

## Transformation of Three-Connected Silicon in BaSi<sub>2</sub>

JÜRGEN EVERS

*Institut für Anorganische Chemie der Universität, Meiserstrasse 1, D-8000 München 2, Germany*

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Solid-solid transitions in trimorphic BaSi<sub>2</sub> have been investigated up to 40 kbar and 1000°C by X-ray powder technique in quenched samples. All transformations between orthorhombic BaSi<sub>2</sub>I with isolated Si-tetrahedra, trigonal BaSi<sub>2</sub>II with corrugated Si-layers, and cubic BaSi<sub>2</sub>III with a three-dimensional three-connected Si-net can be performed in approximately 5 min at high-pressure-high-temperature conditions. At ambient conditions the difference in molar volume between BaSi<sub>2</sub>I and BaSi<sub>2</sub>III is relatively large ( $\Delta V_{I-III} = -6.79 \text{ cm}^3/\text{mole}$ ) and that between BaSi<sub>2</sub>III and BaSi<sub>2</sub>II very small ( $\Delta V_{III-II} = -0.05 \text{ cm}^3/\text{mole}$ ). Consequently in the pressure-temperature phase diagram the boundary (I-III) shows a strong pressure dependence contrary to that of (III-II) which is less dependent on variation of pressure. The triple point between the three solid phases is near 11 kbar and 925°C. Substitution of divalent metal and quadrivalent metalloid can easily influence the phase relations in BaSi<sub>2</sub>.

### Introduction

Barium disilicide is an interesting compound. Up to 40 kbar and 1000°C it exists in three polymorphs. Remarkably, in the silicon and sublattice of its polymorphs the main structural arrangements are found which occur in divalent metal disilicides  $MSi_2$  and digermanides  $MGe_2$  ( $M = Yb, Ca, Eu, Sr, Ba$ ) at all. The metalloid atoms in these polyanionic compounds, always bonded to three other metalloid atoms, build up isolated tetrahedra, layers, and three-dimensional nets.

The room temperature modification BaSi<sub>2</sub>I is orthorhombic (1, 2), space group  $D_{2h}^{16}-Pnma$ , with BaSi<sub>2</sub>-type structure. The most prominent feature of this structure is isolated Si-tetrahedra separated from each other by more than 1.5 Si-Si bond distance. These tetrahedra are only slightly distorted from ideal ones. Bond angles Si<sup>Si</sup>Si vary approximately  $\pm 1^\circ$  around the ideal value of

60° and bond distances Si-Si lie between 2.395 and 2.435 Å (3).

With increasing temperature and pressure BaSi<sub>2</sub> displays an interesting polymorphic behavior. BaSi<sub>2</sub>II, space group  $D_{3d}^3-P\bar{3}m1$ , is trigonal (4-6) with EuGe<sub>2</sub>-type structure (7). In the silicon sublattice of this polymorph corrugated layers of three-connected Si atoms with equidistant bonds (2.43 Å) and equal bond angles (112°) are found.

Cubic BaSi<sub>2</sub>III (8), space group  $O^h-P4_332$ , with SrSi<sub>2</sub>-type structure (9, 2, 10) is stable at lower temperatures and pressures than BaSi<sub>2</sub>II. In the silicon sublattice of this structure type the topologically simplest three-dimensional three-connected (3D3C) net is found only slightly distorted from its ideal configuration (11-16). The repeat unit of four equidistant (2.446 Å) three-connected Si atoms in BaSi<sub>2</sub>III consists of very flat trigonal pyramids with equal bond angles of 118° instead of a coplanar group with bond

angles of  $120^\circ$ . The ideal cubic 3D3C net represents the three-connected analog of the four-connected diamond net (15). In Fig. 1a isolated Si tetrahedra of  $\text{BaSi}_2\text{I}$  are shown; in Fig. 1b corrugated Si layers of  $\text{BaSi}_2\text{II}$  and in Fig. 1c the cubic 3D3C Si net of  $\text{BaSi}_2\text{III}$ .

In continuation of our investigations on the transformation of three-connected silicon nets in  $\text{CaSi}_2$  (17) and in  $\text{SrSi}_2$  (18) the present paper concerns crystal chemical relations in trimorphic  $\text{BaSi}_2$  and the pressure-temperature phase diagram up to 40 kbar and  $1000^\circ\text{C}$ .

## Experimental Procedure

### 1. Sample Preparation

High purity semiconducting (19)  $\text{BaSi}_2$  was prepared in an inductively heated, high-vacuum tight, cold copper boat (20) by direct synthesis. Starting materials were ultrahigh-vacuum distilled barium (21-23) and electronic grade silicon. Typical spark source mass spectrographic analysis showed that the total purity of  $\text{BaSi}_2\text{I}$  is better than 99.9 wt% (24).

