containing equal numbers of sulfur atoms, are about 0.5% smaller in $Sc_{1.37}S_2$ and ScS than in Sc_2S_3. The structural data suggest that the electronic distribution on all the scandium ions is equivalent. The simplest formula for the scandium-rich phases thus becomes $Sc^{III}{}_{2+x}(e^-)_{3x}S^{II-}{}_3$, in which (e^-) represents a delocalized electron participating in metal–metal bonding.

Electrical Properties of Nonstoichiometric Scandium Sesquisulfide.—The sulfur-deficient compound $Sc_{1.37}S_2$ discussed above shows a metallic-type temperature dependence of Q and ρ (Fig. 4) between 300 and 850°K., and the conductivity is n-type as determined from the sign of the thermoelectric power. An estimate of the charge carrier mobility at 300°K., taking for the charge carrier concentration the value 1.5×10^{21} cm.$^{-3}$ calculated from the stoichiometry, is $\mu = 14$ cm.^{2} v.$^{-1}$ sec.$^{-1}$. A more detailed investigation of the electrical transport properties would be required to decide unambiguously between conduction by divalent scandium ions involving an activated hopping model and conduction by electrons involving a band model. The order of magnitude of the mobility, the temperature dependence of the thermoelectric power and resistivity, and the structural data discussed above suggest that conduction is by electrons in a 3d band. Such an interpretation is reasonable, since the overlap of 3d wave functions in the first transition series is largest for scandium.[31] Determination of magnetic susceptibility as a function of temperature would be extremely valuable in determining the valence of scandium and thus the conduction mechanism.

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[31] N. B. Hannay, "Semiconductors," Reinhold Publishing Corp., New York, N. Y., 1959, Chapter 14.

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The Preparation and Crystal Data of the Cadmium Silicates $CdSiO_3$, Cd_2SiO_4, and Cd_3SiO_5

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Three compounds of CdO and SiO_2 exist stably over the temperature range 800–1200° (approximately): $CdSiO_3$, Cd_2SiO_4, and Cd_3SiO_5. These compounds are structurally related to $CaSiO_3$, Na_2SO_4(V), and Ca_3SiO_5, respectively.

Introduction

Although cadmium silicates are of technical interest because of their properties as phosphors, no systematic study of the CdO–SiO_2 system has been reported. $CdSiO_3$ and Cd_2SiO_4 have been prepared by melting CdO and SiO_2,[1] but because of the volatility of CdO it is difficult to prepare pure compounds. The melting points of $CdSiO_3$ and Cd_2SiO_4 were reported as 1241 ± 5° and 1243 ± 1°, respectively, and it was suggested that the latter might be isomorphous with willemite (α-Zn_2SiO_4). Cd_2SiO_4 has also been prepared in autoclaves.[2] There are numerous other scattered references to compounds of CdO and SiO_2, mostly with few preparative details; no structural work appears to have been done.

Experimental

A series of "gels" was prepared containing 20.0, 25.0, 30.0, 33.3, 40.0, 50.0, 60.0, and 80.0 mole % SiO_2. Starting materials were Analar $Cd(NO_3)_2 \cdot 4H_2O$ and colloidal silica (Syton). To each weighed portion of cadmium nitrate the calculated volume of Syton was added, and the mixture was heated gently to drive off water. Ignition at 500° decomposed the nitrate, and the product was shown by X-ray powder photographs to be essentially amorphous.

Several series of heating experiments were made to overcome the problem of CdO loss. Runs were made in gold or platinum envelopes, weighing the envelope and contents before and after each heating in order to determine the CdO loss, and hence the final composition. It was found that loss of CdO from higher temperature runs (>1000°) could be minimized by first allowing the sample to react at 700–800°. Loss of excess CdO from the surface of sintered samples could be controlled by packing the envelopes at the bottom of a larger envelope or crucible filled with CdO.

Results

Phase Relations.—Three binary compounds were detected: $CdSiO_3$, Cd_2SiO_4, and Cd_3SiO_5. The congruent melting points of the first two are 1285 ± 10° and 1270 ± 10°, respectively. The $CdSiO_3$–Cd_2SiO_4 eutectic temperature is 1180 ± 10°. These data and the relatively high volatility of CdO from "open"

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[1] F. M. Jaeger and van Klooster, *Verslag. Akad. Amsterdam*, **24**, 921 (1915).

