THERMODYNAMIC STUDY OF SYNTHESIS OF NEW COMPOUND PHASES UNDER HIGH PRESSURE

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Project No. 5620

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SCIENTIFIC REPORT NO. 1

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Prepared for

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ABSTRACT

A phenomological analysis and correlation of available volumetric and entropy data was performed for the III-V compounds. The results of these procedures were used to predict the volumetric properties of the known high pressure forms of BN and the unknown forms of BSb. In addition, values for compound entropy and the entropy of formation were predicted for the above compounds, BN and BSb, and for several known III-V compounds for which such data are presently lacking. The value for the P-T coefficient, $dP/dT = \Delta S/\Delta V$, was also calculated (from the predicted quantities) for the BN transformations and for the synthesis of BSb from the elements. An experimental program was carried out to attempt to synthesize a new compound BSb. The results obtained suggest that the B-Sb system at 50 kilobars is characterized by a miscibility gap in the liquid phase. High pressure experiments were also carried out for AlN; the results obtained show that solid aluminum nitride and solid boron nitride react by a diffusion process which produces marked changes in the microhardness and morphology of the boron nitride.

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I. INTRODUCTION AND SUMMARY

The objective of this program for the first year effort was to attempt to use high pressure synthesis as a means of preparing a compound in the B-Sb system and new compound phases in the Al-N, Ga-N and In-N systems. Another objective of the program was to perform a phenemological analysis to develop a method of calculating the thermodynamic properties of predictable but, as yet, unknown compounds between elements in Group III and Group V.

High pressure synthesis programs have been carried out in many of the research groups which are active in this technological area. These activities are outgrowths of the earlier successful high pressure synthesis of diamond and cubic boron nitride (1*). In general, the reported successful high pressure synthesis studies do not elaborate on experimental planning and prediction, rather detailed experimental descriptions of the successful experiments are provided. Another aspect of this program is to provide in clear detail a scheme for future high pressure experimental planning.

The experimental program performed in the present investigation included a series of synthesis reactions designed to produce boron antimonide, BSb. Direct elemental synthesis, B + Sb, displacement reaction B + InSb and substitutional reactions B + 0.5 As + 0.5 Sb for which the intended products were BSb, BSb + In and $BAs_{0.5}B_{0.5}$ respectively were attempted with no definite indication of success. These experiments were performed after due consideration of available and predicted thermodynamic properties for the elements and compounds. Some of the experimental findings uncovered shed additional light of the subtleties of high pressure synthesis design considerations. The absence of any stable and/or metastable compounds in this system could be due to the presence of a miscibility gap in the liquid phase. All other III-V systems contain one stable phase (2); metastable phases have been produced in many of these systems by high pressure synthesis procedures (3).

Preliminary experiments were performed for aluminum nitride, gallium nitride and indium nitride. In order to prepare dense solid specimen material for high pressure synthesis reactions, these powders were high pressure hot pressed at 1800°C and 100,000 psi for 10 minutes. In the latter procedure, the sample material is separated from a graphite heater by a boron nitride insulating sleeve. Examination of the billets of aluminum nitride fabricated in this way showed that extensive diffusion of AlN into the BN liner had occurred. This diffusion produced a large increase in the microhardness of the boron nitride. In addition, the morphology of the boron nitride changed and long flake-like precipitates were formed in the boron nitride. Electron microprobe examination of the AlN-BN interface confirmed the diffusion of the aluminum (and presumably the nitrogen) into the boron nitride. These findings are currently under further examination.

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[*] Underscored numbers in parentheses refer to References listed at the end of this report.

A phenemological analysis and correlation of available volumetric and entropy property data was performed for III-V compounds. The volumetric analysis was a refinement of earlier reported (4) results; the entropy analysis was performed for Group IV elements as well as for the isoelectronic III-V compounds. This correlation was used to predict the values of the entropy at 298°K for several known III-V compounds, for the high pressure polymorph, BN (diamond cubic form) and for the predicted compound BSb(diamond cubic form). The correlation can also be used to calculate with the heat capacity and the entropy of the compounds as a function of temperature, that is, Cp[T] and S[T]. Furthermore, by combining the results of the volumetric and entropy property correlations, it was possible to calculate the slope of the P versus T curve, $dP/dT = \Delta S/\Delta V$, for the BN transition from the one atmosphere graphitic form to the high pressure cubic form and for the synthesis reaction $B + Sb \rightarrow BSb$. The comparison of the former calculated value with the experimentally observed value for the "catalyzed" transformation (5) was satisfactory. Results obtained in these analyses were used where feasible in the experimental program.

Some consideration of the problems associated with correlating enthalpy data are presented. The available methods for such calculations are reviewed and their limitations are cited.

A rational scheme for planning high pressure synthesis experiments is presented. The method developed is not unique to the authors and similar procedures are probably used by other workers in this field. However, such a plan of experiment is generally not available in the high pressure literature except as outlined in an earlier publication by the authors (6). As the present program progresses, a more improved plan should evolve.

II. HIGH PRESSURE SYNTHESIS: ANALYTICAL METHODS

A. Design of Experiment

1. General Considerations

The initial step in a high pressure synthesis study is to select a system for study. For purposes of illustration, this discussion will be limited to binary elemental systems. The introduction of more than two elements produces additional factors which have to be considered. The results presented in this report showed one possible effect of third element addition. The system chosen for study should have an established phase diagram at one atmosphere and it is desirable to have a complete thermodynamic description of the elements and phases therein. The compound chosen for high pressure synthesis can be a new phase at a composition in the binary diagram where no compound is formed at one atmosphere or the high pressure phase can be a polymorph of a phase that is stable at one atmosphere. A high pressure phase can also be one that is only stable at one atmosphere over a specific temperature and/or composition range, but which can be quenched to ambient or lower temperature and ambient pressure and retained possibly with a metastable composition.

A rational design for a high pressure synthesis experiment must include:

(1) The selection of the elemental system and the composition

(2) The prediction of the crystal structure of the new material

(3) The prediction of the volumetric properties of the new material

(4) The prediction of the pertinent thermodynamic quantities for the new material, i.e., free energy, enthalpy and entropy parameters

(5) The anticipation of the general characteristics of the new material and the prediction of the magnitude of some physical, eletronic or magnetic properties.

The stability of a new material at high pressure and high temperature will be controlled by thermodynamic quantities and the retention of this material to ambient (metastable) conditions by kinetic factors. Consideration of the stability controlling parameters as a function of temperature and pressure for a generalized reaction for the synthesis of a compound AB with a δ structure leads to

$$\Delta F^{\delta}_{AB}[T,P] = \Delta H^{\delta}_{AB}[T] - T\,\Delta S^{\delta}_{AB}[T] + P\Delta V^{\delta}_{AB}[T] \qquad (1)$$

An analogous expression can be written for a transformation. The calculation of the above parameters at 298°K is one objective of this program. The quantities on the r.h.s. of Eq. (1) are differences, hence the corrections needed for their temperature dependence are second order. Use of appropriate terms for phase changes for the reactants, e.g., melting is a more important consideration. This technique has proven successful in analogous studies of metals and alloys (7).

A partial determination of the parameters on the r.h.s. of Eq. (1) can provide very useful guidelines for a high pressure synthesis. Thus, evaluation of the volume and the entropy terms and consideration of the Claperyon equation given by

$$\left[\frac{dP}{dT}\right]^{\delta}_{AB} = \frac{\Delta S^{\delta}_{AB}[T]}{\Delta V^{\delta}_{AB}[T]} \tag{2}$$

leads to a prediction of the sign and the magnitude of the slope of a P versus T curve for a synthesis or a transformation.

Negative volume changes effect pressure stabilization of AB (δ), but it is necessary and sufficient that ΔF (T, P) be a minimum in the free energy versus composition diagram. Compound synthesis, however, is predicated upon the existence of favorable kinetic factors. Every effort should be made to attempt to predict the volume terms for the reaction of interest. Fortunately, the prediction of the volume characteristics for an unknown material in a given crystal structure presents far less difficulty than the prediction of other characteristic properties. Thus far, the general development of high pressure synthesis design considerations has not required a formal separation between phases which are stable over a range of composition and line compounds. Such a separation would be included in the first refinement of the present method.

