umes of all the ortho- and metasilicates listed by Robie and Waldbaum (*3*) and Helgesson (*2*) except for the Al_2SiO_5 polymorphs, $ZrSiO_4$, and $CaMgSiO_4$. The entropy of $CaMgSiO_4$ listed in Robie and Waldbaum was not determined experimentally; $ZrSiO_4$ is the only silicate with a tetravalent cation. The relationship of Al_2SiO_5 to the other orthosilicates is complicated by the substitution of Al plus O for two divalent cations.

The relationship between the molar volumes and the entropies of orthosilicates of Be, Mg, Ca, and Zn including grossularite ($Ca_3Al_2Si_3O_{12}$) is given by

$$-23.3129 + 1.0365\,n\,V = n\,S \quad (1)$$

where n is one divided by the number of tetrahedrally coordinated ions in the silicate, V is the molar volume (in cubic centimeters per mole), and S is the entropy (in gibbs per mole) (1 gibbs = 1 cal/°K). Entropies estimated by the use of Eq. 1 have been listed in Table 1.

For orthosilicates containing the transition elements Mn and Fe, atoms with unfilled d subshells, Eq. 1 does not hold. (Unfortunately, data on such orthosilicates as Co_2SiO_4 and Ni_2SiO_4 are not available.) From the two data points on the orthosilicates of Mn and Fe we have

$$-38.7322 + 1.5991\,n\,V = n\,S \quad (2)$$

Equation 2 may be improved when more data are available on other orthosilicates with nonspherical ions. It has been included here because it yields an acceptable value of entropy for almandine ($Fe_3Al_2Si_3O_{12}$) as discussed below.

Relations similar to Eqs. 1 and 2 have been obtained for metasilicates. These are

$$-1.1508 + 0.5439\,n\,V = n\,S \quad (3)$$

for the metasilicates of Mg, Ca, and Na-Al and

$$-20.7522 + 1.2870\,n\,V = n\,S \quad (4)$$

for $FeSiO_3$ and $MnSiO_3$. For the metasilicates of transition elements, we have, as with the orthosilicates, only two data points: The entropy for $MnSiO_3$ is from Robie and Waldbaum (*3*), and the value for $FeSiO_3$ has been estimated by Saxena (*4*).

The entropy–molar volume relationship for feldspars and feldspathoids is

$$-2.1205 + 0.4092\,n\,V = nS\,(+\,2R\,\ell n\,2) \quad (5)$$

where R is 1.987 and $2R\,\ell\,n\,2$ is the disorder entropy. The value of n here is the total number of tetrahedrally coordinated cations divided by the total charge on such ions. For example, n for $KAlSi_3O_8$ is 4/15, where the numerator of the fraction represents the number of cations other than K and the denominator represents the sum of the charges.

A comparison of the entropy differences in Table 1 reveals that Eqs. 1, 3, and 5 generally yield better estimates of entropy than the oxide summation method. In particular, the entropies of grossularite, feldspars, and feldspathoids estimated by the method presented here are superior to those estimated by the oxide summation method. However, the entropy of γ-Ca_2SiO_4 calculated from the entropy-volume relationship is grossly erroneous.

The entropy–molar volume relationship for the hydrous silicates is given by

$$2.7468 + 0.4344\,n\,V = n\,S \quad (6)$$

Here n is defined as in Eq. 5. As the data in Table 2 show, this relationship is less useful than those for the anhydrous silicates.

Table 1 shows the standard deviations, σ, for the least-squares fit. It is difficult to determine a reasonable estimate of errors with the entropy-volume method because of uncertainties in the molar volumes and in the experimentally determined entropies.

Garnets are important rock-forming minerals in the deep crust and upper mantle. Therefore, a knowledge of the entropies of almandine ($Fe_3Al_2Si_3O_{12}$) and pyrope ($Mg_3Al_2Si_3O_{12}$) is essential to an understanding of the phase equilibrium relations and to the construction of models of evolution of the earth. The entropy-volume method may be used to estimate the entropies of pyrope and almandine. The molar volumes of these silicates are 113.27 and 115.27 cm³/mole, respectively. Using Eq. 1 for pyrope, we have $-23.3129 + 1.0365\ (113.27/3) = S/3 = 15.82$, or $S = 47.47$ gibbs/mole. The summation of the entropies of the constituent oxides for pyrope is 61.14 gibbs/mole. Considering the difference between the experimental entropy and the oxide sum entropy of grossularite (Table 1), the estimated entropy of pyrope appears to be of the right order. For almandine we have (from Eq. 2) $-38.7322 + 1.5991\ \ (115.27/3) = S/3 = 22.71$, or $S = 68.13$ gibbs/mole, which compares very well with the value of 68.3 ± 3 gibbs/mole calculated by Zen (*5*) using data on phase equilibria.

