions are plotted in Fig. 1 as a function of the composition. Contrary to the results obtained by Rumpf, which are plotted in the same figure for comparison, it is seen that our results obey Vegard's law very closely.

Conditions for the Formation of Solid Solutions.—In the above experiments, solid solutions were obtained by heating a mixture of sulfides with a flux. An attempt was made to obtain a solid solution by the reduction with hydrogen sulfide, of an intimate mixture of calcium and strontium sulfate. With a mixture containing 57 mole per cent. calcium sulfate, the product gave the patterns of the individual sulfides. When fluxed with lithium fluoride this mixture gave a lattice constant of 5.83 Å., corresponding to a composition of 56 mole per cent. calcium sulfide.

Quite different results were obtained when solid solutions of calcium and strontium carbonates were converted to sulfides. Three $(Ca,Sr)CO_3$ precipitates were prepared by adding a solution containing appropriate concentrations of Ca^{+2} and Sr^{+2} to a hot ammonium carbonate solution. They contained 81.7, 59.7 and 32.8 mole per cent. of calcium. Upon conversion to the sulfide by heating in hydrogen sulfide at 1000° the lattice constants of the solid solutions indicated 81.2, 57.7 and 31.0 mole per cent. of calcium, respectively, and on fluxing these products with lithium fluoride 80.5, 57.7 and 30.2 mole per cent. of calcium, respectively. The conversion to sulfide by heating with sulfur at 1000° gave somewhat similar results. The product from the mixture containing the highest percentage of calcium gave a very diffuse pattern before fluxing, and after fluxing a well-defined pattern corresponding to 73.8 mole per cent. calcium. The others yielded sulfides with calcium content 57.7 and 30.4 mole per cent. before fluxing and 59.0 and 30.8 mole per cent. after fluxing. The agreement is reasonably good considering that in the conversion of carbonate to sulfide with sulfur a considerable proportion of sulfate is formed.

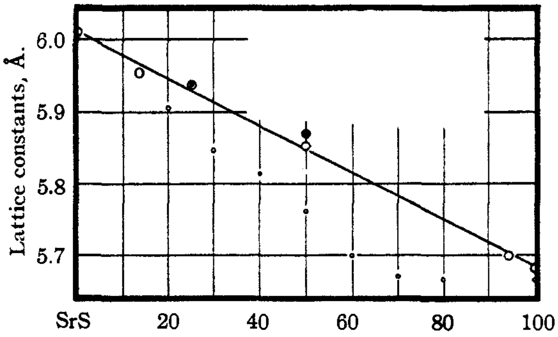

Fig. 1.—Lattice constants (Si,Ca)S: O, LiF fluxes, ● $SO_4^=$ fluxes; o, Rumpf.

Thus solid solutions of sulfides form when a mixture that is itself a solid solution is converted to sulfide. When the starting material is not a solid solution, appreciable solid solution is not obtained. This indicates a low rate of diffusion for these ions at 1000°.

These conclusions serve to explain some of the results previously obtained with mixtures of strontium selenite and other salts.[4] One of these systems ($SrSeO_3$–$CaSeO_3$) gave a lattice constant on reduction which differed widely from that predicted from the expected (Ca,Sr)Se solid solution. This experiment was repeated using a larger proportion (39 mole per cent.) of calcium selenite. The pattern of the selenide phase from the reduced mixture could barely be distinguished from the background but a strong set of lines corresponding to calcium oxide was present. Upon fluxing the mixture with lithium fluoride a distinct pattern of selenide phase appeared with lattice constant corresponding to about 14 mole per cent. calcium. The calcium oxide pattern was unaltered by the fluxing. It would appear, therefore, that the hydrolysis which always occurs when calcium selenite is reduced does not lead to the formation of strontium oxide or to a strontium–calcium oxide solution upon reduction of the mixture of strontium and calcium selenites.

The intersolubility of calcium and strontium oxides was accordingly tested by fluxing (a) a mixture of calcium oxide, strontium fluoride, and lithium fluoride in the proportions of 100:15:5, and (b) a similar mixture composed of strontium oxide, calcium fluoride, and lithium fluoride. From the powder picture of the former, a lattice constant 4.8020 Å. was computed. In the powder picture of the latter were found two sets of lines: from those that corresponded to a strontium oxide phase, the lattice constant 5.1312 Å. was computed; and from those that corresponded to a calcium oxide phase, the lattice constant 4.806 Å. It is obvious that ion exchange between base and flux had occurred in experiment b. The intersolubility of strontium and calcium oxides is apparently quite limited. According to Vegard's law, these results correspond to approximately 2.5

mole per cent. calcium oxide in strontium oxide, and 1 mole per cent. strontium oxide in calcium oxide.