2. Selection Criteria and Prediction of Crystal Structure

The selection of the B-Sb system at the equiatomic composition region for high pressure synthesis experiments was made on the basis of the apparent discontinuity in the compounds formed by the periodically related elements of Group III and Group V. Consideration of the binary compounds formed at one atmosphere between elements of Group III (B, Al, Ga, In) and V (N, P, As, Sb) reveals that the nitrides of aluminum, gallium and indium occur in a hexagonal wurtzite structure. Boron nitride occurs in a graphitic hexagonal form and no compounds are known to exist in the B-Sb system. The remaining combinations of elements from Groups III and V produce compounds with a cubic zinc blende structure. Hence, the absence of any compound in the B-Sb system led to the suggestion of this system for high pressure synthesis study at the equiatomic composition.

If such a discontinuity occurred in a system where all other related compounds have one crystal structure, then it is assumed that the selected composition will have the same structure. The known III-V compounds are primarily formed in two structures: zinc blende and wurtzite. It is worthy of note that Al, Ga and In form nitrides with a wurtzite structure while high pressure syntheses of BN has produced both zinc blende (1) and hexagonal forms (5). Thus, for BSb an a priori choice of the crystal structure cannot be made. However, a comparison of electronegativity differences presented in Table 1 shows that materials which form the zinc blende structure have a lower electronegativity difference than those which form the wurtzite structure; some materials which form both structures have electronegativity differences which are of intermediate values. This generality is particularly applicable to the III-V compounds. The reported pressure transformations (8) for the cuprous halides (stable at one atmosphere in a zinc blende structure) are consistent with the suggested destabilization by the relatively high electronegativity difference. Thus, the zinc blende structure is predicted for the BSb compound.

3. Correlation and Prediction of Volumetric Properties

Volumetric properties of new compounds in a given crystal structure can be predicted from a set of radii which have been deduced from the measured lattice constants of known compounds which form the same structure. Paulings tetrahedral covalent radii (9) were chosen for the zinc blende and the wurtzite structures. These compounds are characterized by tetrahedral symmetry, covalent bonding and semiconducting properties. Linear correlations for these radii with the cubic zinc blende lattice parameter and the hexagonal wurtzite lattice parameter are provided in Figures 1 and 2. These correlations represent a refinement of previous results in that more data were examined and statistical methods were employed to provide the best fit of the data to a linear function. Volumetric parameters were calculated for the zinc blende and wurtzite forms of BSb and BN and for the zinc blende forms of AlN, GaN and InN. These results and the volumetric properties of the known III-V compounds are summarized in Table 2. The calculated volume changes for a series of synthesis reactions are provided in Table 3.

Consideration of the available results indicates that pressure will enhance the synthesis of BSb and the transformation of graphitic BN to both cubic and wurtzite forms. Quantitative prediction of pressure stabilization of the wurtzite or the zinc blende structure cannot be made for BN or BSb, but as discussed above, consideration of the magnitude of the electronegativity differences leads to a prediction that the high pressure form of BSb will be zinc blende. The intermediate value of $1.0(\text{e.v.})^{1/2}$ for the electronegativity difference of BN and the similar volumetric properties of the wurtzite and zinc blende structures suggests that high pressure synthesis experiments could lead to either form. It is well known that Bundy and Wentorf (5) have prepared both forms. The measured volumetric $V^{\delta}_{BN} = 3.563\ \text{cm}^3/\text{g. atom}$ and $V^{\omega}_{BN} = 3.65\ \text{cm}^3/\text{g. atom}$.

The calculated volume changes presented in Table 3 for AlN, GaN and InN are different than those obtained from earlier results (4). The latter had predicted negative volume changes, hence pressure enhancement of the zinc blende form for all these compounds. The present analysis is more extensive and the calculations are performed using a straight line equation based on a least square analysis. A total of thirty (30) data points, which included II-VI and I-VIII compounds in addition to the III-V compounds, were used for the correlation for the zinc blende structure; eleven (11) data points were used for the correlation for the wurtzite structures. The linear

TABLE 1

ELECTRONEGATIVITY DIFFERENCES OF COMPOUNDS WITH ZINC BLENDE, B-3, AND WURTZITE, B-4, STRUCTURES

B-3 Structures	B-3 and B-4 Structures	B-4 Structures
BP (0.1)*	BN (1.0)	AlN (1.5)
AlP (0.6)	ZnS (0.9)	GaN (1.4)
GaP (0.5)	CdS (0.8)	InN (1.3)
InP (0.4)	CdSe (0.7)	BeO (2.0)
BAs (0.0)	AgI (0.6)	ZnO (1.9)
AlAs (0.5)	MnS (1.0)	MgTe (0.9)
GaAs (0.4)	MnSe (0.9)	
InAs (0.3)	SiC (0.7)	
AlSb (0.4)		
GaSb (0.3)		
InSb (0.2)		
HgS (0.6)		
HgSe (0.5)		
HgTe (0.2)		
BeS (1.0)		
BeSe (0.9)		
BeTe (0.6)		
CdTe (0.5)		
ZnTe (0.5)		
CuF (2.1)		
CuCl (1.1)		
CuBr (0.8)		
CuI (0.6)		
BSb (0.1) (predicted B-3)		

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*Electronegativity differences (9) are tabulated in parenthesis beside each compound.

TABLE 2

VOLUMETRIC PROPERTIES OF III-V COMPOUNDS AT 298^{o}K

Compound	Structure[*]	V^{+} cm^3/g. atom	ΔV_f cm^3/g. atom
BN	γ	5.45	-
	ω	(3.65)	-
	δ	(3.66)	-
AlN	ω	(6.25)	-
GaN	ω	(6.80)	-
InN	ω	(9.30)	-
BP	δ	7.04	-3.83
AlP	δ	12.19	-1.38
GaP	δ	12.19	-2.28
InP	δ	15.22	-1.22
BAs	δ	8.21	-0.57
AlAs	δ	13.44	+1.96
GaAs	δ	13.60	+1.22
InAs	δ	16.74	+2.39
BSb	ω	(10.3)	-1.1
	δ	(10.43)	-1.0
AlSb	δ	17.39	+3.30
GaSb	δ	17.05	+2.06
InSb	δ	20.48	+3.52

[*] The symbols γ, ω and δ are used to represent the graphitic hexagonal, wurtzite hexagonal and zinc blende cubic structures respectively.

[+] Crystallographic data taken primarily from Pearson's compilation (10). Parenthetically enclosed quantities calculated from the linear correlations in Figures 1 and 2.

TABLE 3

CALCULATED VOLUME CHANGES FOR PHASE CHANGES OF ZINC BLENDE AND WURTZITE STRUCTURES IN III-V COMPOUNDS AT 298°K

Reaction		ΔV $cm^3/g.$ atom
BN:	$\gamma \rightarrow \delta$	-1.89
	$\gamma \rightarrow \delta$	-1.89
	$\omega \rightarrow \delta$	0.00
AlN:	$\omega \rightarrow \delta$	+0.67
GaN:	$\omega \rightarrow \delta$	+0.09
InN:	$\omega \rightarrow \delta$	-0.24
BSb:	$\omega \rightarrow \delta$	+0.10