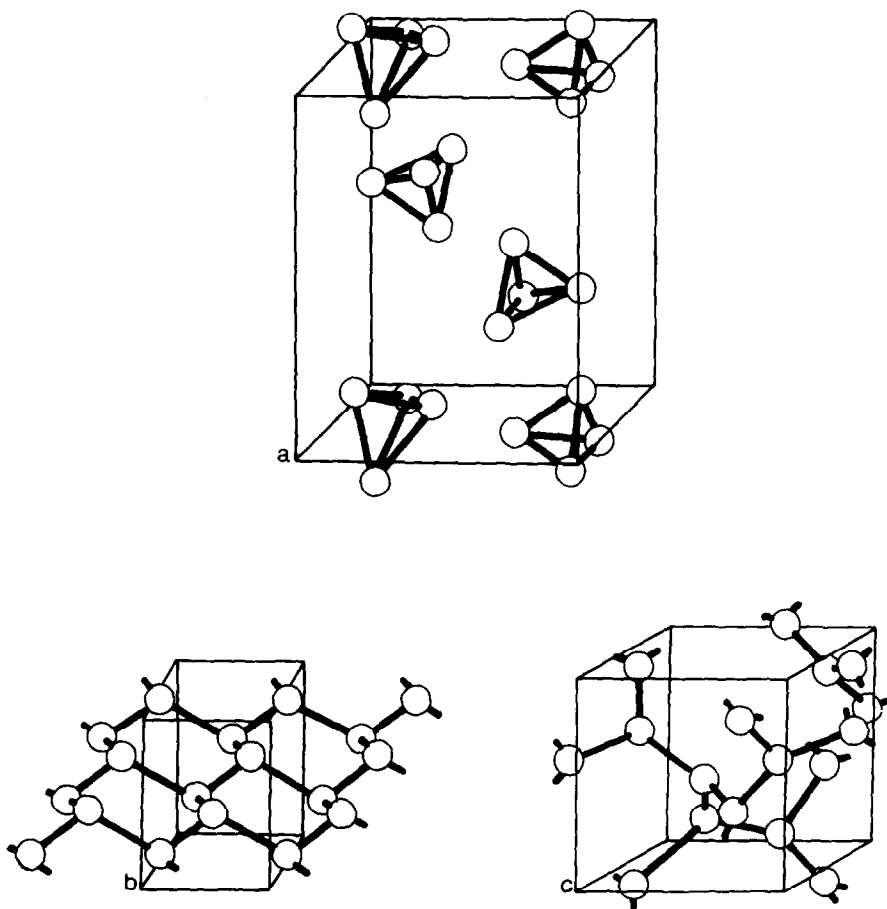


FIG. 1. Structural arrangements of three-connected silicon in trimorphic  $\text{BaSi}_2$ : (a) Si tetrahedra of orthorhombic phase I; (b) corrugated Si layers of trigonal phase II; (c) Si net of cubic phase III in its slightly distorted configuration.

## 2. High-Pressure, High-Temperature Treatment

A belt-type apparatus was used to generate high pressures up to 40 kbar and high temperatures up to 1500°C (25). The discontinuities in resistance during the transformations Ce(I–II), Bi(I–II), and Tl(I–III) at 6–8, 25.5, and 36.7 kbar, respectively, were used for pressure calibration at room temperature. It was assumed that this pressure calibration holds also at high temperatures. Temperatures were measured via wattages calibrated against chromel alumel thermocouples and corrected for pressure dependence (26). For the study of the phase diagram defined  $p$ – $T$  conditions were maintained for 15 min. The samples were rapidly quenched to room temperature before pressure was released. Pressures are believed to be correct within  $\pm 2$  kbar, temperatures within  $\pm 25^\circ\text{C}$ . Additional details have been given elsewhere (27).

Considerable problems were encountered with experiments at lower pressure ( $\leq 10$  kbar) and higher temperature ( $\geq 800^\circ\text{C}$ ). Under these conditions current dropped and voltage increased abruptly after 5–10 min so that wattage was difficult to keep constant. The limited stability of the graphite heaters may result from their reaction with water from the dehydration of pyrophyllite as pressure-transmitting medium.

## 3. X-Ray Characterization

Debye–Scherrer X-ray technique (114.6 mm Seifert camera) with Ni-filtered copper radiation was used for phase analyses.

## 4. Differential Thermal Analyses

In a high-vacuum tight Linseis DTA-apparatus (heating rate  $20^\circ/\text{min}$ , PtRh–Pt thermocouples, dynamic argon flow) nonequilibrium transformations BaSi<sub>2</sub>(II–I) and BaSi<sub>2</sub>(III–I) were studied. Calibration and additional details are quoted elsewhere (18).

## Results

In Table I structural data for orthorhombic BaSi<sub>2</sub>I, trigonal BaSi<sub>2</sub>II, and cubic BaSi<sub>2</sub>III are listed. More detailed data derived from single crystal investigations on a four-circle diffractometer using molybdenum radiation will be published elsewhere (3).

