Cited References

53Hal: R. N. Hall, "Segregation of Impurities During the Growth of Ge and Silicon Crystals", *J. Phys. Chem.*, *57*, 836-839 (1953). (Equi Diagram; Experimental)

56Bar: M.-J. Barbier-Andrieux, "Sur la Préparation par Électrolise Ignée des Alliages du Germanium avec le Silicium et Quelques Autres Métalloides (Preparation of Germanium Alloys with Silicon and Some Other Metalloids by Fusion Electrolysis)", *C.R. Hebd. Séances Acad. Sci.*, *242*, 2352-2354 (1956) in French. (Equi Diagram; Experimental)

56Bri: H. E. Bridgers and E. D. Kolb, "Distribution Coefficient of Boron in Germanium", *J. Chem. Phys.*, *25*, 648-650 (1956). (Equi Diagram; Experimental)

60Sam: G. V. Samsonov, N. N. Zhuravlev, Yu. B. Paderno, O. I. Shulishova, and T. I. Serebryakova, "Interaction of Gallium, Indium, Thallium, Germanium, Tin, and Lead with Boron", *Zh. Strukt. Khim.*, *1*, 458-463 (1960) in Russian; TR: *J. Struct. Chem. (USSR)*, *1*, 425-429 (1960). (Crys Structure; Experimental)

65Wal: F. Wald and R. W. Stormont, "Investigations on the Constitution of Certain Binary Boron-Metal Systems", *J. Less-Common Met.*, *9*, 423-433 (1965). (Crys Structure; Experimental)

***70Bid:** L. R. Bidwell, "The Boron-Germanium System", *J. Less-Common Met.*, *20*, 19-27 (1970). (Equi Diagram; Experimental; #)

70Edw: W. D. Edwards, "The Distribution Coefficient of Boron in Germanium", *J. Electrochem. Soc.*, *117*, 1062-1065 (1970). (Equi Diagram; Experimental)

73Hol: C. E. Holcombe, Jr., D. D. Smith, J. D. Lore, W. K. Duerksen, and D. A. Carpenter, "Physical-Chemical Properties of β-Rhombohedral Boron", *High Temp. Sci.*, *5*, 349-357 (1973). (Equi Diagram; Experimental)

77Cal: B. Callmer, "An Accurate Refinement of the β-Rhombohedral Boron Structure", *Acta Crystallogr.*, *B33*, 1951-1954 (1977). (Crys Structure; Experimental)

81BAP: "Melting Points of the Elements", *Bull. Alloy Phase Diagrams*, *2*(1), 145-146 (1981). (Equi Diagram; Compilation)

81Kin: H. W. King, "Crystal Structures of the Elements at 25 °C", *Bull. Alloy Phase Diagrams*, *2*(3), 401-402 (1981). (Crys Structure; Compilation)

***81Lun:** T. Lundström and L.-E. Tergenius, "A Single-Crystal Study of a Solid Solution of the Composition GeB_{-90}", *J. Less-Common Met.*, *82*, 341-348 (1981). (Crys Structure; Experimental)

*Indicates key paper.
#Indicates presence of a phase diagram.

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The B-Si (Boron-Silicon) System

28.0855 10.81

By R.W. Olesinski and G.J. Abbaschian
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Equilibrium Diagram

The assessed equilibrium phase diagram of the Si-B system is presented in Fig. 1. The diagram includes: (1) a peritectic transformation at 2020 °C involving the B-rich intermediate phase SiB_n ($n \approx 23$), (2) a peritectic transformation involving the intermediate phase SiB_6 at 1850 °C, (3) a eutectic transformation of the liquid of 8 at.% B at 1385 °C, and (4) a peritectoid transformation involving the intermediate phase SiB_3 around 1270 °C.

The monovariant and invariant reactions of the system are listed in Table 1.

Solid Solution of B in Si, (Si). The reported data on the B solid solubility limits in Si, as tabulated in Table 2, are rather conflicting. [68Hes] used electrical conductivity and Hall effect techniques to determine the maximum solubility of B in Si in the temperature range 900 to 1200 °C; the conductivity measurements were conducted on samples cooled from the annealing temperature to room temperature at about 100 °C/min. His values disagree with the X-ray analysis results of [63Sam], who measured lattice parameters of alloys quenched in oil after homogenization for 8 h at different temperatures; to determine the solubility limit of B in Si at room temperature, [63Sam] cooled the samples from 1300 to 600 °C in 5 h, and then to room temperature in 4 h. The solubility limit was also obtained at a single temperature, 1200 °C, by B.T. Howard from diffusion measurements (as quoted by [60Tru]). [54Ful] calculated the solid solubility to be between 0.6 and 1.2 at.% B at 1250 °C, from resistance and Hall effect measurements conducted by A. Uhlir, and by F.J. Marin and J.P. Maita, respectively. [54Ful] listed the work of Uhlir as a private communication, but did not give the source for the latter researchers. The present evaluators were not able to find either source. Metallographic analysis [49Pea] indicated the solid solubility to be <1.3 at.% B at an unspecified temperature.

Table 1 Monovariant and Invariant Reactions in the Si-B System

Phases	Compositions, at.% B			Temperature, °C	Reaction type
$L + (B) \rightleftarrows SiB_n$	90.7	97.0 ± 0.4	95.9 ± 0.4	2020 ± 15	Peritectic
$L + SiB_n \rightleftarrows SiB_6$	65.3	94	85.7	1850 ± 15	Peritectic
$L \rightleftarrows (Si) + SiB_6$	8	3	85.7	1385 ± 15	Eutectic
$(Si) + SiB_6 \rightleftarrows SiB_3$	1	85.7	75.0	1270	Peritectoid
$L \rightleftarrows Si$		0		1414	Melting
$L \rightleftarrows B$		100		2092	Melting

In spite of the disagreement between the solubility limits reported by [68Hes] and [63Sam], both sets of data indicated that the solubility increases with the temperature; [63Sam] estimated that the solubility reaches 3.6 at.% B at 1375 °C. The present evaluators, taking into consideration data of [68Hes], which are generally smaller than those of [63Sam], have assessed the maximum solid solubility to be ~3 at.% B at the eutectic temperature (1385 °C).