[2] C. J. van Nieuwenburg and H. B. Blumendal, *Rec. trav. chim.*, **50**, 989 (1931).

samples were used to prepare single crystals of these phases by a "self-fluxing" method. For example, to grow $CdSiO_3$ crystals a mixture somewhat higher in CdO is selected, *e.g.*, the Cd_2SiO_4 composition. If approximately 100-mg. samples are heated in open envelopes, CdO volatilizes and the bulk composition gradually changes; at about 1200° it reaches $CdSiO_3$ after 10–20 hr. The sample first melts and then refreezes as the composition moves from Cd_2SiO_4 to $CdSiO_3$. This isothermal change in composition results in the growth of large ($\sim$5 mm. long) pale green, lath-shaped crystals of $CdSiO_3$. A similar method was used to produce equant crystals of Cd_2SiO_4; the evaporation of CdO from compositions with $Cd{:}Si > 2{:}1$ is more rapid, and the crystals produced were smaller (0.1–0.2 mm.). Only one heating run yielded crystals of Cd_3SiO_5 of usable size. One possible additional reason for the difficulties in applying this self-fluxing technique to the Cd_3SiO_5 composition is that Cd_3SiO_5 may not melt congruently. Runs were also made in which CdF_2 or $CdCl_2$ (30 wt. %) was added to the Cd_3SiO_5 composition, but the crystals produced after heating at 900 and 1050° were comparatively fine-grained.

Crystal Data.—In all cases, photographs of selected single crystals were compared with reference powder photographs taken on a camera of the same radius. Reference powder photographs were from samples believed to be homogeneous, single-phase preparations.

$CdSiO_3$.—Although the powder pattern showed only a vague resemblance to that of β-$CaSiO_3$ (wollastonite), single-crystal patterns clearly showed that it is the cadmium analog of wollastonite. Table I compares the two unit cells; the dimensions shown refer to the unit cell of the monoclinic polytype (parawollastonite). The single crystals consisted of a mixture of polytypes, hence it was not possible to determine the space group unequivocally. Two specimens of $CdSiO_3$ were examined by selected area electron diffraction using a Vickers EM 3 electron microscope. In one preparation only the monoclinic polytype was detected, the other contained mostly this polytype and some of the triclinic (wollastonite) polytype.

Cd_2SiO_4.—Single-crystal studies and density measurements gave the unit cell, space group, and cell contents (Table I). There are two sets of eightfold special positions in Fddd, both with symmetry 222. The eight silicons must lie on one of these. Both lead to the same spatial arrangement, the choice of one rather than the other corresponding merely to a change of origin. Silicon was therefore placed at 0, 0, 0 and assumed to be surrounded tetrahedrally by four oxygens in the usual way. There are only two ways of placing the SiO_4 tetrahedron so that its twofold axes correspond with the 222 point symmetry, and one of these can be ruled out because it brings the centers of oxygens of adjacent tetrahedra within 1.3 Å. of each other. Assuming the value of 1.63 for the Si–O bond length of an isolated tetrahedron,[3] the 32 oxygens are in the general position with coordinates (−0.156, 0.079, 0.096). The 16 cadmiums must lie on one of the sixteenfold positions (because one of the two sets of eightfold positions is occupied by silicon). All of these give impossible Cd–O distances ($<<$2.0 Å.) except for 0, 0, z with $z \sim 0.3$. Comparison of F_o and F_c for a few reflections (including 004, which is very sensitive to the position of the cadmium) gave excellent agreement for $z = 0.325$. In this position the cadmium is surrounded by six oxygen atoms at the corners of a very distorted octahedron; four of the Cd–O distances ($\sim$2.15–2.35 Å.) are appreciably shorter than the other two ($\sim$2.61 Å.).

TABLE I

SINGLE-CRYSTAL X-RAY DATA FOR THE CADMIUM SILICATES AND RELATED STRUCTURES

(A)

	$CdSiO_3$	β-$CaSiO_3$[a] (wollastonite)
a	15.04 Å.	15.417 Å.
b	7.1 Å.	7.321 Å.
c	6.96 Å.	7.066 Å.
β	94°	95° 24′

d_{obsd} 5.1_0 d_{calcd} 5.07

(B)

	Cd_2SiO_4	Na_2SO_4(V)
a	6.04 Å.	5.85 Å.
b	11.85 Å.	12.29 Å.
c	9.75 Å.	9.75 Å.
Space group	Fddd	Fddd
Z	8	8

d_{obsd} 5.8_0 d_{calcd} 6.03

(C)

	Cd_3SiO_5 Pseudo-rhombohedral	Ca_3SiO_5 Pseudo-rhombohedral
a	6.85 Å.	7.0 Å.
c	8.42 Å.	25.0 Å. (= 3 × 8.33 Å.)

[a] Cell dimensions given by J. Tolliday, *Nature*, **182,** 1012 (1958), for an unanalyzed specimen of parawollastonite from Crestmore, Calif.

This structure is the same type as that described for $Na_2SO_4(V)$[4] and is quite different from that of olivine, α-Zn_2SiO_4, or the polymorphs of Ca_2SiO_4.

Cd_3SiO_5.—Because of the difficulty of preparing single crystals of this compound, X-ray studies are incomplete. Rotation, oscillation, and Weissenberg photographs show that it is pseudo-rhombohedral; the pseudo-cell dimensions are given in Table I. The true cell is larger, and its symmetry has not been properly established.