In Fig. 2 the pressure–temperature phase diagram of BaSi<sub>2</sub> up to 40 kbar and 1000°C is presented. This diagram is based on 31 different  $p$ – $T$  experiments. However, curvature of the phase boundaries could not be resolved by our equipment. The triple point between the three solid phases lies near 11 kbar and 925°C (Fig. 2). Due to the limited stability of the graphite heaters ( $\leq 10$  kbar,  $\geq 800^\circ\text{C}$ ) the equilibrium line BaSi<sub>2</sub>(I–III) was difficult to locate. The phase boundary BaSi<sub>2</sub>(III–II) has a negative slope,  $(\Delta p/\Delta T)_{\text{III–II}} \approx -290$  bar/deg. Further work with improved experimental techniques is needed to determine the slopes  $(\Delta p/\Delta T)_{\text{I–III}}$  and  $(\Delta p/\Delta T)_{\text{I–II}}$  precisely in order to derive thermochemical data via Clausius–Clapeyron equation.

Table II shows the thermochemical data from DTA runs at nonequilibrium conditions for BaSi<sub>2</sub>(II–I) and BaSi<sub>2</sub>(III–I) using samples of equal weights. In Fig. 3 the exothermic, irreversible transformations at ambient pressure are shown. Increasing sample weights does not yield higher resolution since then base lines deviate more. The nonequilibrium transformation enthalpies are  $\Delta H_{\text{II–I}} = -1.1 \pm 0.2$  and  $\Delta H_{\text{III–I}} = -0.8 \pm 0.4$  kcal/mole. Complete retractions (II–I) and (III–I) are achieved at a heating rate of  $20^\circ/\text{min}$  within 5 and 8 min, respectively (Table II, Fig. 3). Data of transformation (II–I) agree with those quoted earlier (28) before transformation orthorhombic into cubic BaSi<sub>2</sub> was known.

## Discussion

By high pressure–high temperature treatment of BaSi<sub>2</sub>I a density increase of

TABLE I  
STRUCTURAL DATA FOR ORTHORHOMBIC, TRIGONAL, AND CUBIC BaSi<sub>2</sub><sup>a</sup>

Phase	Normal pressure(I)	High Pressure(II)	High pressure(III)
Crystal class	Orthorhombic	Trigonal	Cubic
Space group	$D_{2h}^{16}-Pnma^b$	$D_{3d}^3-P\bar{3}m1$	$O^6-P4_332$ (or $O^7-P4_132$ ) <sup>c</sup>
Lattice parameters (Å)	$a = 8.942(4)$ $b = 6.733(3)$ $c = 11.555(5)$	$a = 4.047(3)$ $c = 5.330(5)$	$a = 6.715(3)$
Cell volume (Å <sup>3</sup> )	695.7 = 8·86.96	75.60	302.8 = 4·75.70
Density (g/cm <sup>3</sup> )			
Observed	3.54	4.2 <sub>6</sub>	4.2 <sub>7</sub>
Calculated	3.696	4.251	4.246
Molar volume (cm <sup>3</sup> /mole)	52.37	45.53	45.58
Formula units	8	1	4
Positions	4 Ba <sub>I</sub> in 4c  4 Ba <sub>II</sub> in 4c 4 Si <sub>I</sub> in 4c 4 Si <sub>II</sub> in 4c 8 Si <sub>III</sub> in 8d	1 Ba in 1a 2 Si in 2d	4 Ba in 4a 8 Si in 8c

<sup>a</sup> Numbers in parentheses are the experimental uncertainties on the last digit.

<sup>b</sup> From systematic extinctions acentric space group  $Pna2_1$  is also allowed. But for  $z = 1/4$  position 4a in  $Pna2_1$  is identical with 4c in  $Pnma$  (n.b. interchange  $z$  with  $y$ ). Refinement from 3200 independent reflections yield for Ba positions in  $Pna2_1$  only very slight deviation from  $z = 1/4$ ;  $x$  and  $y$  are identical with 4c; RF value is not significantly lowered.

<sup>c</sup> The investigated single crystal has absolute configuration  $P4_332$ . By Hamilton test (346 reflections,  $R_{4332} = 3.79$ ,  $R_{4132} = 4.09$ ) enantiomorphic space group  $P4_132$  is rejected at a lower than the 0.005 level of significance.