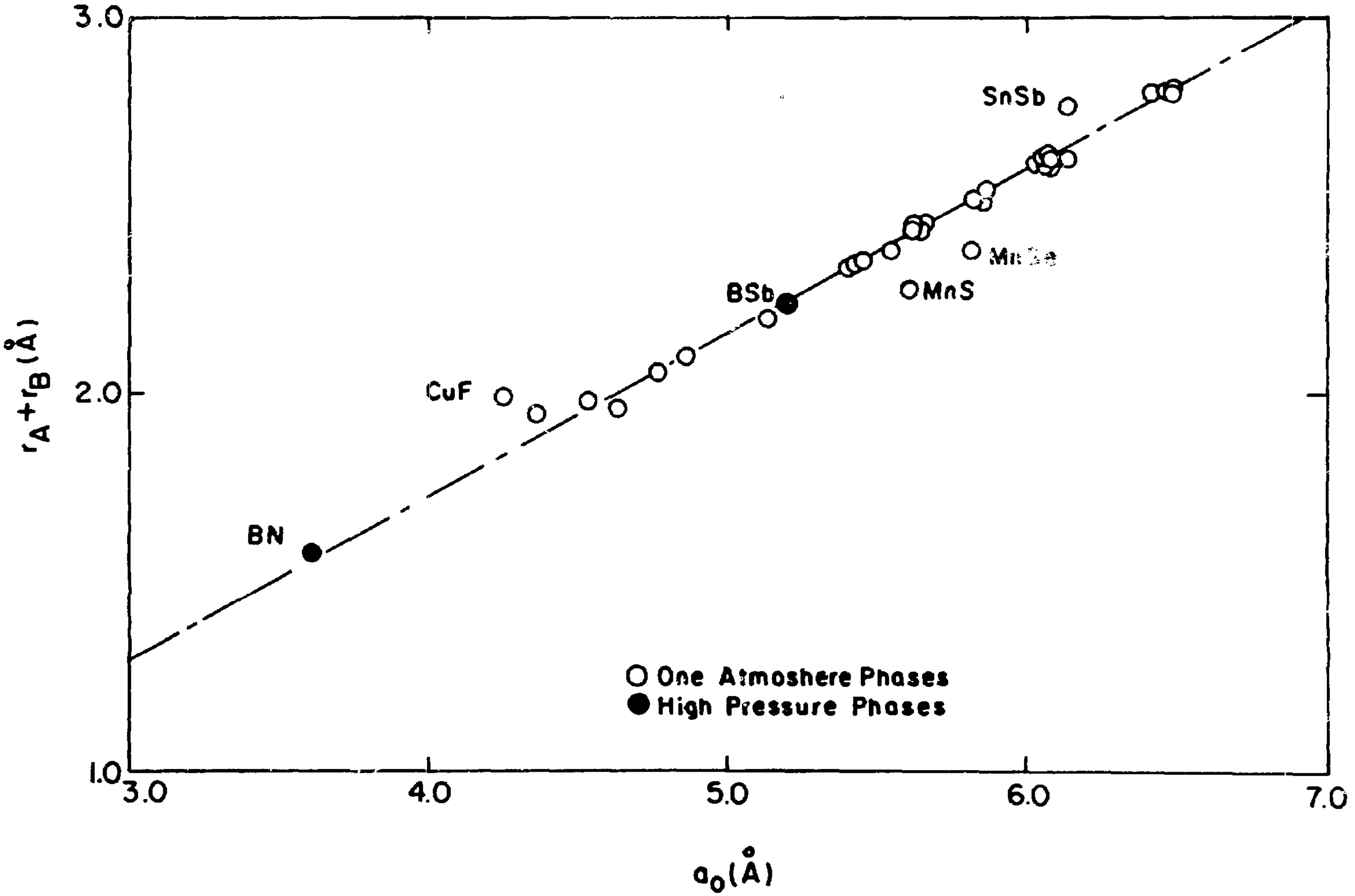

Figure 1. Linear Correlation for the Sum of Pauling's Tetrahedral Covalent Radii with Cubic Lattice Parameter, a_0, for Zinc Blende Structures.

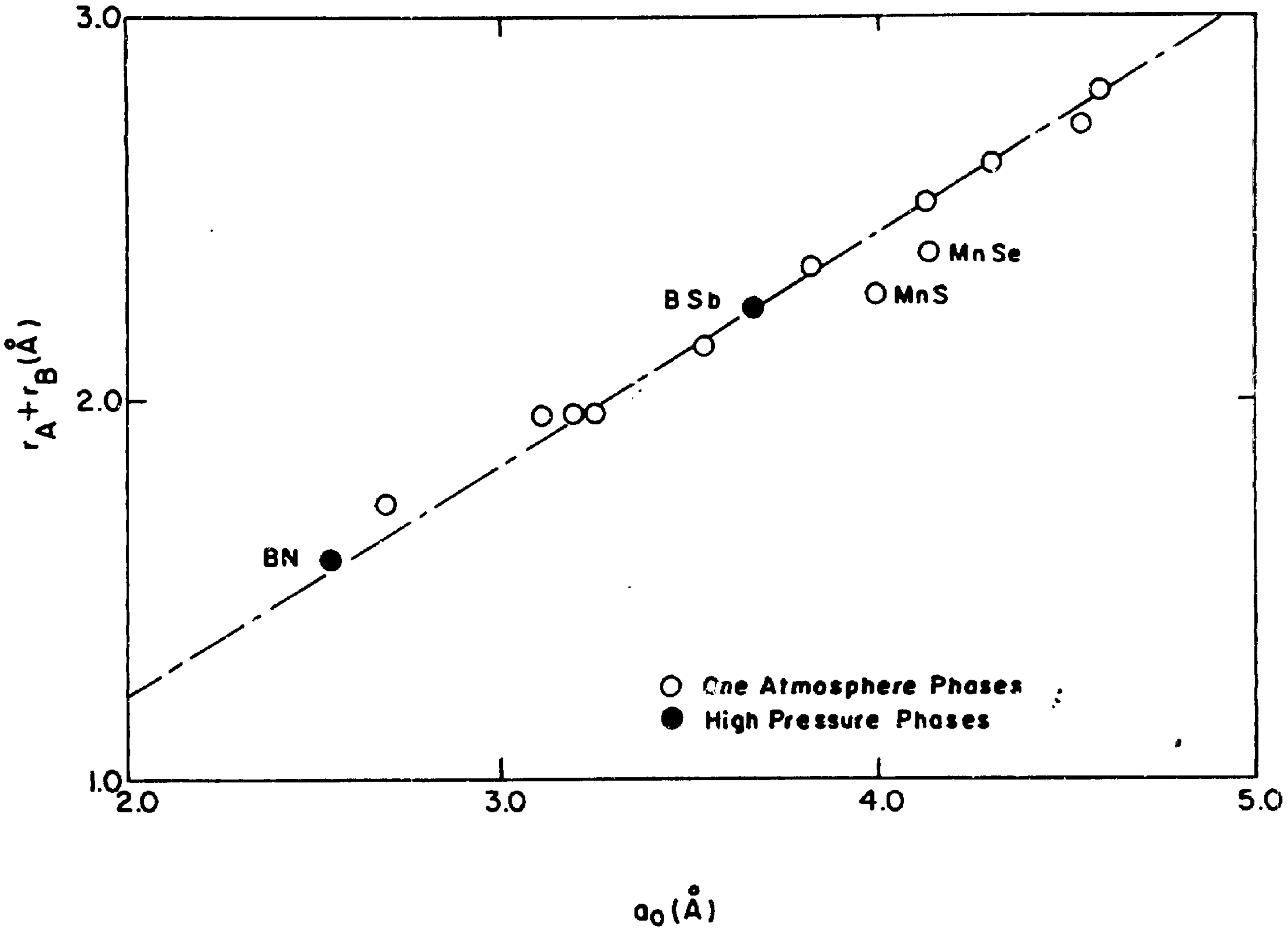

Figure 2. Linear Correlation for the Sum of Pauling's Tetrahedral Covalent Radii with Hexagonal Lattice Parameter, a_o, for Wurtzite Structures.

correlations developed in this program can be expressed analytically as,

$$a_o\ (B\text{-}3) = 2.347\ (r_A + r_B) - 0.082 \qquad (4)$$

$$a_o\ (B\text{-}4) = 1.729\ (r_A + r_B) - 0.217 \qquad (5)$$

where $c_o/a_o = 1.621$ and r_A, r_B are the tetrahedral radii (9)

The previous results (5) gave:

$$a_o\ (B\text{-}3) = 2.441\ (r_A + r_B) - 0.303 \qquad (6)$$

$$a_o\ (B\text{-}4) = 1.756\ (r_A + r_B) - 0.267 \qquad (7)$$

where $c_o/a_o = 1.625$ and r_A, r_B are the tetrahedral radii (9)

The results in Table 3 indicate that pressure enhanced synthesis of AlN in a zinc blende structure is not feasible. The calculated volume change for GaN is close to zero, but in view of the successful synthesis of BN in both the wurtzite and zinc blende forms even though the volumetric properties of these structures are virtually identical suggests that a limited number of synthesis experiments should still be performed for GaN. The results for InN predict a pressure enhancement of the zinc blende structure in agreement with previous findings (1).

Recently, Hall and Compton (11) have set forth a series of compounds which are Group IV analogs of carbon for future high pressure research. The authors provide a tabulation of symmetrical and unsymmetrical two-atom analogs of carbon. The list is provided in Table 4.