The solid solution, as discussed later, is substitutional, and the Si lattice parameter contracts upon alloying with B.

The equilibrium distribution coefficient of B in Si near the Si melting point was reported as 0.8 to 0.9 in [53Hal], [54Bur], and [60Tru].

Intermediate Phase SiB_3. The formation of a boride containing roughly 75 at.% B was first reported by [00Moi]. The existence of the stable rhombohedral phase is well documented, although its ranges of thermal stability and homogeneity are still uncertain. The compound was obtained by direct synthesis of Si and B [55Sam, 60Col, 62Mag], by fusion of SiB_6 with Si [60Cli], and by reduction of B_2O_3 with Si [60Riz]. Because of the difficulties involved in the separation of SiB_3 from SiB_6, chemical analyses by various investigators often indicated the B/Si molar ratio around 4 [60Bro, 60Cli, 60Mat, 60Riz, 60Col]. These results are erroneous, because more precise investigations revealed the composition of the phase to correspond to $SiB_{2.89}$ [62Mag] and $SiB_{3.65}$ [70Ett]. [62Mag] prepared crystals by melting a Si-B mixture containing 10 at.% B in a high-frequency induction furnace in an argon atmosphere. The crystals were analyzed by X-ray methods, using a Guinier-type camera and Weissenberg photographs, with Cu Kα radiation. [70Ett] used electron beam microanalysis of samples melted at 1600 °C and rapidly cooled. No reliable information is available regarding the homogeneity range of SiB_3. Therefore, $SiB_{2.89}$ and $SiB_{3.65}$, representing 74.3 and 78.5 at.% B, respectively, are accepted by the present evaluators as the limits of the homogeneity range for SiB_3.

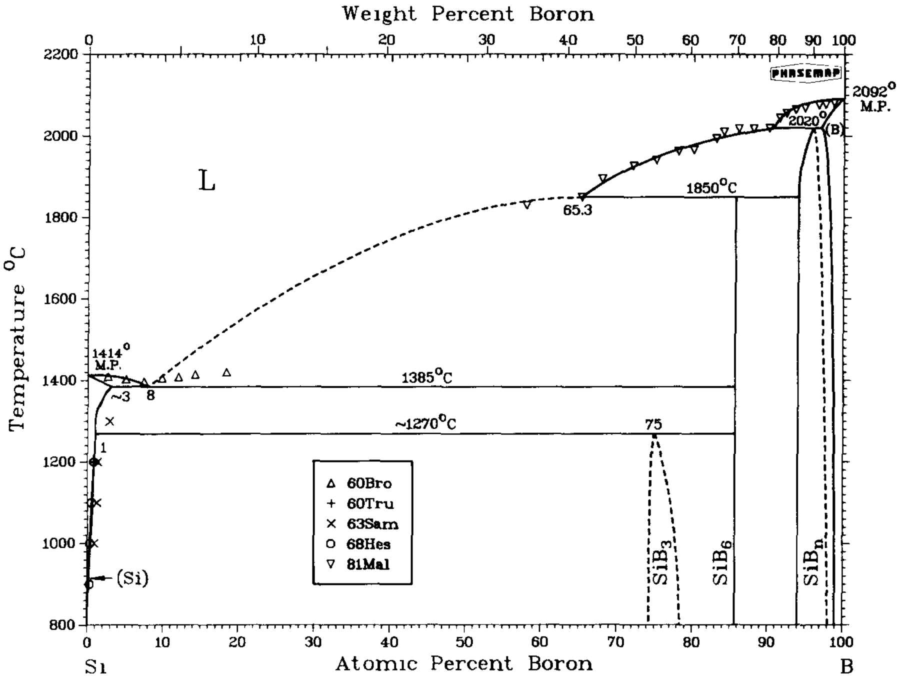
In regard to the thermal stability range of SiB_3, it is generally agreed that the compound is unstable above 1200 to 1400 °C [59Kna, 60Bro, 79Ara]. [60Bro] indicated that during sintering of Si and B powder mixtures at temperatures between 1200 and 1380 °C, a new compound, which they identified as SiB_4, formed at first, but it slowly decomposed into SiB_6 and (Si). At temperatures below 1200 °C, the compound was stable for "long periods". [59Kna] showed that when a mixture with 77.8 at.% B was heated to 1258 °C and quenched, it contained only SiB_3 and SiB_6. However, when the material was

Table 2 Experimental (*T*, *x*) Coordinates of the Si Solvus Curve in Si-B Alloys

Temperature, °C	Composition, at.% B	Reference
1385	3	This work(a)
1300	2.88	[63Sam]
1200	1.28	[63Sam]
	0.95	[60Tru]
	0.85	[68Hes]
1100	1.20	[63Sam]
	0.52	[68Hes]
1000	0.92	[63Sam]
	0.32	[68Hes]
900	0.21	[68Hes]
25	0.81	[63Sam]

(a) Estimated from combined data of [68Hes] and [63Sam].

Fig. 1 Assessed Si-B Phase Diagram



R.W. Olesinski and G.J. Abbaschian, 1984.