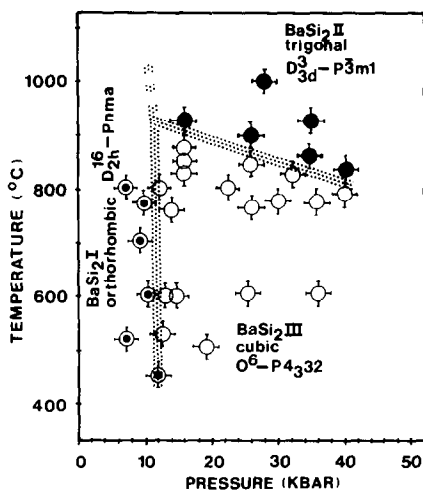


FIG. 2. Pressure-temperature phase diagram of BaSi<sub>2</sub> up to 40 kbar and 1000°C.

approximate 15% is achieved for both BaSi<sub>2</sub>II and III. Astonishingly, a higher formal coordination number of BaSi<sub>2</sub>II (12:6, Ba has 12 Si, Si has 6 Ba neighbors) than of BaSi<sub>2</sub>III (8:4) is not adequately reflected in their densities; the latter is only 0.1% lower in density than the first (Table I). On the other hand, high pressure-high temperature treatment (max. 40 kbar, max. 1000°C) is yet not sufficient enough to change the bond character in BaSi<sub>2</sub>II or III. Also here the silicon atoms remain three-connected.

Therefore it is possible that large difficulties must not be overcome in order to transform phases I, II, and III into each other. Indeed, at high pressure-high temperature conditions all transformations

TABLE II

THERMOCHEMICAL DATA OF THE NONEQUILIBRIUM TRANSFORMATIONS TRIGONAL INTO ORTHORHOMBIC AND CUBIC INTO ORTHORHOMBIC BaSi<sub>2</sub> AT AMBIENT PRESSURE

	Transformation	
	Trigonal into orthorhombic	Cubic into orthorhombic
Transformation character at ambient pressure	Exothermic, irreversible	Exothermic, irreversible
Sample weight (mg)	69.4	69.4
Heating rate (°/min)	20	20
Transformation peak (°C)		
Start	420	490
End	520	640
Enthalpy of transformation at ambient pressure (kcal/mole)	-1.1 ± 0.2	-0.8 ± 0.4

in trimorphic BaSi<sub>2</sub> can be performed in 5 min with a yield of at least 90%, as can be easily shown by X-ray investigations in quenched samples. Due to the rapidity of these transformations one can speculate that

a total breakdown of lattices during transformation is quite improbable. Total reconstructive transformations (29, 30) are expected to be rather sluggish.

However, obvious structural relations between BaSi<sub>2</sub>I with Si tetrahedra, BaSi<sub>2</sub>II with corrugated Si layers, and BaSi<sub>2</sub>III with cubic 3D3C Si net do not appear at first sight. In Fig. 4a Si tetrahedra of four unit-cells of orthorhombic BaSi<sub>2</sub>I are projected on (010). The tetrahedra, related by a center of symmetry, are tilted against each other, perhaps due to more efficient packing. Thus, one inversion tetrad of each tetrahedron lies in a plane parallel to the (a, c) plane at  $y = 1/4$  or  $y = 3/4$ . In the upper left cell of Fig. 4b one inversion tetrad is shown. A rotation of 45° around this axis results in a second group of inversion tetrads lying already parallel to the  $b_{\text{orth}}$  axis. Now, structural relations in trimorphic BaSi<sub>2</sub> become more evident (Figs. 4a-d). In order to transform the Si tetrahedra the inversion tetrads parallel  $b_{\text{orth}}$  axis have to be converted into 4<sub>3</sub> helices (or the enantiomorphic 4<sub>1</sub> ones) if the cubic 3D3C Si net of BaSi<sub>2</sub>III is created or into flat distorted "helices" if the corrugated Si layers of BaSi<sub>2</sub>II are built up.

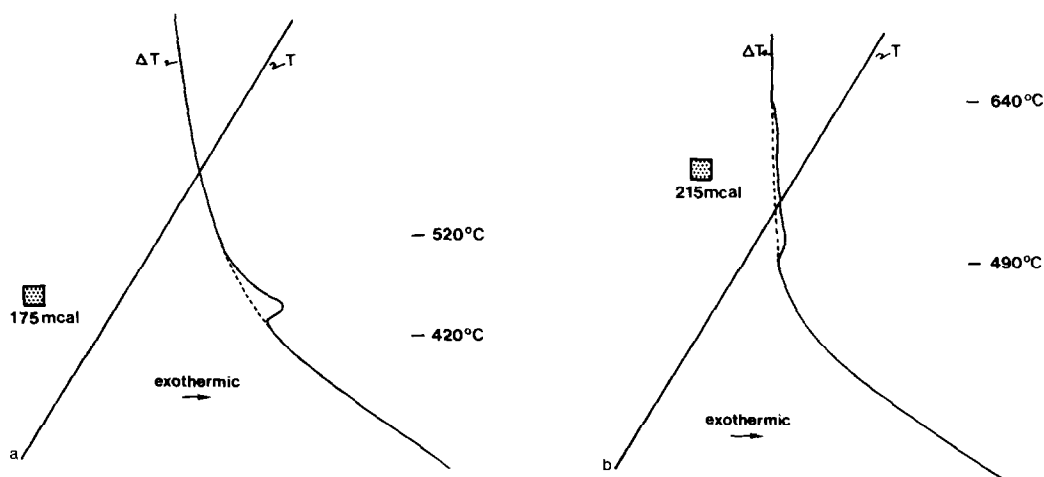


FIG. 3. Thermogram of nonequilibrium transformation of 69.4 mg BaSi<sub>2</sub> at a heating rate of 20°/min: (a) trigonal into orthorhombic; (b) cubic into orthorhombic.