TABLE 4*

ISOELECTRONIC, TWO-ATOM ANALOGS OF CARBON

Symmetrical	Unsymmetrical	
BN (1.0)*	B_2O (1.5)	B_3F (2.0)
BeO (2.0)	BeN_2 (1.5)	Be_3F_2 (2.5)
LiF (3.0)	LiN_3 (2.0)	Li_2O_3 (2.5)

*Electronegativity differences are tabulated in parenthesis as in original reference (11).

The authors report the successful synthesis of B_2O. This material was found to have a hexagonal crystal structure similar to graphite and the one atmosphere form of boron nitride. One of the reported synthesis reactions is given in Eq. (8).

$$4B + B_2O_3 \rightarrow 3\ B_2O \tag{8}$$

Successful synthesis was obtained by thermally quenching the sample from pressures of the order of 50 to 75 kilobars at temperatures from 1200° to 1800°C after 3 minute reaction times. It is interesting that the volumetric calculations at room temperature employing 4.6 cm^3/g.atom for B, 5.26 cm^3/g.atom for B_2O_3 and 5.56 cm^3/g.atom for B_2O (calculated from the reported (11) density of 2.24 g/cm^3) afford a positive net volume change of 0.38 cm^3/g.atom. This apparent conflict, with the reported successful pressure enhanced synthesis, should be further investigated. It is, of course, possible that the temperature dependence of ΔV for the reaction could be such as to change the sign of ΔV at elevated temperatures.

The volumetric correlations obtained in the present research can be used to calculate the volume parameters of BeO and B_2O in a zinc blende structure and ΔV for the phase transformations. Thus,

$$BeO\ (\omega) \rightarrow BeO\ (\delta);\ \Delta V = +\ 0.50\ cm^3/g.\text{atom} \tag{9}$$

$$B_2O\ (\gamma) \rightarrow B_2O\ (\delta);\ \Delta V = -1.76\ cm^3/g.\text{atom} \tag{10}$$

The previous correlation (Eq. 6) gave $\Delta V^{\omega \rightarrow \delta} = +0.28\ cm^3/g$.atom for BeO. The predicted lattice parameter for B_2O in a pseudo zinc blende, B-3, structure is 3.70Å ($V^{\delta} = 3.80\ cm^3/g$.atom). This value was calculated by assuming that for one gram atom half of the B-3 sites are occupied by boron and the other half are occupied by oxygen, 2/6, and the rest of the boron, 1/6. Such manipulations are a consequence of the normal B-3 structure which is formed by two elements in a one to one atomic ratio. Similar calculations would have to be made to calculate the volumetric properties of the remaining unsymmetrical carbon analogs in Table 4. The calculations would be further complicated by the absence of tabulated values for tetrahedral covalent radii for Li.

4. Correlation and Prediction of Entropy Data

In order to develop a method for predicting the entropy property values which are needed in Eqs. (1) and (2) to define the conditions of pressure and temperature under which the compound to be synthesized will be stabilized, it is convenient to expand a technique developed by Kaufman (12, 13) for calculating phase equilibria at one atmosphere. The entropy of a compound AB in the diamond cubic (zinc blende) structure, δ, is given by Eq. (11).

$$S^{\delta}_{AB} = 1/2\ S^{\alpha}_{A} + 1/2\ S^{\beta}_{B} + \Delta S^{\delta}_{f} \tag{11}$$

where α and β are the normal, one atmosphere crystallographic forms of elements A and B and ΔS^δ_f is the entropy of formation. The Gibbsiam mixing term is excluded as the compounds are considered fully ordered. The quantity S^δ_{AB} can be alternately defined as :

$$S^\delta_{AB} = 1/2 \ S^\delta_A + 1/2 \ S^\delta_B + S^\delta_E \tag{12}$$

where S^δ_E is the excess entropy of formation of AB^δ from two elements having the same crystal structure as AB^δ.

If as a first approximation, S^δ_E is assumed to be equal to zero then from Eq. (12)

$$S^\delta_{AB} \simeq 1/2 \ S^\delta_A + 1/2 \ S^\delta_B \tag{13}$$

Inspection of the available data at 298°K for III-V compounds composed of elements in the same period reveals that

$$S^\delta_{InSb} = 10.30 \text{ e.u./g. atom} \qquad (\underline{14}) \tag{14}$$

$$S^\delta_{Sn} = 10.55 \text{ e.u./g. atom} \qquad (\underline{15}) \tag{15}$$

$$S^\delta_{GaAs} = 7.67 \text{ e.u./g. atom} \qquad (\underline{14}) \tag{16}$$

$$S^\delta_{Ge} = 7.46 \text{ e.u./g. atom} \qquad (\underline{14}) \tag{17}$$

Entropy data are available for S^δ_{Si} and S^δ_C but are lacking from S^δ_{AlP} and S^δ_{BN}. Consideration of Eqs. (14) through (17) on the basis of Eq. (13) lead to the following results:

$$S^\delta_{In} = S^\delta_{Sb} = S^\delta_{Sn} = 10.55 \text{ e.u./g. atom } (\underline{15}) \tag{18}$$

$$S^\delta_{Ga} = S^\delta_{As} = S^\delta_{Ge} = 7.46 \text{ e.u./g. atom } (\underline{14}) \tag{19}$$

$$S^\delta_{Al} = S^\delta_P = S^\delta_{Si} = 4.44 \text{ e.u./g. atom } (\underline{16}) \tag{20}$$

$$S^\delta_B = S^\delta_N = S^\delta_c = 0.58 \text{ e.u./g. atom } (\underline{17}) \tag{21}$$

from which the quantities S^δ_{AB} [298] and $\Delta S^\delta_{AB,f}$ [298] can be calculated for all III-V compounds including BSb(δ), BN(δ) and other compounds for which no entropy data are available. Further, entropy data are available for InAs, InP, GaSb and AlSb, thus it is possible to check this method of approximating the entropy. The results presented in Table 5 provide a comparison of calculated and experimentally observed entropy values.

The calculated entropy values for the remaining III-V compounds are provided in Table 6; the parenthetically enclosed compounds are of interest as regards high pressure synthesis. The results in Table 6 can be used to calculate the entropy change for the elemental synthesis of BSB(δ) and for the transformation of the graphitic hexagonal boron nitride to BN(δ). The calculated results summarized in Table 7 were obtained using S[298] = 1.42 e.u./g.atom for B (17), 10.92 e.u./g.atom for Sb (18) and 1.84 e.u./g.atom for γ BN (19).

TABLE 7

CALCULATED THERMODYNAMIC QUANTITIES AT 298°K FOR HIGH PRESSURE SYNTHESIS OF CUBIC III-V COMPOUNDS

Reactions	ΔV (cm^3/g. atom)	ΔS (e.u./g. atom)	(dP/dT) + ($\Delta S/\Delta V$) (atm/deg K)
$B + Sb \rightarrow BSb(\delta)$	-1.1	-0.6	+22.5
$BN(\gamma) \rightarrow BN(\delta)$	-1.89	-1.3	+28.4

A comparison of the slope of the P versus T curve established by Bundy and Wentorf (5) for the "catalyzed" transformation of γ to δ for BN (36.9 atm/deg K) yields fair agreement.

The results obtained thus far for BSb(δ) indicate that experiments should be carried out at low temperatures and high pressures to maximize possibilities for successful synthesis. The negative entropy of formation calculated for BSb(δ) is compared with the experimental and calculated entropy change at 298°K for the other III-V compounds in Table 8. Examination of these results shows that all of the compounds have a negative entropy of formation. Accordingly, their stability is primarily controlled by the enthalpy of formation. For BSb, the relatively small negative entropy of formation would provide a small positive free energy term in Eq. (1). For example, at 1000°K, $T\Delta S$ is +600 cal/g. atom. The total free energy change given by Eq. (1) would be negative with a relatively small negative enthalpy of formation. The latter quantity varies from -3 to -18 kcal/g. atom for those III-V compounds for which such property data are available The pressure enhancement by the negative volume of formation would provide a term equal to -1314 cal/g. atom for a pressure of 50 kilobars. The problems associated with calculating the enthalpy of formation are discussed in the next section. The results obtained thus far indicate that high pressure will assist in the stabilization of BSb(δ) and that the use of elevated temperatures such as 1000°K will not contribute significantly to destabilization.