Table 3 Experimental (*T*, *x*) Coordinates of the Liquidus Curve in Si-B Alloys

Temperature, °C	Composition, at.% B	Reference
1414 (Si Melting)	0	[81BAP]
1409	2.6	[60Bro]
1402	5.0	[60Bro]
1397	7.4	[60Bro]
1385 (eutectic)	8.0	See text
1405	9.8	[60Bro]
1408	12.0	[60Bro]
1414	14.2	[60Bro]
1420	18.4	[60Bro]
1830	58	[81Mal]
1850 (SiB_6 peritectic)	65.3	[81Mal]
1895	68	[81Mal]
1927	72	[81Mal]
1941(a)	75(a)	[81Mal]
1963	78	[81Mal]
1967	80	[81Mal]
1994	83	[81Mal]
2010	84	[81Mal]
2018	86	[81Mal]
2019(a)	88	[81Mal]
2020 (SiB_n peritectic)	90.7	[81Mal]
2045(a, b)	91.5(a)	[81Mal]
2056(a, b)	92.4(a)	[81Mal]
2065(a, b)	93.6(a)	[81Mal]
2069(a, b)	94.8(a)	[81Mal]
2077(a, b)	96.7(a)	[81Mal]
2078(a, b)	97.6	[81Mal]
2082(a, b)	98.7	[81Mal]
2092 (B melting)	100	[81BAP]

(a) Averaged values for 2 to 5 measurements. (b) Because the melting point of B was given by the reference as 2070 °C and the presently accepted value is 2092 °C, this temperature has been adjusted to avoid discontinuity in plotting the liquidus curve.

heated to 1279 °C and quenched, it contained three phases, (Si), SiB_3, and SiB_6, indicating that some SiB_3 had decomposed into (Si) and SiB_6. According to [79Ara], who reported X-ray measurements corroborated with DTA and metallographic analysis, SiB_3 undergoes a peritectic transformation around 1400 °C. However, this conclusion seems to be based solely on the X-ray examination of Si-B samples annealed for 10 h at 1300 °C; DTA did not indicate any transformation besides the eutectic at 1385 °C. The author attempted to explain the discrepancy between his results and those of the previous researchers by attributing the previously reported decomposition temperature of SiB_3, slightly above 1200 °C, to transformations of SiO_2 or Al_2O_3 which, he presumed, were used by others for the thermocouple sheath. It should be noted, however, that [59Kna] used an optical pyrometer rather than thermocouples. Because data of [59Kna] have been found by the present evaluators to be the most consistent and best documented among the three cited references, SiB_3 is believed to transform peritectoidally around 1270 °C.

Intermediate Phase SiB_6. SiB_6 was first obtained by [00Moi], who synthesized it from Si and B in an electric arc furnace. The structural properties of the orthorhombic boride were satisfactorily determined by [58Ada] and [59Cli], who investigated crystals obtained by fusion of the elements at 2250 °C in an argon atmosphere. Thermal analysis studies revealed that SiB_6 decomposes peritectically at 1850 ±15 °C [81Mal, 81Arml, 79Ara] into a liquid of 65.3 at.% B and a B-rich solid phase [81Mal, 81Arml]. The solid phase may contain 94.6 ± 0.4 at.% B, as determined by [81Arml] from X-ray diffraction analysis, or 93.87 ± 0.05 at.% B, as determined by [80Vial] from metallographic and microprobe analyses. The homogeneity range of SiB_6 has not been definitely documented, although some unspecified "narrow" range was tentatively suggested in [81Arml]. [79Ara] claimed the homogeneity range of SiB_6 to be 78 to 81 at.% B. However, his graphical and tabular data showed the homogeneity range of ~82 to 91 at.% B. Because of this contradiction, the author's claim cannot be accepted by these evaluators.

Intermediate Phase SiB_n. Recently obtained thermal analysis results in conjunction with the X-ray, microprobe, and microhardness analyses were interpreted by [81Mal] and [81Arml] as evidence of the formation of a B-rich solid phase distinct from, though isotypic with, the solid solution of Si in B, (B). It was reported [81Mal] that the phase containing 95.9 ± 0.4 at.% B decomposes peritectically at 2020 ± 15 °C to a liquid of 90.7 at.% B and a B solid solution of 97.0 ± 0.4 at.% B. The homogeneity range of SiB_n was reported to be from 94.6 to ~98.5 at.% B at 1600 °C [81Arml].

The results of thermodynamic measurements by differential mass spectrometry reported in [81Arml] and [81Arm2] were claimed to support the existence of the SiB_n phase in the range 93.3 to 97.6 at.% B at 1427 °C and 93.75 to 97.6 at.% B at 1527 °C. However, because the determined activities in the solid are not very accurate and the plots of composition functions can be interpreted either way (i.e., for or against the existence of SiB_n), this claim is not particularly convincing.

The existence of a stable, solid, rhombohedral phase containing roughly 95 at.% B is rather indisputable. The evidence, apart from the earlier mentioned sources [81Mal] and [81Arml], includes a metallographic study by [57Now] and X-ray diffraction investigations by [65Gie]. The latter identified the phase as SiB_{14}, and this notation may be encountered in the literature when referring to the B-rich phase. [72Por] reported the peritectic transformation of the phase to be at 1970 °C.

On the other hand, the SiB_n phase is regarded by some researchers as the extension of the (B) solid solution [80Vial], as discussed later.