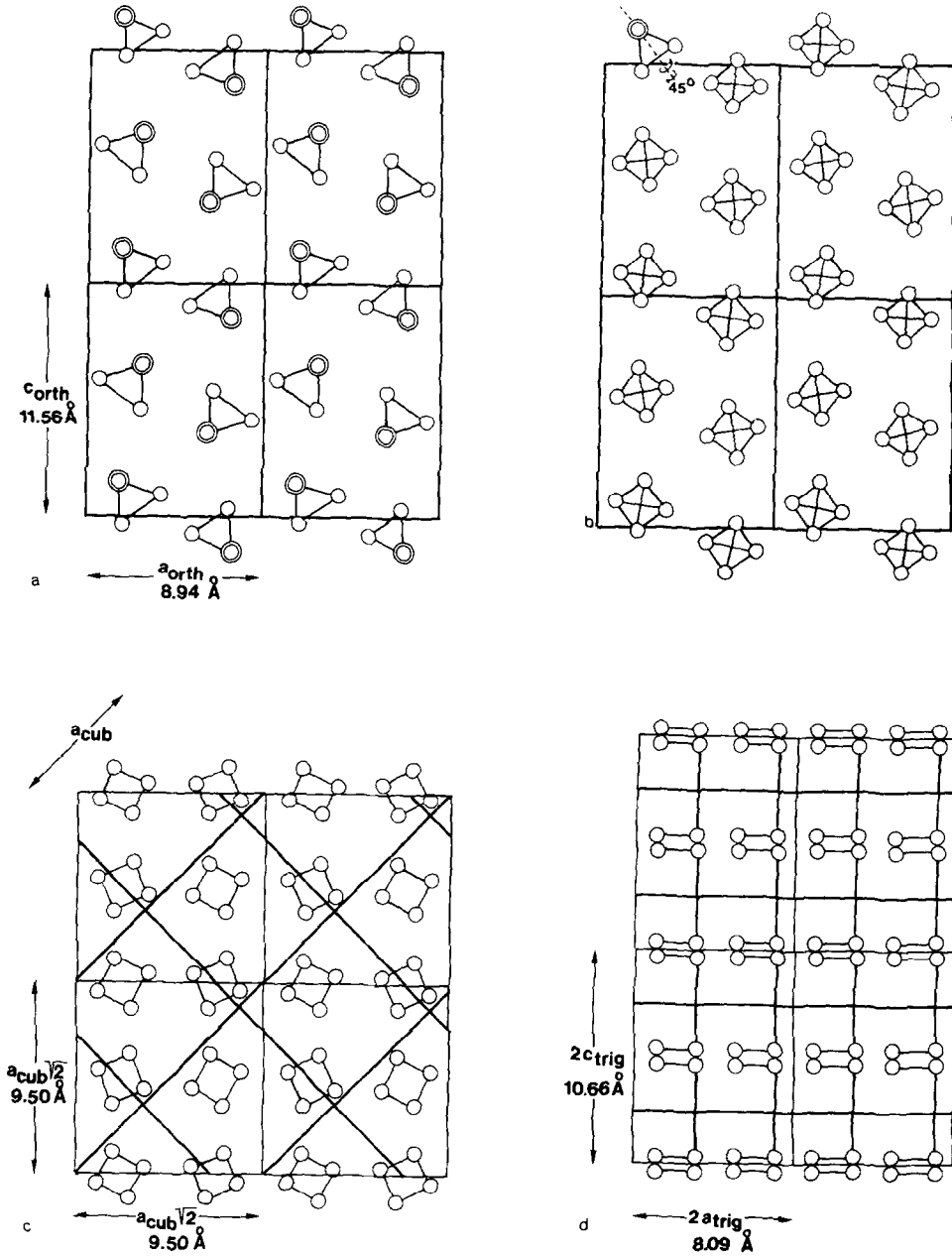


FIG. 4. (A) Projection on (010) of Si tetrahedra of four orthorhombic unit-cells of BaSi<sub>2</sub>I. Symmetry related tetrahedra are tilted against each other. (b) Projection on (010) of Si tetrahedra after 45° rotation. One tetrahedron before rotation is shown in the upper left cell. (c) Projection on (001) of the Si net of eight unit-cells on cubic BaSi<sub>2</sub>III. For the positional parameter  $x_{\text{Si}} = 0.419$  the 4<sub>3</sub>-Si helices are rotated against each other. (d) Projection on (010) of corrugated Si layers of 16 orthohexagonal unit-cells of trigonal BaSi<sub>2</sub>II. Silicon atoms are arranged in flat distorted "helices." For reasons of clearness bonds between the "helices" are not shown.