TABLE 5

COMPARISON OF CALCULATED AND OBSERVED ENTROPIES OF III-V ZINC BLENDE COMPOUNDS AT 298°K

Compound	$S^{\delta}[\cdot 298]$, e.u./g.atom	
	Calculated	Observed
InAs	9.01	9.05
InP	7.50	7.14
GaSb	9.01	9.09
AlSb	7.50	7.68
InSb	10.55	10.30
GaAs	7.46	7.67

TABLE 6

CALCULATED ENTROPY OF III-V ZINC BLENDE COMPOUNDS AT 298°K

Compound	$S^{\delta}[298]$, e.u./g.atom
(BN)	0.58
AlN	2.51
(GaN)	4.02
(InN)	5.57
BP	2.51
AlP	4.44
GaP	5.95
BAs	4.02
AlAs	5.95
(BSb)	5.57

TABLE 8

CALCULATED* AND OBSERVED ENTROPY OF FORMATION OF ZINC BLENDE III-V COMPOUNDS AT 298°K

Compound	S^{δ}_{AB} cal/°K g. atom	$1/2\ (S_A + S_B)$ cal/°K g. atom	ΔS_f cal/°K g. atom
InSb	10.30	12.40	-2.10
InAs	9.05	11.14	-2.09
InP	7.14	12.24	-5.10
InN	(5.4)	18.38	(-13.0)
GaSb	9.09	10.37	-1.28
GaAs	7.67	9.11	-1.44
GaP	(6.0)	10.21	(-4.2)
GaN	(3.9)	16.35	(-12.5)
AlSb	7.68	8.85	-1.16
AlAs	(6.0)	7.59	(-1.6)
AlP	(4.6)	8.68	(-4.1)
AlN	(2.5)	14.83	(-12.3)
BSb	(5.6)	6.17	(-0.6)
BAs	(4.1)	4.91	(-0.8)
BP	(2.6)	6.01	(-3.4)
BN	(0.6)	12.15	(-11.6)

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*Parenthetically enclosed values were calculated by the method developed in this section.

5. Correlation and Prediction of Enthalpy Data

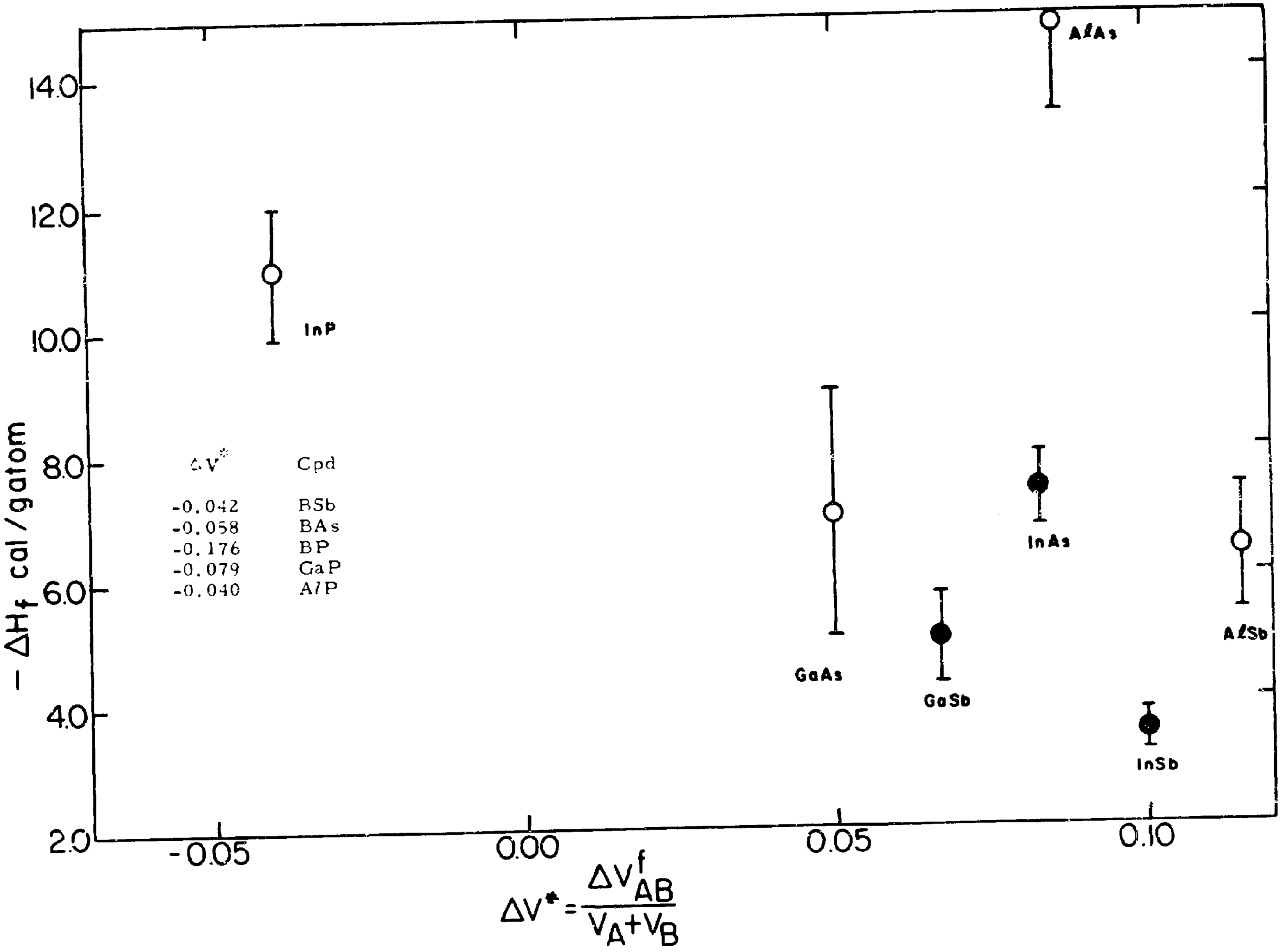
Enthalpy correlations have been developed for various types of compounds. Kubaschewski (20) derived an expression for metallic compounds in which the increase in effective co-ordination number in the compound relative to the elements is combined with thermal properties of the elements. Pauling (9) developed expressions relating electronegativity differences to the heat of formation of a variety of compounds. Other authors, for example, Robinson and Bever (21) have suggested that ΔH formation is a simple linear function of ΔS formation. In analyzing the available entropy data for III-V compounds it was noted that data were lacking for many of the systems. Heat of formation data are not available for a longer number of these compounds.

In order to develop, or use, a method for predicting the sign and magnitude of the enthalpy of formation, the following observations should be recalled: the zinc blende structure has tetrahedral co-ordination and the solid elements which form many of the compounds have higher co-ordination. Thus, Kubaschewski's method (20) would not be directly applicable. The antimonides of aluminum, gallium and indium are characterized by negative volumes of formation and small (less than -8 kilocalories per gram atom) heats of formation. Pauling procedure for calculating the enthalpy of formation (9) is not particularly applicable to compounds in which the bonding is predominately covalent. The available and the calculated entropy of formation data do not show a large variation among the III-V compounds, hence Robinson and Bever's method (21) cannot be applied.

From an examination of various correlation functions such as the methods mentioned above, it was found that some degree of linear behavior could be obtained between the enthalpy of formation and a quantity ΔV^* defined as:

$$\Delta V^* = \frac{\Delta V_f^{AB}}{V_A + V_B} \tag{22}$$

where ΔV_{AB}^f is the volume change for formation of AB and V_A and V_B are the volume change per gram atom of elements A and B. The data are presented graphically in Figure 3. The indicated spread in the available enthalpy data are estimates of experimental uncertainty. Figure 3 also contains a tabulated list of ΔV^* of compounds for which data are presently unavailable. It should be noted that the positive ΔV^f for several of the III-V compounds leads to positive ΔV^* for these compounds. At present it is not possible to calculate ΔH^f for BSb nor for BAs and BP, but this analysis indicates that these three compounds should have negative heats of formation. Further, it is probable that ΔH^f will be more negative for BP than for BAs than for BSb. From these considerations, it is predicted that the ΔF^f of BSb^{δ} will be negative and that high pressure should further enhance the stability of the compound. Although it is necessary for ΔV_{AB}^f to be negative, it is necessary and sufficient that the free energy versus



ΔV^*	Cpd
-0.042	BSb
-0.058	BAs
-0.176	BP
-0.079	GaP
-0.040	AlP

Figure 3. Volumetric Correlation of Enthalpy of Formation for III-V Compounds.

composition curve be a minimum relative to all other phases and combinations of phases at the equi-atomic composition. The calculation of such free energy curves for the one atmosphere phase relations would constitute the next step in this development.