Solid Solution of Si in B, (B). Under equilibrium conditions, the solid solution of Si in B can contain up to 1.6 at.% Si at 1600 °C, 2.4 at.% Si at 1900 and 2000 °C, and 3.0 ± 0.4 at.% Si at the peritectic temperature of 2020 °C [81Arml]. [80Vial] investigated X-ray powder patterns of Si-B mixtures containing up to 14.3 at.% Si and reacted at 1600 °C in an argon atmosphere, and rapidly cooled. From the variation of the unit cell parameters with the composition, they concluded that the single-phase solid solution can contain up to 5.6 at.% Si at this temperature. The results of additional microscopic and microprobe analyses were claimed by the authors to support their findings, and to extend the solid solubility limit to 6.13 at.% Si at a peritectic temperature of 1850 °C. On the other hand, the homogeneous samples obtained by zone melting at about 2000 °C by [80Via2] contained only up to 4 at.% Si, and the single crystals grown by the same investigators contained only up to 3 at.% Si.

Liquid Solution. The experimental liquidus coordinates, listed in Table 3, have been selected from [81Mal] and [60Bro]. Because [60Bro] used 1420 °C as the melting temperature of Si, their reported temperatures are corrected down by 6 °C to make them compatible with the Si melting point of 1414 °C [81BAP]. The eutectic temperature has been accepted after [81Mal] and [79Ara] as 1385 ± 15 °C, and the eutectic composition has been estimated at 8 at.% B from [60Bro] measurements. The eutectic composition of 14 at.% B estimated by [81Arml] for the samples that were cooled at a rate of 50 °C/min has not been accepted because of the high cooling rate.

The liquidus boundary calculated by the present evaluators on the optimization of the experimental points and the thermodynamic data discussed later is plotted in Fig. 1. The calculations have been conducted assuming the Henrian character of the solid solutions and identifying the thermodynamic properties of the SiB_n phase with those of the B-rich solid solution.

It may be advisable to emphasize the often ambiguous and conflicting character of the literature data available for this system, particularly those concerning the intermediate phases. Some metallographic and X-ray diffraction studies, for instance those of [51Bre] and [56Sta], failed to produce evidence of the existence of a silicon boride. On the other hand, [82Chu] performed thermodynamic calculations for an SiB_4 that, they assumed, did not melt or decompose until 1900 °C. [56Zhu] claimed SiB_6 to have a cubic structure. [59Sle] and [62Sam], based on poor experimental evidence, constructed a phase diagram substantially different from Fig. 1.

Metastable Phases

Homogeneous B-rich chemical vapor deposits were obtained and studied by [76Arm] and [79Arm]. The deposition technique consisted of the pyrolysis of a BBr_3-$SiBr_4$ mixture onto a graphite substrate under reduced pressure in the temperature range 1000 to 1500 °C. The dependence of the Si concentration of the deposit on the temperature, pressure, and initial gas composition was determined in [79Arm]. The maximum Si concentration was close to 4 at.% at 1400 °C and 2×10^{-2} Torr, compared to 3 at.% allowed by equilibrium under these conditions. Thermodynamic calculations of [80Via2] indicated that any equilibrium Si-B phase can form from the BBr_3-$SiBr_4$ mixture in the temperature range 1000 to 1800 °C, but only under a very low pressure.

Table 4 Si-B Crystal Structure and Lattice Parameter Data

Phase	Composition range, at.% B	Pearson symbol	Space group	Prototype	Lattice parameters, nm a	b	c	Composition, at.% B	Reference
Si	0	*cF*8	*Fd*3*m*	C (diamond)	0.54306	···	···	···	[81Kin](a)
					0.54299	···	···	···	[63Sam]
					0.54295	···	···	···	[55Hor]
SiII (H.P.)	···	*tI*4	$I4_1/amd$	βSn	0.4686	···	0.2585	···	[Pearson]
(Si)	0.1 to 3.0	*cF*8	*Fd*3*m*	C (diamond)	0.54286	···	···	0.1	[63Sam]
					0.54281	···	···	0.1	[55Hor]
					0.54282	···	···	0.2	[63Sam]
					0.5428	···	···	0.26	[49Pea]
					0.54279	···	···	0.3	[63Sam]
					0.54249	···	···	0.3	[55Hor]
					0.54264	···	···	0.5	[63Sam]
					0.54250	···	···	1.0	[63Sam]
					0.5422	···	···	2.0	[63Sam]
					0.5412	···	···	3.0	[63Sam]
SiB_3	74.3 to 78.5	*hR*15	$R\bar{3}m$	B_4C	0.6319	···	1.2713	74.3	[62Mag]
					0.632	···	1.275	(b)	[60Riz]
					0.6330	···	1.2736	(b)	[60Mat]
					0.635	···	1.269	(b)	[60Cli]
SiB_6	85.7	*oP*280	*Pnnm*	SiB_6	1.439	1.827	0.988	···	[59Cli]
					1.4392	1.8267	0.9885	···	[58Ada](a)
SiB_n(c)	93.3 to ~97	*hR*12	$R\bar{3}m$	B	1.113	···	2.383	93.3	[65Gie]
					1.111	···	2.387	94.4	[80Via1]
					1.110	···	2.387	94.5	[80Via1]
					1.109	···	2.385	95	[80Via1]
					1.106	···	2.386	95.5	[80Via1]
					1.106	···	2.386	96	[80Via1]
					1.0989	···	2.3998	96	[79Ara]
					1.104	···	2.383	96.7	[80Via1]
(B)	~97 to ~100	*hR*12	$R\bar{3}m$	B	1.0973	···	2.3861	97.3	[79Ara]
					1.100	···	2.386	97.5	[80Via1]
					1.097	···	2.386	98	[80Via1]
					1.097	···	2.386	98.5	[80Via1]
					1.094	···	2.385	99	[80Via1]
					1.094	···	2.385	99.5	[80Via1]
βB(d)	100	*hR*12	$R\bar{3}m$	B	1.09251	···	2.38143	···	[77Cal](a)
					1.0926	···	2.381	···	[80Via1]
					1.0931	···	2.3825	···	[79Ara]
					1.0944	···	2.3811	···	[65Gie]