TABLE III  
LATTICE PARAMETERS FOR THE Sr<sub>1-x</sub>Ba<sub>x</sub>Si<sub>2</sub> SYSTEM<sup>a</sup>

Composition x	Structure					
	SrSi <sub>2</sub> type			BaSi <sub>2</sub> type		
	Phase	a axis (Å)	Phase	a axis (Å)	b axis (Å)	c axis (Å)
0.00	NP	6.0535(3)				
0.10	NP	6.555(5)				
0.25	HP	6.579(5)	NP	8.69(5)	6.56(4)	11.23(8)
0.50	HP	6.622(8)	NP	8.77(5)	6.62(4)	11.33(8)
0.75	HP	6.672(5)	NP	8.88(5)	6.70(4)	11.48(8)
0.90	HP	6.695(5)	NP	8.90(5)	6.72(4)	11.54(8)
1.00	HP	6.715(3)	NP	8.942(4)	6.733(3)	11.555(5)

<sup>a</sup> NP, Normal pressure; HP, high pressure. Numbers in parentheses are experimental uncertainties on the last digit.

For transformation of orthorhombic BaSi<sub>2</sub>I into cubic BaSi<sub>2</sub>III  $b_{\text{orth}} = 6.73 \text{ \AA}$  has to become  $a_{\text{cub}} = 6.72 \text{ \AA}$ . This agreement of unit-cell parameters  $b_{\text{orth}}$  and  $a_{\text{cub}}$  is also fulfilled in solid solutions Sr<sub>1-x</sub>Ba<sub>x</sub>Si<sub>2</sub> (Table III) (31) which can be prepared dimorphically. Since the Si tetrahedra (Fig. 4b) also have to rearrange, shortening in the  $c_{\text{orth}}$  direction ( $c_{\text{orth}} = 11.56 \text{ \AA} \rightarrow a_{\text{cub}} \cdot 2^{1/2} = 9.50 \text{ \AA}$ ) and elongation in the  $a_{\text{orth}}$  direction ( $a_{\text{orth}} = 8.94 \text{ \AA} \rightarrow a_{\text{cub}} \cdot 2^{1/2} = 9.50 \text{ \AA}$ ) is necessary in order to transform them into the cubic 3D3C Si net. One orthorhombic unit-cell ( $V_{\text{orth}} = a_{\text{orth}} \cdot b_{\text{orth}} \cdot c_{\text{orth}}$ ) with eight formula units BaSi<sub>2</sub> (= 16 Si atoms) is then converted into two cubic unit-cells ( $V_{\text{orth}} = a_{\text{cub}} \cdot 2^{1/2} \cdot a_{\text{cub}} \cdot a_{\text{cub}} \cdot 2^{1/2} = 2 V_{\text{cub}}$ ) with  $2 \cdot 4$  formula units (= 2 · 8 Si atoms). For the change of one inversion tetrad (parallel  $b_{\text{orth}}$ ) of one Si tetrahedron into a  $4_3$  helix three of the six Si-Si bonds within one tetrahedron have to be broken (Figs. 5a and b) and the Si<sup>Si</sup>Si bond angle has to increase from approximately 60 to 118°. For creation of the cubic 3D3C Si net from the  $4_3$  helices every Si atom in such a helix has to use one bond for connection with other helices. Further details of the cubic 3D3C net are discussed in (18).

On the other hand, for transformation of Si tetrahedra (BaSi<sub>2</sub>I) into corrugated Si layers (BaSi<sub>2</sub>II)  $b_{\text{orth}} = 6.73 \text{ \AA}$  has to become orthohexagonal  $b_{\text{orth hex}} = a_{\text{trig}} 3^{1/2} = 7.01 \text{ \AA}$ . The flat distorted "helices" (Fig. 5c) which have to be created from Si tetrahedra are not true helices since, e.g., a constant sense of screw motion is missing. Additional details are quoted in (17). For the transformation BaSi<sub>2</sub>(I-II) shortening both in the  $c_{\text{orth}}$  direction ( $c_{\text{orth}} = 11.56 \text{ \AA} \rightarrow 2 c_{\text{orth hex}} = 2 c_{\text{trig}} = 10.66 \text{ \AA}$ ) and  $a_{\text{orth}}$  direction ( $a_{\text{orth}} = 8.94 \text{ \AA} \rightarrow 2 a_{\text{orth hex}} = 2 a_{\text{trig}} = 8.09 \text{ \AA}$ ) is required. One orthorhombic unit-cell has therefore to be changed into four orthohexagonal cells of BaSi<sub>2</sub>II with  $2 \cdot 4 = 8$  formula units (= 2 · 4 · 2 Si atoms). Also here three of the six Si-Si bonds within one Si tetrahedron have to be broken in order to be converted into corrugated Si layers. In addition, Si<sup>Si</sup>Si bond angles have to be increased from approximately 60 to 112°, slightly lower than for BaSi<sub>2</sub>(I-III) transformation (60 → 118°) (Figs. 5a-c).