III. HIGH PRESSURE SYNTHESIS: EXPERIMENTAL

A. Procedure

High pressure synthesis experiments are performed in an MIA (6) conical piston/die arrangement which is capable of generating pressures of the order of 50 to 90 kilobars and temperatures up to 2000°C on relatively small samples, 0.10 inch diameter x 0.40 inch high. A schematic diagram of this apparatus is provided in Figure 4. In previous work (6) solid reactant powders were hand punched into a graphite furnace and subjected to the synthesis conditions. An improvement in experimental technique was effected in the present program by utilizing high pressure hot pressing techniques (22, 23) to fabricate dense solid mixtures of reactant powders which could be characterized by metallographic procedures prior to, and after, a high pressure synthesis experiment. The apparatus for high pressure hot pressing shown digramatically in Figure 5 is capable of generating pressures of the order of 100,000 to 300,000 psi and temperatures up to 2000°C on specimens of 0.40 inch diameter x 1.0 inch long. This technique is extremely useful in the preparation of a uniform mixture of two, or more, substances when one material has a substantially higher vapor pressure than the other(s).

In practice, synthesis experiments are carried out by loading the reactants to the desired pressure, then increasing the temperature to the reaction range for a defined, but usually limited (e.g., 5 minutes) time, and next thermally quenching the reaction mixture by cutting off the heating power while maintaining the pressure at the reaction condition. Finally, the pressure is released to ambient conditions and the high pressure cell assembly is removed and the reaction product is separated. The latter is subjected to metallographic and X-ray procedures for analysis. Additional procedures such as chemical analysis or electron microprobe are used as necessary.

B. Attempted Synthesis of Boron Antimonide

Synthesis experiments designed to produce experimental data on the stability of the compound BSb (zinc-blende structure) were performed according to reaction schemes which can be classified as:

(1) Elemental Synthesis: $0.5B + 0.5Sb \rightarrow B_{0.5}Sb_{0.5}$

(2) Substitutional Synthesis: $0.5B + (0.5-x)As + xSb \rightarrow B_{0.5}As_{0.5-x}Sb_{x}$ (a)

$0.5Sb + (0.5-x)Al + xB \rightarrow Sb_{0.5}Al_{0.5-x}B_{x}$ (b)

(3) Replacement Synthesis: $0.5B + In_{0.5}Sb_{0.5} \rightarrow B_{0.5}Sb_{0.5} + 0.5In$

The substitutional schemes provide data for the effect of pressure on the replacement of arsenic by antimony in the compound $B_{0.5}As_{0.5}$, and of aluminum by boron in the compound $Al_{0.5}Sb_{0.5}$. Both of the binary compounds are stable at one atmosphere in the zinc-blende form. The elemental synthesis and the replacement synthesis experiments were designed to provide reaction paths leading to BSb at relatively low reaction temperatures to maximize the

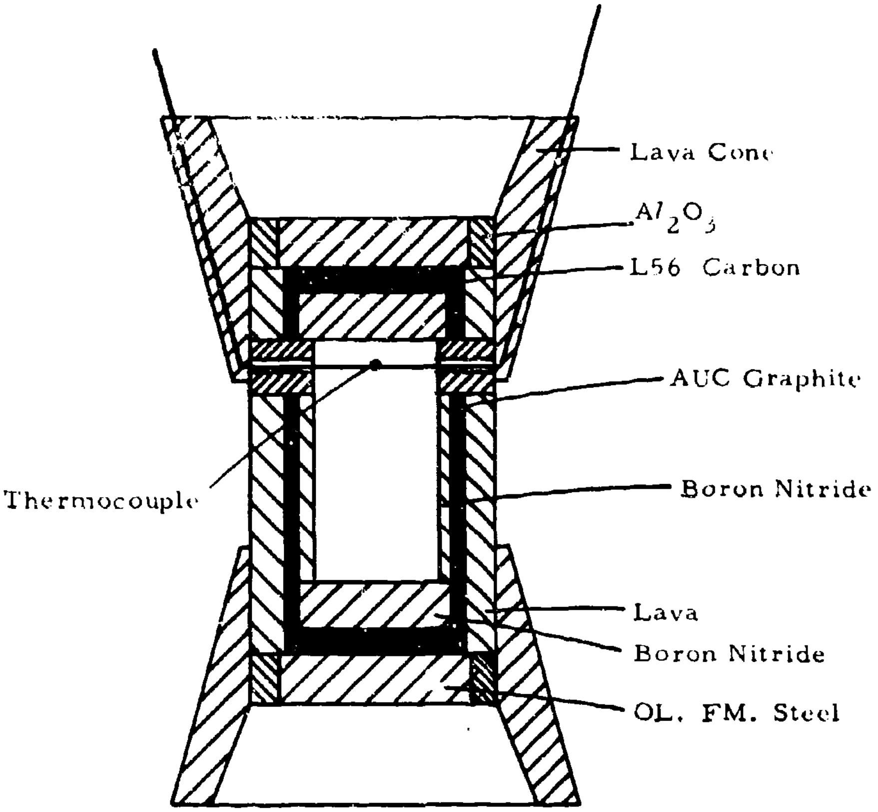
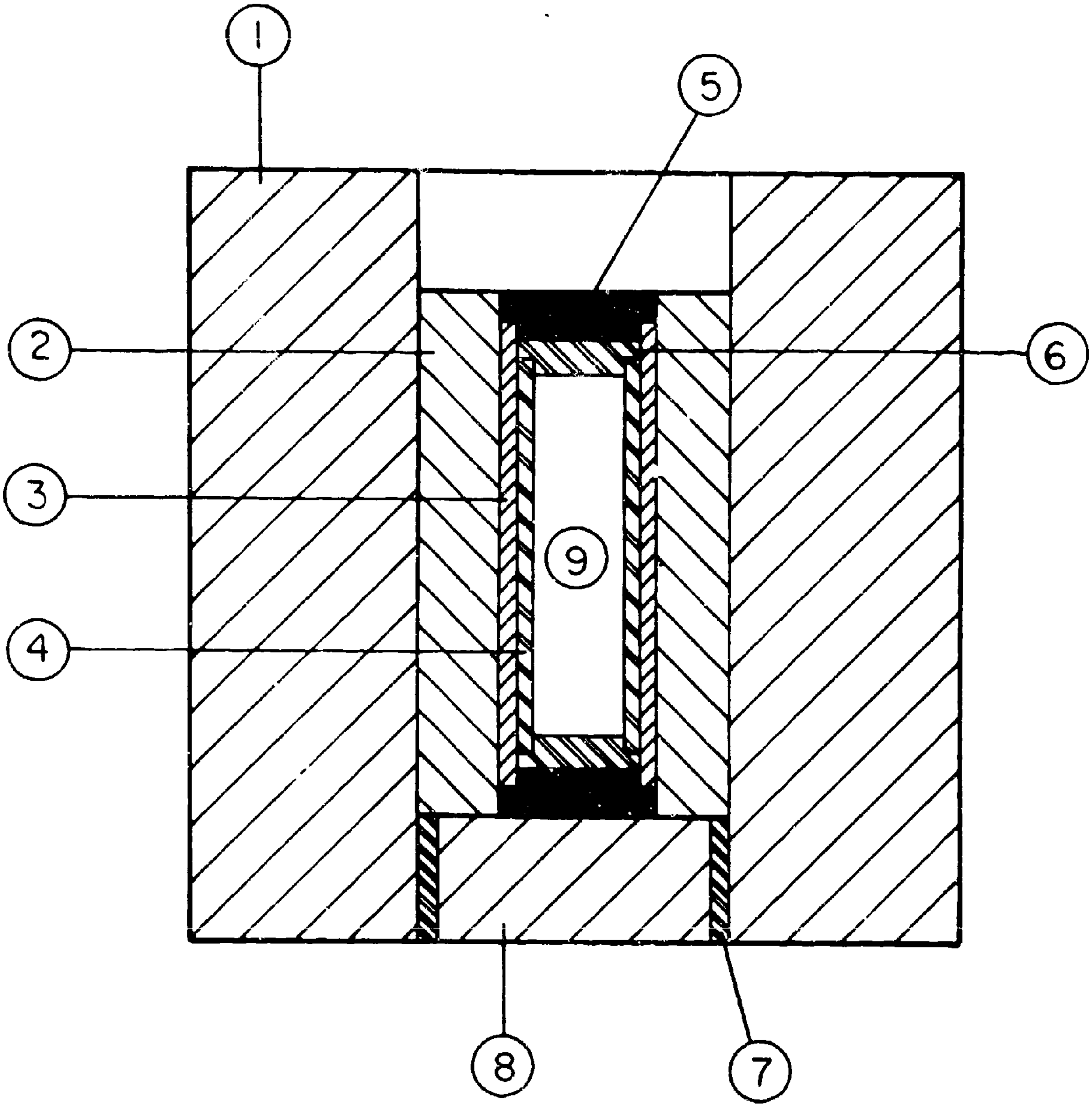


Figure 4. High Pressure (MIA) Synthesis Apparatus.