(a) The most reliable data (b) "SiB_4" was erroneously assigned to SiB_3 by the reference. (c) Some references [80Via1, 79Ara] regarded the phase to be the (B) solid solution (d) Assumed to be the only stable phase of pure B

The concentration of B in ion-implanted and laser annealed Si was obtained in a range up to 2.5 at.% B [78Lar, 78Whi]. The implantation was performed with 35-keV ions to doses of up to 2.5 × 10^{16}cm^{-2}; the implanted crystals were annealed using 50 ns laser pulses. It should be noted that the obtained concentrations do not exceed the maximum equilibrium composition of the (Si) solution adopted in this evaluation (3 at.% B).

Crystal Structure and Lattice Parameters

At normal pressure, Si has a cubic diamond-type structure; the high-pressure Si is tetragonal, of βSn type. B is listed in [Pearson] as forming four different phases; however, it is these evaluators' belief that the only stable phase of B is rhombohedral, with the lattice parameters listed in Table 4. The other structures [59Dec, 60Tal, 63Bec] were probably stabilized by the presence of impurities.

The lattice parameter measurements of the Si-rich solid solution by [49Pea, 55Hor, 59Epe] revealed contraction of the Si lattice on alloying with B, implying substitutional character of the solution. More recent studies of [67Coh, 72Mcq] led to the determination of the lattice contraction coefficient. [81Vla] indicated that the B-rich solid solution may form through a substitutional- interstitial mechanism. In alloys containing less than 1 at.% Si, substitution is believed to be the more probable mechanism.

The crystallographic description of the Si-B phases is presented in Table 4. Because SiB_n phase is isotypic with B-rich solid solution, some investigators made no distinction between crystallographic data of both phases. According to [81Arm1] and [81Mal], the unit cell of the B-rich solid solution expands along both crystallographic axes with increasing Si content, whereas for the SiB_n phase, the expansion takes place only in the "*a*" direction.

For the reasons presented earlier, the crystallographic data reported in the literature for SiB_4 have been assigned to SiB_3 in Table 4. The results of [55Sam], who assigned tetragonal structure to SiB_3, have not been included in Table 4, because the quality and adequacy of their measurements were convincingly questioned by [57Gur].

Thermodynamics

The published thermodynamic data on the Si-B system are rather scant, and the reported results leave much to be desired. [81Arm2] conducted a thermodynamic study on the solid Si-B system by differential mass spectrometry. The partial pressure measurements were used to determine activities of the components as a function of composition at 1423 and 1523 °C, and subsequently to thermodynamically describe the solid phases. The measurements, however, lack sufficient accuracy. [78Esi] gave the enthalpy of mixing function for the liquid solution as:

$$\Delta H = x_{Si}x_B(-38 - 86x_B - 240x_B^2 + 440x_B^3) \quad \text{kJ/mol}$$

which has been used by the present evaluators to optimize the liquidus boundary. From the enthalpy of mixing function and the experimental liquidus data of Table 3, the excess entropy function of the liquid was evaluated; the liquidus boundary was then determined from the Gibbs energy functions of the liquid and solid phases using the common tangent method. The Gibbs free energy of fusion functions for pure Si and B have been determined as:

$$\Delta_{fus}G_{Si} = 48\,531 + 0.5298T - 4.3723T \ln T + 1.9288\cdot 10^{-3}T^2 - 1.77\,10^5 T^{-1} \quad \text{J/mol}$$

$$\Delta_{fus}G_B = 30\,513 - 24.18T + 1.552T \ln T + 3.556\cdot 10^{-5}T^2 - 4.83\,10^6 T^{-1} \quad \text{J/mol}$$

The heat capacities and heats of fusion have been taken from [77Bar], and the melting points from [81BAP].

Various computational techniques were used to calculate the phase diagram by utilizing the enthalpy function given by [78Esi], the solubility data of Tables 2 and 3, and other solid solubilities given in the text. The calculations were done by assuming Henrian behavior for the solid solutions, and thermodynamically identifying the SiB_n phase with the (B) solid solution. The calculated liquidus curve agreed with the experimental features of the diagram only upon weighting the solubility data. Thus, results of [60Bro] were assigned half of unity weight of values by [81Mal], whereas the eutectic and SiB_6 peritectic points were given a weight of five. The Henrian activity coefficients of the solutes in (Si) and (B) with respect to pure solid standard state were arbitrarily selected in the following form:

$$RT \ln \gamma_B^0 = -235 + \Delta_{fus}G_B \quad \text{kJ/mol}$$

$$RT \ln \gamma_{Si}^0 = -95 + \Delta_{fus}G_{Si} \quad \text{kJ/mol}$$

It must be noted that the calculated liquidus boundary has a point of inflection around 20 at.% B. Although this behavior of the liquid is supported by experimental points of [60Bro], there is no conclusive evidence that the inflection is actually warranted by a change in the nature of the liquid around 20 at.% B. The calculated coordinates of the eutectic and SiB_6 peritectic points agree well with the experimental data. With regard to the SiB_n peritectic transformation, which was not included in the optimization procedure, its congruent point has been taken from [81Mal], as listed in Table 3.

It should be emphasized that the generated liquidus boundary serves mostly interpolation purposes and may not necessarily reflect true thermodynamic relations in the system.