From a structural point of view one would expect the transformation between the cubic 3D3C Si net (BaSi<sub>2</sub>III) and corrugated Si layers (BaSi<sub>2</sub>II) to be more rapid than

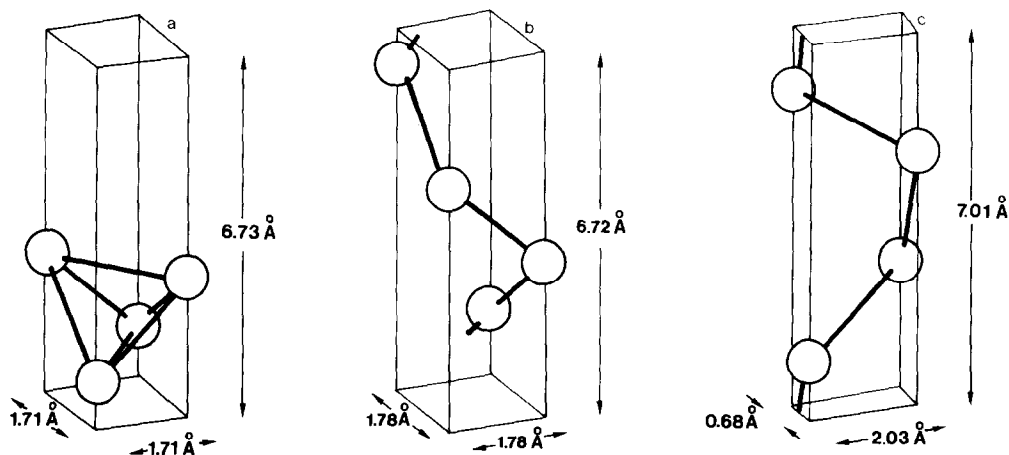


FIG. 5. Comparison of four Si atoms within a: (a) tetrahedron of  $\text{BaSi}_2\text{I}$  after  $45^\circ$  rotation; (b)  $4_3$ -helix of  $\text{BaSi}_2\text{III}$ ; (c) flat distorted "helix" of  $\text{BaSi}_2\text{II}$ .

between  $\text{BaSi}_2\text{I}$  and  $\text{BaSi}_2\text{II}$  and also between  $\text{BaSi}_2\text{I}$  and  $\text{BaSi}_2\text{III}$ . For the transformation  $\text{BaSi}_2(\text{III-II})$  only 33% of the Si-Si bonds within the nets have to be broken and bond angles  $\text{Si}^i\text{Si}^j$  must only change from  $118$  to  $112^\circ$ . But for transformations  $\text{BaSi}_2(\text{I-II})$  and  $\text{BaSi}_2(\text{I-III})$  50% of the Si-Si bonds must be broken. The change in bond angles  $\text{Si}^i\text{Si}^j$  from  $60$  to  $112$  and  $118^\circ$ , respectively, is also larger. However, experimental transformation kinetics are a rather complex subject.

In addition, the transformation of the cubic 3D3C Si net ( $\text{BaSi}_2\text{III}$ ) into two-dimensional Si layers is also the first example for  $M\text{Si}_2$  and  $M\text{Ge}_2$  compounds ( $M = \text{Yb}, \text{Ca}, \text{Eu}, \text{Sr}, \text{Ba}$ ) where by increasing pressure and temperature (e.g.,  $\text{BaSi}_2\text{III}$  at 20 kbar,  $900^\circ\text{C}$ ; Fig. 2) the dimension of the arrangement of the metalloid atoms is lowered. Dimension increasing is much more common and known for five transformations in these compounds ( $\text{CaSi}_2(\text{I-II})$  (20, 17),  $\text{BaSi}_2(\text{I-II})$  (6),  $\text{BaSi}_2(\text{I-III})$  (8),  $\text{SrGe}_2(\text{I-II})$  (32),  $\text{BaGe}_2(\text{I-II})$  (33)).

Better understanding of the thermochemical relations in trimorphic  $\text{BaSi}_2$  results from comparison of the pressure-tempera-

ture phase diagram (Fig. 2) with the differences in molar volume between phase I, II, and III (Table I). It is obvious that  $\Delta V_{\text{I-II}}$  and  $\Delta V_{\text{I-III}}$  are very large contrary to  $\Delta V_{\text{III-II}}$  which is very small. Internal work  $-p\Delta V$  contributes then in the transformations I-II and I-III strongly and in III-II only a little. Therefore the phase boundaries I-II and I-III show a strong pressure dependence whereas phase boundary III-II is less dependent on variation of pressure (Fig. 2, n.b. abscissa and ordinate are interchanged). These relations are also supported by the data derived by nonequilibrium DTA experiments (Table II, Fig. 3). However, this comparison is restricted to a certain degree since thermodynamic equilibrium conditions are missing if quenched high-pressure-high-temperature samples are retransformed at ambient pressure in a DTA-apparatus. But one has to consider that from equilibrium DTA experiments at high pressure-high-temperature conditions, a particularly difficult experimental technique, up to now only transformation temperatures, but no quantitative transformation energies can be obtained. Therefore, nonequilibrium energies derived by a simpler DTA technique at