1. DIE (TUNGSTEN CARBIDE)
2. OUTER INSULATION (LAVA)
3. FURNACE (GRAPHITE)
4. BORON NITRIDE LINER
5. CARBON PAD
6. BORON NITRIDE PAD
7. LAVA SLEEVE
8. CLOSURE (HARDENED STEEL)
9. SPECIMEN (0.40 IN. DIA. X 1.0 IN. LONG)

Figure 5. High Pressure Hot Pressing Apparatus.

probability of successful synthesis. The results of the phenomenological stability analysis indicate that the anticipated intermetallic compound BSb should be stabilized by high pressure and low temperature although the latter parameter appears to be second order. The compositions of the starting materials for the various reaction schemes are summarized in Table 9.

The conditions employed for the experiments performed are provided in Tables 10 through 13. Product characterization results are also reported therein. All high pressure experiments were terminated by a temperature quench; the pressure was released at room temperature. The synthesis experiments are distinguished from the prefabrication experiments by the pressure range used; that is, synthesis experiments are performed in the 50 kilobar range and prefabrications in the 100,000 psi range.

1. Elemental Synthesis

Elemental synthesis results presented in Table 10 do not show conclusive evidence for the formation of BSb but can be used to provide information regarding the phase diagram of B-Sb. Elemental antimony was identified by X-ray methods and elemental boron was identified by metallographic analysis in all experiments. X-ray analysis of the reaction product from Experiment No.'s 58, 60 and 61 show the presence of BN which is an impurity from the container of the reactants. In addition, the X-ray patterns from these reaction mixtures produce weak d-spacing values of 2.81, 2.48 and 1.814Å (the latter could be the 004 reflection for BN). The nearest d-spacing values calculated for BSb(δ), a_o = 5.16Å, are 2.99, 2.58 and 1.82Å. The latter procedure produced clear evidence that the boron in the high pressure is present as unreacted relatively large grains similar to those found in the high pressure hot pressed starting materials, Figure 6 and as an extremely fine grain boundary precipitate which apparently forms from a liquid phase, Figure 7. Observation of two thermal effects in the DTA experiments in which the larger grains of boron did not dissolve, Experiment No. 70 (DTA) and the determination of an experimental limitation for the production of the fine grain boundary precipitate to the temperature range between 500° and 550°C, Experiment No.'s 32, 18 and 37, can not be explained by assuming simple eutectic system. Further, the presence of thermal effect below the melting point of antimony, 585°C at 50 kilobars (24), is not consistent for a peritectic system.

The available results are consistent with a monotectic system as shown in Figure 8. This type of system was suggested for B-Sb at one atmosphere by Wald and Stormont (25). The latter based their prediction on calculations employing Hildebrands rule (26) concerning the tendency of binary systems to form miscibility gaps in the liquid state. In order to check the applicability of this type of calculation to the systems under investigation, the method developed by Kaufman and Bernstein (27) which is analogous to that developed by Hildebrand (26) was used to estimate the interaction parameter, L, for the liquid phase. According to this method L is defined as

TABLE 7

COMPOSITION OF STARTING MATERIALS FOR HIGH PRESSURE SYNTHESIS

Mixture No.	Reactants (Relative Atomic Amounts)	Remarks*
1	$0.5B + 0.5Sb$	(1), (2)
8	$0.5B^* + 0.5Sb$	(6), (2)
2	$0.5B + 0.5In + 0.5Sb$	(1), (2), (3)
6	$0.5B + In_{0.5}Sb_{0.5}$	(1), (5)
7	$0.5B^* + In_{0.5}Sb_{0.5}$	(6), (5)
3	$0.5B + 0.5As$	(1), (4)
13	$0.5B + 0.5As$	(1), (7)
4	$0.5B + 0.4As + 0.1Sb$	(1), (4), (2)
5	$0.5B + 0.3As + 0.2Sb$	(1), (4), (2)
9	$0.5B + 0.2As + 0.3Sb$	(1), (4), (2)
14	$0.5Al + 0.5Sb$	(8), (2)
11	$0.1B + 0.4Al + 0.5Sb$	(1), (8), (2)

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[*] Reactants are identified as follows:
(1) -400 Mesh, Crystalline, 99%B.
(2) -300 Mesh, United Mineral and Chemical Antimony.
(3) A. D. MacKay, 99.97% In.
(4) Mallinckrodt Reagent Arsenic, Ground to -325 Mesh.
(5) Cominco, Grade 12 InSb; Polycrystalline, Ground to -325 Mesh.
(6) Fine particle size boron labeled "amorphous" but found to crystalline and a lower purity material than (1).
(7) Fisher Reagent, Ground to -325 Mesh.
(8) Alcoa, Al Pigment 123, Code #10005.

TABLE 10

EXPERIMENTAL CONDITIONS AND RESULTS FOR ELEMENTAL SYNTHESES

Exp. No.	Mixture No.*	Pressure	Temp. (°C)	Time (min.)	Results
10	1	100 kpsi	1400	10	No Reaction
11	1	50 kilobars	700	30	Grain Boundary Precipitate
18	1	50 kilobars	530	45	Grain Boundary Precipitate
19	1	50 kilobars	600	45	Grain Boundary Precipitate
29	1	50 kilobars	500	45	No Reaction
32	8	50 kilobars	500	45	No Reaction
37	1	50 kilobars	500-550	Cycle[1]	Grain Boundary Precipitate
58 (DTA)	1	50 kilobars	25-600		Large thermal effect at 590°C. BN identified, BSb suggested.
60 (DTA)	1	50 kilobars	25-400		No conclusive data for a thermal effect. X-ray result same as No. 58.
61 (DTA)	1	50 kilobars	25-450		No conclusive data for a thermal effect. X-ray result same as No. 58.
70 (DTA)	1	40 kilobars	25-		Thermal effect evidenced at 400°C (see foot note 2).

---

* See Table 1 for identification of reaction mixtures.

1. Cycled 500° to 550°C, 5 minutes at each temperature, 4 cycles performed, then quenched from 550°C.
2. Independent research carried out by H. Posen at AFCRL gave a thermal arrest at 530°C followed by a large thermal effect at 624°C at 40 kilobars.

TABLE 11

EXPERIMENTAL CONDITIONS AND RESULTS FOR REPLACEMENT REACTION SYNTHESIS

Exp. No.	Mixture No.*	Pressure	Temp. (°C)	Time (min.)	Results
14	2	100 kpsi	1000	45	B, InSb, Sb Identified InSb/Sb Eutectic Structure
21	Product No. 14	50 kilobars	300	45	B, InSb, Sb Identified Diffraction Line at 3.02 Å InSb severely cracked
22	Product No. 14	50 kilobars	410	45	B, InSb, Sb Identified Diffraction Line at 3.02 Å
24	Product No. 14	50 kilobars	500	45	B, InSb, Sb Identified Diffraction Line at 3.02 Å
31	7	50 kilobars	300	45	No Reaction, No Line at 3.02 Å
36	6	50 kilobars	500	45	B, InSb Identified, Diffraction Line at 3.91 Å
38	6	50 kilobars	400	45	B, InSb Identified, Diffraction Line at 3.91 Å with Increased Intensity

---

[*] See Table 9 for identification of reaction mixtures.