Cited References

00Moi: H. Moissan and A. Stock, "Preparation et Proprietes de Deux Borures de Silicium: SiB^3 et SiB^6", *C.R. Acad. Sci. (Paris)*, *131*, 139-143 (1900) in French. (Equi Diagram; Experimental)

49Pea: G.L. Pearson and J. Bardeen, "Electrical Properties of Pure Silicon and Silicon Alloys Containing Boron and Phosphorus", *Phys. Rev.*, *75*, 865-883 (1949). (Crys Structure, Equi Diagram; Experimental)

51Bre: L. Brewer, D.L. Sawyer, D.H. Templeton and C.H. Dauben, "A Study of the Refractory Borides", *J. Am. Ceram. Soc.*, *34*, 173-179 (1951). (Equi Diagram; Experimental)

53Hal: R.N. Hall, "Segregation of Impurities During the Growth of Germanium and Silicon Crystals", *J. Phys. Chem.*, *57*, 836-839 (1953). (Equi Diagram; Experimental)

54Bur: J.A. Burton, "Impurity Centers in Ge and Si", *Phys.*, *20*, 845-854 (1954). (Equi Diagram; Theory)

54Ful: C.S. Fuller and J.A. Ditzenberger, "Diffusion of Boron and Phosphorus into Silicon", *J. Appl. Phys.*, *25*, 1439-1440 (1954). (Equi Diagram; Experimental)

55Hor: F.H. Horn, "Densitometric and Electrical Investigation of Boron in Silicon", *Phys. Rev.*, *97*, 1521-1525 (1955). (Equi Diagram, Crys Structure; Experimental)

55Sam: G.V. Samsonov and V.P. Latysheva, "K Voprosu o Khimicheskikh Soyedinenyakh Bora s Kremnyem (On the Question of Chemical Compounds of Boron with Silicon)", *Dokl. Akad. Nauk SSSR*, *105*, 499 (1955). (Crys Structure; Experimental)

56Sta: J.A. Stavrolakis, H.N. Barr, and H.H. Rice, "An Investigation of Boride Cermets", *Am. Ceram. Soc. Bull.*, *35*, 47-52 (1956). (Equi Diagram; Experimental)

56Zhu: N.N. Zhuravlev, "Rentgenograficheskoye Opredelenye Struktury SiB_6 (X-Ray Determination of the SiB_6 Structure)", *Kristallografiya*, *1*, 666-668 (1956). (Crys Structure; Experimental)

57Gur: M.A. Gurevich, V.A. Epelbaum, and B.F. Ormont, "Ob Obrazovanii Fazy SiB_3 v Sisteme Kremnij-bor (On the Formation of SiB_3 Phase in the Silicon-Boron System)", *Zh. Neorg. Khim.*, *2*, 206-208 (1957). in Russian; TR: *Russ. J. Inorg. Chem.*, *2*(1), 315-318 (1957). (Crys Structure; Review)

57Now: H. Nowotny, E. Dimakopoulou, and H. Kudielka, "Untersuchungen in den Dreistoffsystemen Molybdän-Silizium-Bor, Wolfram-Silizium-Bor und in dem System: VSi_2-$TaSi_2$ (Investigation of the Ternary Systems Molybdenum-Silicon-Boron, Tungsten-Silicon-Boron, and of the System VSi_2-$TaSi_2$)", *Monatsch. Chem.*, *88*, 180-192 (1957) in German. (Equi Diagram; Experimental)

58Ada: R.F. Adamsky, "Unit Cell and Space Group of Orthorhombic SiB_6", *Acta Crystallogr.*, *11*, 744-745 (1958). (Crys Structure; Experimental)

59Cli: C.F. Cline, "An Investigation of the Compound Silicon Boride SiB_6", *J. Electrochem. Soc.*, *106*, 322-325 (1959). (Crys Structure; Experimental)

59Dec: B.F. Decker and J.S. Kasper, "The Crystal Structure of a Simple Rhombohedral Form of Boron", *Acta Crystallogr.*, *12*, 503-506 (1959). (Crys Structure; Experimental)

59Epe: V.A. Epelbaum, M.A. Gurevich, and M.S. Starostina, "The Solubility of Boron in Silicon", *Zh. Neorg. Khim.*, *4*, 1881-1884 (1959) in Russian; TR: *Russ. J. Inorg. Chem.*, *4*, 851-853 (1959). (Equi Diagram, Crys Structure; Experimental)

59Kna: W.A. Knarr, "A Study of the Silicon-Boron Phases and a Determination of the Enthalpy of Vaporization and Formation of Silicon Hexaboride", Ph.D. thesis, University of Kansas (1959). (Equi Diagram, Thermo; Experimental; #)

59Sle: V.M. Sleptsov and G.V. Samsonov, "Do Pitannia pro Rozchinnist Boru v Kremnij (On the Solubility of Boron in Silicon)", *Dop. Akad. Nauk Ukr. RSR*, 982-984 (1959) in Russian. (Crys Structure, Equi Diagram; Experimental)

60Bro: C. Brosset and B. Magnusson, "The Silicon-Boron System", *Nature*, *187*, 54-55 (1960). (Equi Diagram, Crys Structure; Experimental)

60Cli: C.F. Cline and D.E. Sands, "A New Silicon Boride, SiB_4", *Nature*, *185*, 456 (1960). (Crys Structure; Experimental)

60Col: E. Colton, "Preparation of Tetraboron Silicide, B_4Si", *J. Am. Chem. Soc.*, *82*, 1002 (1960). (Equi Diagram; Experimental)

60Mat: V.I. Matkovich, "A New Form of Boron Silicide, B_4Si", *Acta Crystallogr.*, *13*, 679-680 (1960). (Crys Structure; Experimental)

