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High Pressure Synthesis of New Silicon Sulfides

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By heating mixtures of silicon and sulfur in various atomic ratios to temperatures of 700–2300° at pressures of 25–80 kbars, we have obtained a variety of reaction products. In addition to the previously known SiS_2 and SiS, these include several colored glasses and three new crystalline materials with distinctive X-ray diffraction patterns.

Experimental

Compressed pellets of 99.99+% silicon and 99.99+% sulfur, prepared in 1:1, 2:3, 1:2, and 1:2.2 atomic ratios, were placed in pyrophyllite tetrahedrons with graphite heating elements which have been described previously.[1] A tetrahedral anvil apparatus of National Bureau of Standards design[2] was used in all of the experiments. Discussion of temperature and pressure calibrations and experimental procedure have been reported earlier.[3]

Results and Discussion

Products from 33 runs above 50 kbars and 700° gave a new X-ray diffraction powder pattern, the strongest lines of which are shown in Table I, column (a). The relative intensities were similar in all samples, and neither Si nor S treated alone under the same conditions gave this pattern. These and the 14 weaker lines in the pattern can be indexed on the basis of a tetragonal structure with lattice constants $a = 5.43$ Å. and $c = 8.67$ Å. A 1Si:2.2S mixture held at 75 kbars and 1430° for 2 min. gave highest yields of this crystalline product. With a 1:1 Si + S starting mixture, Si lines were also always present; sulfur lines plus the new pattern resulted from 1 Si:2.2S mixtures. Microscopic examination indicated that the products from 1:2 and 1:2.2 starting mixtures consisted of 95% colorless, translucent, birefringent crystals. These appear to be of quality sufficiently good for a single crystal X-ray structural study. Several of these products were purified by repeated CS_2 washings, or by gentle heating *in vacuo* to remove excess sulfur, and then sealed under a dry N_2 atmosphere in polyethylene vials. These were cut open in $NaOH–H_2O_2$ solutions as the first step of analysis. *Anal.* Calcd. for SiS_2: Si, 30.5; S, 69.5. Found: Si, 30.6, 30.5; S, 73.6, 74.6. Two other samples examined[4] gave 1.46 and 1.48 ± 0.05% oxygen by neutron activation analysis, indicating slight hydrolysis even under careful handling conditions. Earlier Si and S analyses indicated extensive hydrolysis in atmospheric moisture when no special precautions were taken.

TABLE I
X-RAY DIFFRACTION POWDER PATTERNS FOR HIGH PRESSURE Si–S COMPOUNDS[a]

(a)		(b)		(c)	
d, Å.	*I*/*I*₀	*d*, Å.	*I*/*I*₀	*d*, Å.	*I*/*I*₀
4.60	40	6.0	40	5.2	30
2.88	100	4.74	20	4.04	30
1.92	40	4.55	20	2.95	100
1.699	45	4.02	20	2.61	30
1.598	45	2.99	100	1.79	35
1.356	30	2.82	35	1.75	45
1.060	25	1.81	25	1.561	30
		1.73	30		

[a] See text for significance of columns (a), (b), and (c).

Thermogravimetric analysis (TGA) of the purified crystalline product in air showed 28.9% weight loss up to 650°. Pure O_2 was then introduced and the temperature raised to 1000°, resulting in 33.8% total weight loss, slightly less than the 34.8% loss calculated for the reaction: $SiS_2 + 3O_2 \rightarrow SiO_2 + 2SO_2\uparrow$. Residue analysis showed 45.8% Si, compared with 46.0% calculated for the oxidation observed (97.1% complete). A plateau occurred at about 600° at a weight consistent with the composition Si_2OS_3. When pure oxygen was used from the beginning of heating, the TGA curve of the product showed a very sharp drop at 470° to a final weight loss of 34.0%, almost theoretical for SiS_2 oxidation. In nitrogen, TGA required 825° for major loss to begin and was slow and incomplete even after 16 hr. at 1050°.

The TGA results thus indicate a composition close to SiS_2. Wet chemical analyses agree exactly with Si in SiS_2, but S is somewhat high and the Si + S sum thus exceeds 100%. Failure to remove all excess sulfur from the high pressure products together with the uncertainty limits of the analyses may account for this.

We conclude therefore that this is a new, high-pressure modification of SiS_2, but cannot rule out entirely the possibility of a range of compositions near the 1Si:2S ratio with the same structure.[5] The measured density of this new SiS_2 polymorph is 2.23 ± 0.04 g./cc., 9% greater than the 2.05 g./cc. calculated from the lattice constants for normal SiS_2 which has an orthorhombic structure.[6]

Colored glasses ranging from canary-yellow to orange to green were obtained as minor or major products from many very high pressure Si–S reactions. Holding Si–S mixtures with atomic ratios from 1:1 to 1:2.2 at 45 kbars and 700° for 2 min. gave high yields. Distinct color differences and different degrees of transparency related to the atomic ratios indicate a wide range of compositions. X-Ray diffraction exposures up to 16 hr. showed these products to be amorphous. Elemental analyses were unsatisfactory, Si and S totalling to

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(1) H. T. Hall, *Science*, **128**, 446 (1958).

(2) E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **63C**, 59 (1959).

(3) J. R. Soulen and M. S. Silverman, *J. Polymer Sci.*, **1**, 823 (1963).

(4) J. C. Cooper, Am. Iso Metrics Corp., College Station, Texas.