The pronounced effect of oxide upon the luminescent properties of phosphors[9] suggested that solid solution with the sulfide or selenide might occur. The lattice constants obtained by fluxing strontium oxide and sulfide and oxide and selenide mixtures are shown in Table IV. It can be seen that the amount of oxide which disssolves in either selenide or sulfide is quite small and lies almost within the limits of determination by X-ray diffraction.

TABLE IV

LATTICE CONSTANTS OF MIXTURES CONTAINING OXIDE

Composition by weight		Fluxing time, hours	Lattice constant Å.	
Base	Flux		SrO	Other base
SrSe 5, SrO 5	LiF 1	30	5.145	6.230
SrSe 100, SrO 0, 1, 2, 4[a]	SrF_2 7.5, $SrSO_4$ 7.5	0.75		6.232
SrS 2, SrO 1	LiF 0.3	30	5.140	6.0050
SrS 100, SrO 3	LiF 9	1.5		6.0075
SrS 100, SrO 10	LiF 9	1.5		6.0070
SrS 100, SrO 2	$SrCl_2$ 12	1.5		6.0065

[a] Phillip's Straumanis camera used.

The intersolubility of magnesium sulfide with calcium and strontium sulfides was also tested by the same procedures. The lattice constants for these mixtures are listed in Table V and should be compared with the values for the pure sulfides given in Table I. There is very little intersolubility in the MgS–SrS systems but with the CaS–MgS system about 11 weight per cent. magnesium sulfide dissolves in the calcium sulfide and about 15 weight per cent. of calcium sulfide in the magnesium sulfide lattice. This is perhaps a greater intersolubility than one would expect with a difference in cationic radii of some 50 per cent.

TABLE V

LATTICE CONSTANTS OF MIXTURES CONTAINING MAGNESIUM SULFIDE

Composition by weight		Fluxing time, hours	Lattice constant, Å.	
Base	Flux		MgS	Other base
MgS 5, SrS 10	LiF 2.2	3	5.194	6.0058
SrS 10	LiF 0.5, MgF_2 1	3		6.0062
MgS 9, SrS 1	$SrCl_2$ 1	3		6.0012
MgS 6, SrS 4	$SrCl_2$ 1	1		6.0030
MgS 3, SrS 7	$SrCl_2$ 1	1		6.0020
MgS 1, CaS 5	NaCl 1.2	1		5.614
MgS 5, CaS 1	NaCl 1.2	1	5.251	

Acknowledgments.—The authors wish to thank Professor Fankuchen for his advice and Mr. Milton Schneider for his assistance in taking some powder diagrams. We are also indebted to Miss Hilda Texin and Messrs. Richard Hall and Kenneth Stripp for some of the samples used.

Summary

Precision lattice constants were determined for magnesium, calcium and strontium sulfides, strontium selenide, calcium and magnesium oxides. The extent of solid solution among these compounds and some of the methods for forming solid solutions were studied.

Complete intersolubility exists among calcium sulfide, strontium sulfide and strontium selenide. Magnesium and calcium sulfides are intersoluble to a limited extent. Solid solution formation among the other pairs appears to be negligible.

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

[CONTRIBUTION FROM RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION, KEARNY, NEW JERSEY]

Melting Points of Iron Oxides on Silica; Phase Equilibria in the System Fe–Si–O as a Function of Gas Composition and Temperature

BY L. S. DARKEN

The phase relations in the ternary system Fe–O–Si are of considerable interest to the steel industry, particularly in two respects: (1) the oxidation (scaling) of silicon steels produces in some cases a subscale and in other cases a so-called "silicon skin" (mainly metallic Fe + SiO_2). Since the primary requisite for scaling is the production of a gradient of the partial pressure of oxygen in the vicinity of the surface scaled, it is believed that a knowledge of the stability of the different oxides under various partial pressures of oxygen will aid in interpreting the observed phenomena. (2) The behavior of refractories is influenced in some cases by the form of iron oxide contained therein or deposited thereon. This is particularly so in blast furnace brick, in which metallic iron is thought to act as a catalyst for the deposition of carbon which in extreme cases disintegrates the brick. It has been observed that brick fired at high temperatures are less susceptible to this form of attack. It seems reasonable that higher temperatures effect fusion of the iron oxides forming silicates, etc., which are less easily reduced and less catalytic. The present investigation demonstrates that the temperature of fusion of iron oxides in contact with silica is a rather sensitive function of gas composition (varying from 1120 to 1447°), hence that fusion may be accomplished in some