60Riz: H.F. Rizzo and L.R. Bidwell, "Formation and Structure of SiB_4", *J. Am. Ceram. Soc.*, *43*, 550-552 (1960). (Crys Structure; Experimental)

60Tal: C.P. Talley, "A New Polymorph of Boron", *Acta Crystallogr.*, *13*, 271-272 (1960). (Crys Structure; Experimental)

60Tru: F.A. Trumbore, "Solid Solubilities of Impurity Elements in Germanium and Silicon", *Bell Syst. Tech. J.*, *39*, 205-233 (1960). (Equi Diagram, Thermo; Theory)

62Mag: B. Magnusson and C. Brosset, "The Crystal Structure of $B_{2.89}Si$", *Acta. Chem. Scand.*, *16*, 449-455 (1962). (Crys Structure; Experimental)

62Sam: G.V. Samsonov and V.M. Sleptsov, "Poperednij Variant Diagrami Sistemi Bor-Kremnij (Preliminary Variation of the Diagram of the Boron-Silicon System)", *Dop. Akad. Nauk Ukr. RSR*, 1066-1068 (1962). (Equi Diagram; Experimental; #)

63Bec: H.J. Becher, "Uber die Bildung der Tetragonalen Bormodifikation durch Substitution der Berylliumatome im Gitter des BeB_{12} (On the Formation of Tetragonal Modification of Boron Through Substitution of Beryllium Atoms in the Lattice of BeB_{12}", *Z. Anorg. Chem.*, *321*, 217-223 (1963) in German. (Crys Structure; Experimental)

***63Sam:** G.V. Samsonov and V.M. Sleptsov, "Investigation of the Solubility of Boron in Silicon", *Zh. Neorg. Khim*, *8*, 2009-2011 (1963) in Russian; TR: *Russ. J. Inorg. Chem.*, *8*, 1047-1048 (1963). (Crys Structure, Equi Diagram; Experimental)

65Gie: R.F. Giese, Jr., J. Economy, and V.I. Matkovich, "Interstitial Derivatives of β Boron", *Z. Krist.*, *122*, 144-147 (1965). (Crys Structure; Experimental)

67Coh: B.G. Cohen, "X-Ray Measurement of Elastic Strain and Lattice Constant of Diffused Silicon", *Solid State Electron.*, *10*, 33-37 (1967). (Crys Structure; Experimental)

***68Hes:** J. Hesse, "Loeslichkeit und Ausscheidungskinetik von Bor in Polykristallinem Silizium (Solubility and Kinetics of Precipitation of Boron in Polycrystalline Silicon)", *Z. Metallkd.*, *59*, 499-502 (1968) in German. (Crys Structure, Equi Diagram; Experimental)

70Ett: P. Ettmayer, H.C. Horn, and K.A. Schwetz, "Untersuchungen im System Silicium-Bor mit Hilfe der Elektronenstrahl-Mikroanalyse (Investigation of the Silicon-Boron System by Means of X-Ray Microanalysis)", *Mikrochim. Acta Suppl.*, *4*, 87-95 (1970) in German. (Crys Structure, Equi Diagram; Experimental; #)

72Mcq: K.G. McQuhae and A.S. Brown, "The Lattice Contraction Coefficient of Boron and Phosphorus in Silicon", *Solid State Electron*, *15*, 259-264 (1972). (Crys Structure; Experimental)

72Por: K.I. Portnoi and V.M. Romashov, "Binary Constitution Diagrams of Systems Composed of Various Elements and Boron — a Review", *Poroshk. Metall.*, *5*(113), 48-56 (1972) in Russian; TR: *Sov. Powder Metall. Met. Ceram.*, *11*, 378-384 (1972). (Equi Diagram; Experimental)

76Arm: B. Armas, C. Combescure, J.M. Dusseau, T.P. Lepetre, J.L. Robert, and B. Pistoulet, "Fabrication and Study of Electrical Properties of Boron-Silicon Compounds with High Boron Concentration", *J. Less-Common Met.*, *47*, 135-140 (1976). (Meta Phases, Experimental)

77Bar: I. Barin, O. Knacke, and O. Kubaschewski, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, New York (1977). (Thermo; Compilation)

77Cal: B. Callmer, "An Accurate Refinement of the β-Rhombohedral Boron Structure", *Acta. Crystallogr.*, *B33*, 1951-1954 (1977). (Crys Structure; Experimental)

***78Esi:** Yu.O. Esin, S.P. Kolesnikov, V.M. Baev, and A.F. Ermakov, "Entalpij Obrazovanya Zhidkikh Splavov Kremnya s Borom (Enthalpies of Formation of Liquid Alloys of Silicon with Boron)", *Tezisy Nauchn. Soobshch. Vses. Konf. Str. Svoistvam Met. Shlakovykh Rasplavov*, 3rd ed., Vol. 2, 182-183 (1978). (Thermo; Experimental)

78Lar: B.C. Larson, C.W. White, and B.R. Appleton, "Unidirectional Contraction in Boron-Implanted Laser-Annealed Silicon", *Appl. Phys. Lett.*, *32*, 801-803 (1978). (Meta Phases; Experimental)

78Whi: C.W. White, W.H. Christie, B.R. Appleton, S.R. Wilson, P.P. Pronko, and C.W. Magee, "Redistribution of Dopants in Ion-Implanted Silicon by Pulsed-Laser Annealing", *Appl. Phys. Lett.*, *33*, 662-664 (1978). (Meta Phases; Experimental)

79Ara: B.G. Arabey, "Vzaimodeystvie v Sisteme Si-B (Interaction in the Si-B System)", *Izv. Akad. Nauk. SSSR Neorg. Mater.*, *15*, 1589-1592 (1979) in Russian. (Crys Structure, Equi Diagram; Experimental; #)