(5) Recently we have found a high pressure form of germanium sulfide which analyzes $Ge_{0.94}S_{2.05}$. This material was produced when a 1:2.2 Ge + S mixture was subjected to 45 kbars and 1100° for 5 min. Its X-ray diffraction powder pattern is very similar to that of this new form of SiS_2, and the materials are thus probably isomorphous. The *d*-spacings (Å.) and relative intensities for this high pressure form are: 4.7, 75; 2.93, 100; 1.94, 25; 1.75, 40; and 1.62, 25.

(6) R. W. G. Wyckoff, "Crystal Structures," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Vol. I, p. 330.

80–90% of the sample weights, with oxygen only 0.25 to 1.5% in four products analyzed by neutron activation analysis.

Because of the possibility that the Si–S mixture could react with the pyrophyllite (a hydrated aluminum silicate) sample containers under extreme conditions, we also carried out reactions in boron nitride tetrahedrons. The same glassy products were obtained in the latter, and we thus believe that, in spite of the poor analysis, the glasses contain essentially silicon and sulfur. Oxidation of these glasses in air begins at 425° as shown by initial weight loss in TGA and the beginning of a large exotherm in differential thermal analysis. Preliminary density measurements yielded 2.07 ± 0.02 g./cc.

The most remarkable property of these glassy products is their hydrolytic stability, which is much greater than that of normal silicon mono- and disulfides. Even with finely ground material, reaction with water to give H_2S and amorphous silica took many hours to complete, compared to minutes for the normal sulfide, or even less for the monosulfide. We prepared samples of the latter by passing CS_2 over hot Si in a quartz tube at 1000° according to a procedure previously described.[7] The solid condensate obtained was mainly a fluffy pale yellow powder which was pyrophoric when dropped onto water. Careful examination of the quartz reaction tube revealed a small amount of orange, transparent glass similar in appearance to some of the high pressure products. This was amorphous in X-ray examination and also of much greater hydrolytic stability than the normal silicon sulfides. Hydrolysis of this glass, however, gave a soft, white material quite different in appearance from the tan, grainy residue obtained on hydrolysis of the high pressure glass.[8]

A second crystalline silicon sulfide occurred as gray needle-like crystals radiating toward the center of the product. The X-ray diffraction powder pattern characteristic of this product (Table I, column (b)) was obtained in about 20 runs. Preliminary attempts to index this powder pattern yielded several sets of tetragonal lattice constants which gave fair agreement with observed $\sin^2 \theta$ values. We hope the structure of this compound can be resolved by a single crystal X-ray study. Many products containing this material were heterogeneous, but it could be obtained in good yield from approximately 1Si:2S mixtures held at 45 kbars and 1100° for 5 min. Microscopic observation of its hydrolysis showed it to be similar to that of normal SiS_2.

A dull, opaque, hard bronze to tan solid that reacted vigorously in water was found in various amounts in 12 runs. It was the major product from Si–S mixtures held 5 min. at 44 kbars and 1400°. The strongest lines in its X-ray diffraction powder pattern are listed in Table I, column (c).

Acknowledgment.—We thank Dr. W. Clavan and Mr. R. Hamilton for obtaining the X-ray patterns and the Pennsalt analytical and shop groups for their help in this work. It was supported in part by the Office of Naval Research.

(7) R. F. Barrow and W. Jevons, *Proc. Roy. Soc.* (London), **A169**, 46 (1939).

(8) Barrow and Jevons[7] reported glassy products from vacuum sublimation of the monosulfide. They found that the band spectra of vapor from glasses and the yellow monosulfide powder were the same.

Correspondence

Hydrogen Bonding to Manganese(III) β-Ketoenolates: Influence on the Low Energy Electronic Band

Sir:

The visible and near-infrared region of the spectra of manganese(III) acetylacetonate, $Mn(AA)_3$, and other β-ketoenolate compounds of this ion is known to contain two bands of comparable intensity.[1–5] The recent publication by Morosin and Brathovde[6] of the X-ray crystal structure of $Mn(AA)_3$ prompts us to communicate some of our findings with regard to the spectral properties of β-ketoenolates of manganese(III), particularly since the most recently proposed[2,5] assignment can now be ruled out, while an earlier one[3,4] has several features suggesting it to be incorrect also.

In high-spin $3d^4$ complexes with O_h symmetry, one expects a ^5E_g ground state with single spin-allowed crystal-field transition to the $^5T_{2g}$ level. Lowering the symmetry to D_3 does not remove the degeneracy of the ground state but does split[3,5] the $^5T_{2g}$ state. This splitting has been observed by Piper and Carlin[3] in polarized spectral studies.

Since Morosin and Brathovde[6] have found that crystalline $Mn(AA)_3$ contains six Mn–O bonds of essentially equal length and that the molecule as a whole is only slightly distorted from the structure observed[7] for $Fe(AA)_3$, spectral assignments must be made within the crystal-field framework of an octahedral configuration with a rhombic perturbation. The above authors[6] have discussed the implications of the structure of $Mn(AA)_3$ on the question of Jahn–Teller distortion,

(1) J. P. Fackler, Jr., and I. D. Chawla, *Inorg. Chem.*, **3**, 1130 (1964).

(2) R. Dingle, *J. Mol. Spectry.*, **9**, 426 (1962).

(3) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

(4) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962).

(6) B. Morosin and J. R. Brathovde, *Acta Cryst.*, **17**, 705 (1964).

(7) R. B. Roof, Jr., *ibid.*, **9**, 781 (1956).