The symmetry and dimensions of the pseudo-cell show a striking resemblance to the pseudo-cell of Ca_3SiO_5[5] (Table I). Studies to be reported elsewhere[6] show that both structures are based on similar structural units, with Cd_3SiO_5 representing a simpler type of stacking.

Powder X-Ray Data.—Powder data were obtained from both film and diffractometer measurements. The data for $CdSiO_3$ agree with those in the X-ray Powder Data File, card 2-0719, with the exception of the line

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(3) J. V. Smith and S. W. Bailey, *Acta Cryst.*, **16**, 801 (1963).
(4) W. H. Zachariasen and G. E. Ziegler, *Z. Krist.*, **81**, 92 (1932).
(5) J. W. Jeffrey, *Acta Cryst.*, **5**, 26 (1952).
(6) L. S. D. Glasser, *ibid.*, in press.

reported at $d = 4.07$ Å. This reflection is not observed in completely reacted mixtures and can be attributed to the strongest reflection of cristobalite ($d = 4.04$ Å.). Indexed powder data for Cd_2SiO_4 are shown in Table II; the pattern was indexed by direct comparison of single-crystal and powder photographs taken on the same camera. The intensities recorded on the diffractometer agreed well with those observed on film. Powder data for Cd_3SiO_5 (Table III) have not been indexed, but comparison of single crystal and powder photographs taken on the same camera shows that all the reported reflections belong to Cd_3SiO_5.

Table II

Powder Data for Cd_2SiO_4[a]

d_{obsd}, Å.	I	hkl	d_{calcd}, Å.
4.705	15	111	4.706
3.775	40	022	3.774
2.951	60	040	2.955
2.791	100	113	2.794
2.680	75	220	2.682
2.563	25	202	2.565
2.449	3	004	2.452
2.354	6	222	2.352
2.321	35	133	2.322
2.146	10	151	2.147
1.936	20	311	1.939
		242	1.936
1.842	30	115	1.842
1.824	40	062	1.827
		153	1.825
1.691	30	313	1.692
1.684	8	135	1.685
1.646	25	260	1.648
1.603	2	171	1.600
		244	1.597
1.575	7	026	1.575
1.567	16	333	1.568
1.504	10	400	1.504
1.476	10	080	1.477
1.463	2	155	1.464
1.455	13	173	1.456
1.436	8	206	1.437
1.395	10	226	1.396
1.394	7	422	1.398
1.384	10	353	1.385
1.340	10	440	1.341
1.320	3	335	1.322
1.291	8	442	1.293
		246	1.292
		137	1.289
1.279	2	404	1.283
1.257	3	066	1.258

[a] Data obtained using a Philips Type PW 1051 X-ray diffractometer with Cu Kα radiation. Observed spacings and intensities were measured by both scanning and counting techniques, with silicon as an internal standard.

Table III

Powder Data for Cd_3SiO_5[a]

d, Å.	I	
4.87 ± 0.02	vw	
3.43 ± 0.01	vvw	
2.823 ± 0.003	vvs	doublet
2.764	w	
2.478	vw	
2.418	m	
2.324	vvw	
2.17–2.18	mw, broad	
2.072	vvw	
1.981	vw	
1.737	s	doublet
1.716	s	
1.666 ± 0.002	vvw	
1.609	vw	
1.491	m	
1.461	vs	
1.413	ms	
1.241	vvw	
1.208	vw	
1.176	vvw	
1.142	vw	
1.123	m	
1.113	vvw	
1.103	vvw	
1.085	m, broad	

[a] Data obtained using a 6-cm. diameter camera with Cu Kα radiation. Estimated errors (second column) apply to the value against which they occur and also to the succeeding values.

Discussion

The formulas $CdSiO_3$ and Cd_2SiO_4 deduced from direct heating experiments are confirmed by X-ray diffraction studies on single crystals. The Cd_3SiO_5 formula is based on two lines of evidence: (1) the occurrence of this phase in mixtures having a Cd:Si ratio of ~3:1, and (2) the analogy between its cell dimensions and those of the well-known Ca_3SiO_5 compound.

The analogy between Ca and Cd silicates is interesting. The metasilicates are structurally identical, even to forming the same two polytypes. The 3:1 compounds probably represent different methods of stacking similar structural units. The orthosilicates are not related. This is surprising in view of the relatively large tolerance of the olivine structure for divalent cations of different size and electronic structures (Mg, Fe, Co, Ni, Ca, etc.). Among the cations of medium size only Zn and Cd do not adopt the olivine structure; zinc orthosilicate has the phenacite structure, presumably because of the ease with which zinc forms four tetrahedral bonds. The large Sr^{2+} and Ba^{2+} ions occur in structures permitting higher coordination numbers. The structure of the cadmium orthosilicate still provides six-coordination for the Cd^{2+} ions, but the surrounding oxygen atoms form a highly distorted octahedron instead of the regular one provided by the olivine structure.

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