The results of these calculations indicate that the entropies of most anhydrous silicates can be estimated with accuracy with the use of these entropy-volume relationships. These relationships, however, depend upon the nature of the cations, and, although significant correlations have been found here for silicates of several ions, these relations must be used with caution for silicates of other ions.

SURENDRA K. SAXENA
Department of Geology,
Brooklyn College, City University
of New York, New York 11210

References

1. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions* (Prentice-Hall, Engelwood Cliffs, N.J., 1952); W. S. Fyfe, F. J. Turner, J. Verhoogen, *Geol. Soc. Am. Mem. 73* (1958).
2. H. C. Helgesson, *Am. J. Sci.* **267**, 729 (1969).
3. R. A. Robie and D. R. Waldbaum, *U.S. Geol. Surv. Bull.* **1259**, 256 (1968).
4. S. K. Saxena, unpublished data.
5. E-An Zen, *Contrib. Mineral. Petrol.* **39**, 65 (1973).

20 February 1976; revised 21 April 1976

A Hexagonal (Wurtzite) Form of Silicon

Abstract. *The existence of a hexagonal (wurtzite) form of silicon, similar to that form of diamond (carbon) observed in meteorites and in the laboratory, has been identified by x-ray diffraction in reaction-bonded silicon nitride containing unreacted silicon. The presence of this phase is due to stresses created in the silicon by the nitridation reaction.*

We prepared reaction-bonded silicon nitride (Si_3N_4) by maintaining a compacted volume of finely powdered (−200 mesh) silicon in a nitrogen atmosphere at temperatures between 1250° and 1500°C for several hours to several days. During an extensive microstructural characterization of this material, we used x-ray diffraction to check the relative amounts of α- and β-Si_3N_4, the extent of reaction, and the existence of any impurity compounds. We obtained powder patterns with CuKα radiation on a Nonius diffractometer using monochromatic radiation (graphite-focusing crystal); the intensity as a function of 2θ (where θ is the dispersion angle) was recorded between 12° and 72°. Unreacted silicon was always present and was used as a standard. All of the x-ray peaks expected for α- and β-Si_3N_4 and unreacted silicon (diamond cubic) were observed and easily identified by reference to the Joint Committee on Powder Diffraction Studies powder diffraction file (numbers 9-250, 9-259, and 5-0565).

Table 1. X-ray data assembled from 49 specimens. Abbreviations: s+, very strong; s, strong; m, medium; w, weak; −, not observed; 0 indicates reflection coincident or overlapping with Si_3N_4 or diamond cubic silicon. The calculated intensities differ somewhat from the observed ones because the structure is distorted as a result of stresses. The experimental technique used by Jamieson (*3*) made it difficult for him to assign intensities.

Wurtzite (c = 6.60 Å, a = 4.04 Å)		d_{obs} (Å)	Intensity		Jamieson's d_{obs} (Å)	Jamieson's tetragonal structure (c/a 0.552, c = 2.585 Å, a = 4.686 Å)	
hkl	d_{calc}(Å)		I_{calc}	I_{obs}		d_{calc}	*hkl*
100	3.5	3.79	32	m to s+			
002	3.3	3.276	18	s			
101	3.08	3.138	16	0 Si	3.085s+		
		2.88		m			
		2.67		s	2.613s		
		2.46		m			
102	2.4	2.378	7	s	2.351s	2.343	(200)
		2.244		0 Si_3N_4	2.265m+	2.263	(101)
110	2.03	2.03	13	m			
103	1.86	1.86	13	s	1.865s		
200	1.74	1.75	2	s			
112	1.72	1.70	8	w	1.713w+		
						1.657	(220)
201	1.69	1.638	2	0 Si			
						1.628	(211)
004	1.65		0	−			
202	1.54	1.54	2	s	1.592s		
104	1.496	1.52	0	w			

In a number of samples, especially those where the β form was predominant, there was a family of peaks that could not be identified. Although not intense by comparison with the other phases present, many samples contained all or some of these peaks. One sample of silicon powder (nominally −200 mesh particle size and 99 percent pure, with no impurities detectable by x-rays before heat treatment) that had been maintained at a temperature of 1000°C for 12 hours exhibited unidentified peaks. This temperature is sufficiently low to preclude nitride formation, and, when diffraction patterns were taken, only unidentified and diamond cubic silicon peaks were observed. After 3 months at ambient temperature, some of the unidentified peaks either vanished or were replaced by new peaks, indicating the instability of the unidentified phase. In order to explain these peaks, we considered the possibility of another crystallographic form of silicon.