ambient pressure may serve as first information. By inspection of Table II it is obvious that these values in BaSi<sub>2</sub> ( $\Delta H_{\text{II-I,n.e.}} = -1.1 \pm 0.2$ ,  $\Delta H_{\text{III-I,n.e.}} = -0.8 \pm 0.4$ , in kcal/mole) are relatively small compared to those in CaSi<sub>2</sub> (17) and SrSi<sub>2</sub> (18) with  $\Delta H_{\text{II-I,n.e.}} = -4.2 \pm 0.8$  and  $\Delta H_{\text{III-I,n.e.}} = -1.6 \pm 0.3$  (in kcal/mole), respectively. These low values in BaSi<sub>2</sub> are compatible with small changes in entropy  $\Delta S$ . A small entropy change is correlated for BaSi<sub>2</sub>(I-II) and BaSi<sub>2</sub>(I-III) to a relatively large change in molar volume and, on the other hand, in BaSi<sub>2</sub>(III-II) to a very small one. Due to the Clausius-Clapeyron equation  $\Delta p/\Delta T = \Delta S/\Delta V$  the phase boundaries (I-II) and (I-III) show slight slopes, contrary to (III-I) with a steep slope. Unfortunately, these extreme values of the slopes  $\Delta p/\Delta T$  are difficult to evaluate accurately (Fig. 2, n.b. abscissa and ordinate are interchanged, as mentioned above) if one bears in mind the uncertainty in pressure and temperature measurement.

Although the thermochemical separation between orthorhombic BaSi<sub>2</sub>I with isolated Si tetrahedra, trigonal BaSi<sub>2</sub>II with corrugated Si layers, and cubic BaSi<sub>2</sub>III with 3D3C Si net seems smaller than that in dimorphic CaSi<sub>2</sub> or SrSi<sub>2</sub>, there has been found no hint up to now that BaSi<sub>2</sub>II or III are high-temperature phases at ambient pressure. If melts of composition Ba:2Si in a water-cooled copper boat at ambient pressure are quenched by abruptly switching off HF-energy phase I is always obtained. At this condition  $T\Delta S$  does not alone stabilize phase II or III. By heating to the melting point phase I takes up thermal energy without transformation. However, the situation is changed if in addition to heating, pressure is applied. Most probably increasing of cell volume due to thermal expansion is overcompensated by compression due to applying high pressures. Now the cubic 3D3C Si net and the corrugated Si layers in BaSi<sub>2</sub> can take up better thermal energy than

the phase with isolated tetrahedra, tilted against each other.

Substitution of both constituents, divalent metal and quadrivalent metalloid, can easily influence the thermochemical relations between the phases with tetrahedra, layers, and 3D3C nets. Corrugated Si layers can be prepared using high-pressure-high-temperature conditions in limited ranges of solid solutions between SrSi<sub>2</sub> and BaSi<sub>2</sub> and also between BaGe<sub>2</sub> and BaSi<sub>2</sub>. In solid solutions Sr<sub>1-x</sub>Ba<sub>x</sub>Si<sub>2</sub> layers are obtained in the small range  $0.9 < x \leq 1.0$ . For higher Sr contents only the cubic 3D3C Si net is stable up to 40 kbar and 1000°C. Also in solid solutions BaSi<sub>2-x</sub>Ge<sub>x</sub> the range of existence of layers ( $0.0 \leq x < 0.5$ ) is smaller than the cubic 3D3C net ( $0.0 \leq x \leq 1.0$ ). For  $1.0 \leq x \leq 2.0$  the tetragonal 3D3C net (11-16) ( $\alpha$ -ThSi<sub>2</sub>-type structure) (34) is found at high pressures and high temperatures.

Interestingly, although in BaSi<sub>-1.0</sub>Ge<sub>-1.0</sub> the cubic 3D3C net is more densely packed than the tetragonal one ( $V_{\text{cub}} = 312$ ,  $V_{\text{tetr}} = 326$ , in Å<sup>3</sup> for four formula units) the first is destabilized. This is possible only if the gain in  $T\Delta S$  is higher than the loss in  $p\Delta V$ . For attempts to prepare the cubic 3D3C net as third polymorph of BaGe<sub>2</sub> (phase I: BaSi<sub>2</sub>-type structure with Ge tetrahedra; phase II:  $\alpha$ -ThSi<sub>2</sub>-type structure with tetragonal 3D3C Ge net) from the investigation of the thermochemical relations in BaSi<sub>2</sub> and some solid solutions, low temperatures (e.g., 400°C) and very high pressures ( $\gg 40$  kbar) are therefore recommended.

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