79Arm: B. Armas, C. Combescure, G. Male, and M. Morales, "A Study of the Thermal Decomposition of Gaseous Si-B Bromides under Reduced Pressure", *J. Less-common Met.*, *67*, 449-453 (1979). (Meta Phases; Experimental)

***80Via1:** J.C. Viala and J. Bouix, "Alliages Bore-Silicium Riches en Bore. Partie I", *J. Less-Common Met.*, *71*, 195-206 (1980). (Equi Diagram, Crys Structure; Experimental)

80Via2: J.C. Viala, R. Hillel, and J. Bouix, "Alliages Bore-

Silicium Riches en Bore. Partie II", *J. Less-Common Met.*, *71*, 207-218 (1980). (Crys Structure; Experimental)

***81Arm1:** B. Armas, G. Malé, and D. Salanoubat, "Determination of the Boron-Rich Side of the B-Si Phase Diagram", *J. Less-Common Met.*, *82*, 245-254 (1981). (Equi Diagram, Crys Structure; Experimental; #)

81Arm2: B. Armas, C. Chatillon, and M. Allibert, "Determination des Activites dans le Systeme Bore-Silicium par Spectrometrie de Masse Differentielle", *Rev. Int. Hautes Temp. Refract.*, *18*, 153-165 (1981). (Thermo; Experimental)

81Kin: H.W. King, "Crystal Structures of the Elements at 25 °C", *Bull. Alloy Phase Diagrams*, *2*(3), 401-402 (1981). (Crys Structure; Compilation)

***81Mal:** G. Male and D. Salanoubat, "Sur l'Existence d'Une Phase Riche en Bore dans le Systeme Bore-Silicium", *Rev. Int. Hautes Temp. Refract.*, *18*, 109-120 (1981). (Equi Diagram; Experimental; #)

81Vla: M. Vlasse and J.C. Viala, "The Boron-Silicon Solid Solution: A Structural Study of the SiB_{36} Composition", *J. Solid State Chem.*, *37*, 181-188 (1981). (Crys Structure; Experimental)

82Chu: T.A. Chubinidze, A.L. Okley, and M.A. Zhuruli, "Ob Energii Vzaimodeystvya v Sisteme Si-B (On the Interaction Energy in the Si-B System)", *Izv. Akad. Nauk SSSR. Met.*, 199-201 (1982). (Thermo; Theory)

*Indicates key paper.
#Indicates presence of a phase diagram.

B-Si evaluation contributed by **R.W. Olesinski** and **G.J. Abbaschian**, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This program was supported by ASM under grant No. FG101-1 to the University of Florida. Thermodynamic calculations were made by using the computer program developed by Drs. A.D. Pelton, W.T. Thompson, and C.W. Bale of McGill University, Montreal, Quebec. Literature was searched through 1982. Professor G.J. Abbaschian is the ASM/NBS Data Program Category Editor for binary silicon alloys.

The C-Ge (Carbon-Germanium) System

12.011 72.59

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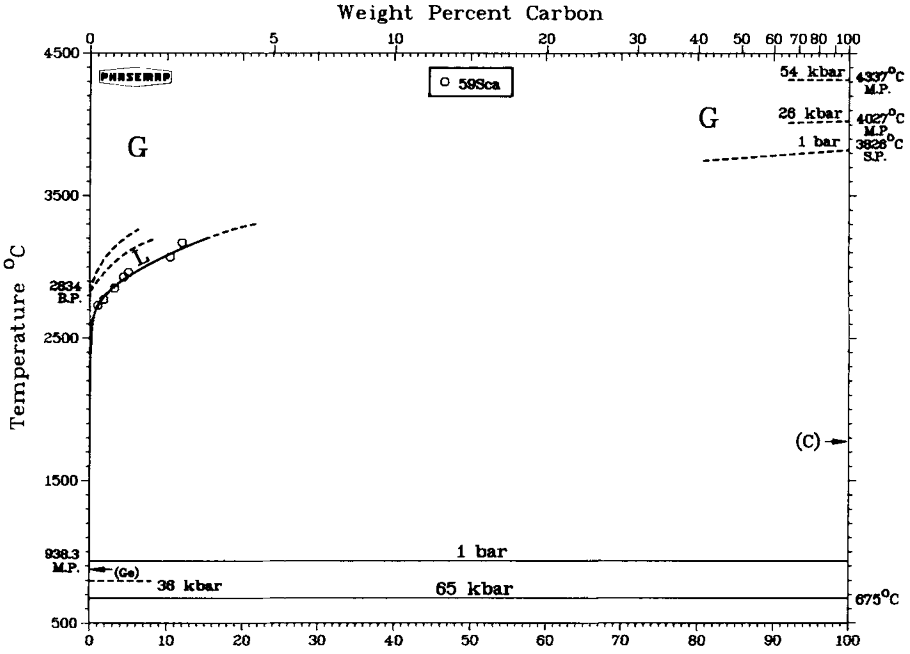
Equilibrium Diagram

The assessed equilibrium phase diagram of the Ge-C system is shown in Fig. 1.* The diagram includes a eutectic transformation at a composition very close to pure Ge and at a temperature slightly below the melting point of Ge. The components indicate no appreciable solubility in the solid state, as indicated in Table 1.

Because of difficult experimental requirements, only a few investigations have been conducted on the Ge-C system, and the results leave much to be desired.

Fig. 1 Assessed Ge-C Phase Diagram



R.W. Olesinski and G.J. Abbaschian, 1984.

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*All temperatures in this evaluation have been adjusted to the 1968 Temperature Scale (IPTS-68).