A literature search revealed a number of investigations which set forth evidence both for and against the existence of forms of silicon other than the diamond cubic. In 1947, using crude Debye-Scherrer x-ray diffraction equipment, Heyd *et al.* (*1*) reported the observation of a phase change in silicon when very fine powder was heated to 1050°C. Drawing an analogy with carbon, they suggested that the new phase was hexagonal. Only limited experimental detail was reported: it was stated that some impurities might help the conversion and that it was reversible. In 1956, Wood (*2*), having carried out some related experiments, argued that the hexagonal phase does not exist.

A number of investigations have revealed several phases of both silicon and germanium at high temperature and pressure. Tetragonal (*3*) (see Table 1), body-centered cubic (*4*), and hexagonal (*5*) structures have been proposed for silicon. It was found that transformations of the first two of these structures were encouraged by shear or compressive stresses, or both, and both had specific volumes about 1.9 percent less than the diamond cubic form of silicon. More particularly, it has been proposed (*6*) that the white tin (tetragonal) structure could be formed by compression along one of the cubic axes and by expansion along the [110] direction. It has been observed (*5*) that the dense phase (body-centered cubic), upon heating, might undergo a phase change to a hexagonal structure with lattice parameters of a = 3.80 Å and c = 6.28 Å. However, no corresponding x-ray data have been published.

After we had explored all possible known phases of silicon, we calculated the expected d-spacings (interatomic distances) for a new hexagonal form of silicon. The data could be fitted for a wurtzite type structure with a unit cell composed of four atoms at 0 0 0, 0 0 ⅜, ⅔ ⅓ ½, and ⅔ ⅓ ⅞. The lattice parameters are a = 4.04 Å and c = 6.60 Å (Table 1). The c/a ratio is 1.63, which is exactly the same as the c/a ratio reported for a similar form of carbon found in meteorites (*7*) and produced in the laboratory (*8*).

The experimental observations summarized in Table 1 were reduced from x-ray data taken from 49 samples. Because the intensities for each unidentified peak varied from sample to sample, the letters s, m, and w are used to represent strong, medium, and weak as compared to the strongest unidentified lines present. The value reported is the most often observed intensity. In only one case (d = 3.79 Å) was this value difficult to assign.

Further substantiation of the possibility of this new phase was obtained from an electron diffraction study (*9*), which identified a hexagonal substance with a d-spacing of 1.89 Å. No explanation could be found for this observation other than hexagonal silicon.

We believe that during the formation of Si_3N_4, especially the β phase, there are stresses in the interior of the silicon grain due to the 22 percent volume increase during nitridation (*10*). The hexagonal (wurtzite) phase may form along with, or as a result of, the formation of the dense tetragonal silicon under the influence of stress and heat. The observed x-ray data (Table 1) suggest that both phases may be present in our unidentified substance. Some of Jamieson's unidentified lines (*3*) match well with lines of the proposed hexagonal phase and suggest that he also may have had both phases present.

H. M. JENNINGS
M. H. RICHMAN

Division of Engineering,
Brown University,
Providence, Rhode Island 02912

References and Notes

1. F. Heyd, F. Kohl, A. Kochanovaska, *Collect. Czech. Chem. Commun.* **12**, 502 (1947).
2. F. Wood, *J. Phys. Chem.* **60**, 506 (1956).
3. J. C. Jamieson, *Science* **139**, 762 (1963).
4. J. Kasper and S. Richards, *Acta Crystollogr.* **17**, 752 (1964).
5. R. H. Wentorf, Jr., and J. S. Kasper, *Science* **139**, 338 (1963).
6. M. J. P. Musgrave and J. A. Pople, *J. Phys. Chem. Solids* **23**, 321 (1962).
7. R. E. Hanneman, H. M. Strong, F. P. Bundy, *Science* **155**, 995 (1967).
8. F. P. Bundy and J. S. Kasper, *J. Chem. Phys.* **46**, 3437 (1967).
9. S. C. Danforth, thesis, Brown University (June 1975).
10. H. M. Jennings and M. H. Richman, *J. Mater. Sci.*, in press.
11. Research supported by the U.S. Army Research Office under grant DS-ARO-D-31-127-72-6183 (Project No. 10618-mc).

14 July 1975; revised 14 June 1976