TABLE 12

EXPERIMENTAL CONDITIONS AND RESULTS FOR SUBSTITUTIONAL REACTION SYNTHESIS IN THE B-As-Sb SYSTEM

Exp. No.	Mixture No.*	Atomic Ratio As/Sb	Pressure	Temp. (°C)	Time (min.)	Results
13	3	5:0	102 kpsi	1000	45	No Reaction
20	Product No. 13	5:0	50 kilobars	700	45	High BAs; low B, As
46	13	5:0	50 kilobars	700	45	Very weak X-ray diffraction
47	13	5:0	50 kilobars	850	10	High As, B; low BAs
				700	35	
48	13	5:0	50 kilobars	1000	10	High As, B; low BAs
				700	35	High As, B; low BAs
54	13	5:0	100 kpsi	1000	10	As, B; many unidentified X-ray lines; trace BAs
57	Product No. 54	5:0	50 kilobars	700	45	As; many unidentified X-ray lines; completely different from No. 20
15	4	4:1	100 kpsi	1000	45	B, As, As/Sb solid solution
23	Product No. 15	4:1	50 kilobars	700	45	High BAs; low B, As/Sb solid soln; trace As
59	Product No. 23	4:1	50 kilobars	400	45	BAs; As/Sb solid soln; As
16	5	3:2	100 kpsi	800	45	B, As, As/Sb Solid Solution
34	5	3:2	55 kilobars	500	45	High As/Sb solid solution; low As, B; 4 extra X-ray lines
41	5	3:2	50 kilobars	700	45	High As/Sb solid soln; low B, As; trace Sb; four extra X-ray lines very weak
35	9	2:3	50 kilobars	500	45	As, Sb, B; four extra X-ray lines
39	9	2:3	50 kilobars	570	45	Two As/Sb solid solns; B
40	9	2:3	50 kilobars	850	45	One As/Sb solid solution; B
42	9	2:3	50 kilobars	700	45	One As/Sb solid solution; B

*See Table 9 for identification of reaction mixtures.

TABLE 13

EXPERIMENTAL CONDITIONS AND RESULTS FOR SUBSTITUTIONAL REACTION SYNTHESES IN THE B-Al-Sb SYSTEM

Exp. No.	Mixture No.*	Atomic Ratio Al:B	Pressure	Temp. (°C)	Time (min.)	Results[1]
43	11	4:1	108 kpsi	1000	10	High AlSb; low Al, Sb;B
44	11	4:1	108 kpsi	800	10	moderate AlSb, Al, Sb; B
45	11	4:1	118 kpsi	1000	10	High AlSb; low Al, Sb;B
52	14	5:0	104 kpsi	1000	10	AlSb, Al, Sb
53	14	5:0	100 kpsi	800	10	AlSb, Al, Sb
55	Product No. 43		50 kilobars	700	45	AlSb, Al, Sb, B
56	Product No. 43		50 kilobars	1000	45	Same as No. 55

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* See Table 9 for identification of reaction mixtures.

[1] Extensive room temperature oxidation was noted for AlSb and for the Al-Sb-B hot pressed billets.

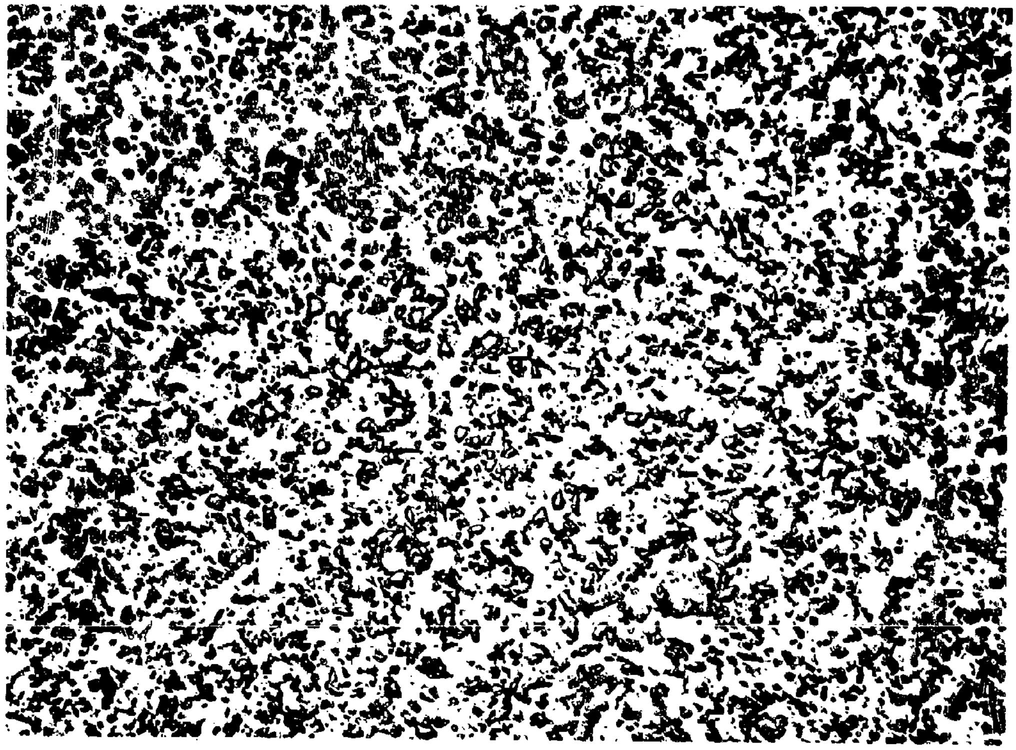

Figure 6. High Pressure Hot Pressed Mixture of Boron and Antimony.

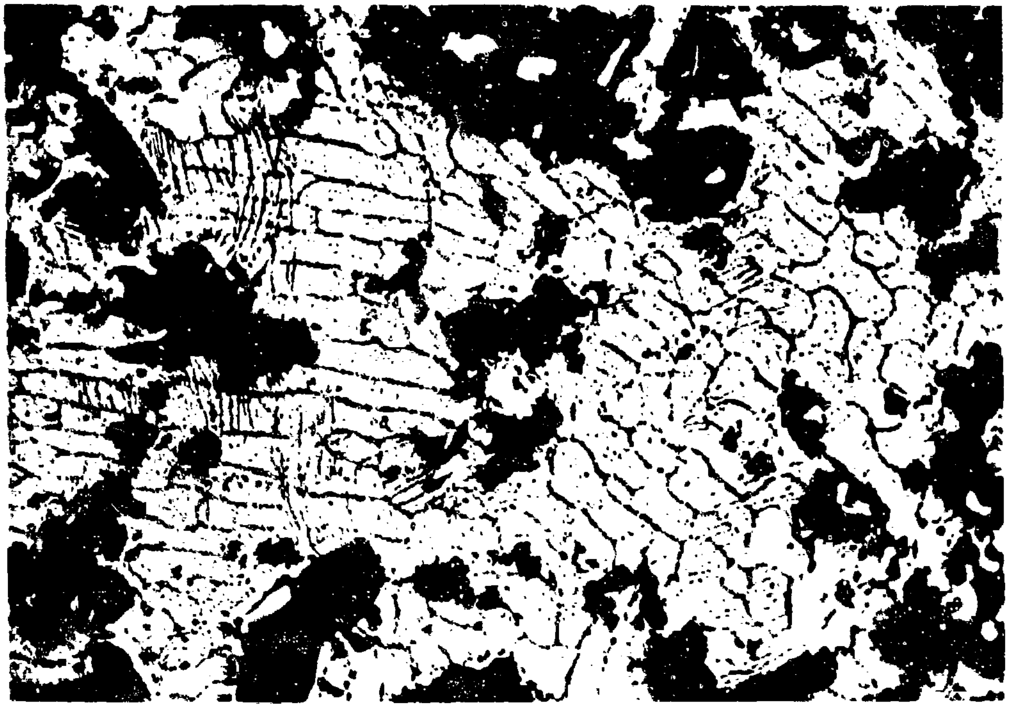

Plate 8328

Etched Etchant: 30 HCl: $5H_2O_2$(5%) : $65H_2O$ 500X

Note: Precipitate at subgrain boundaries of antimony unreacted boron indicated by black areas.

Figure 7. Reaction Product of Experiment No. 37, 0.5B + 0.5Sb.

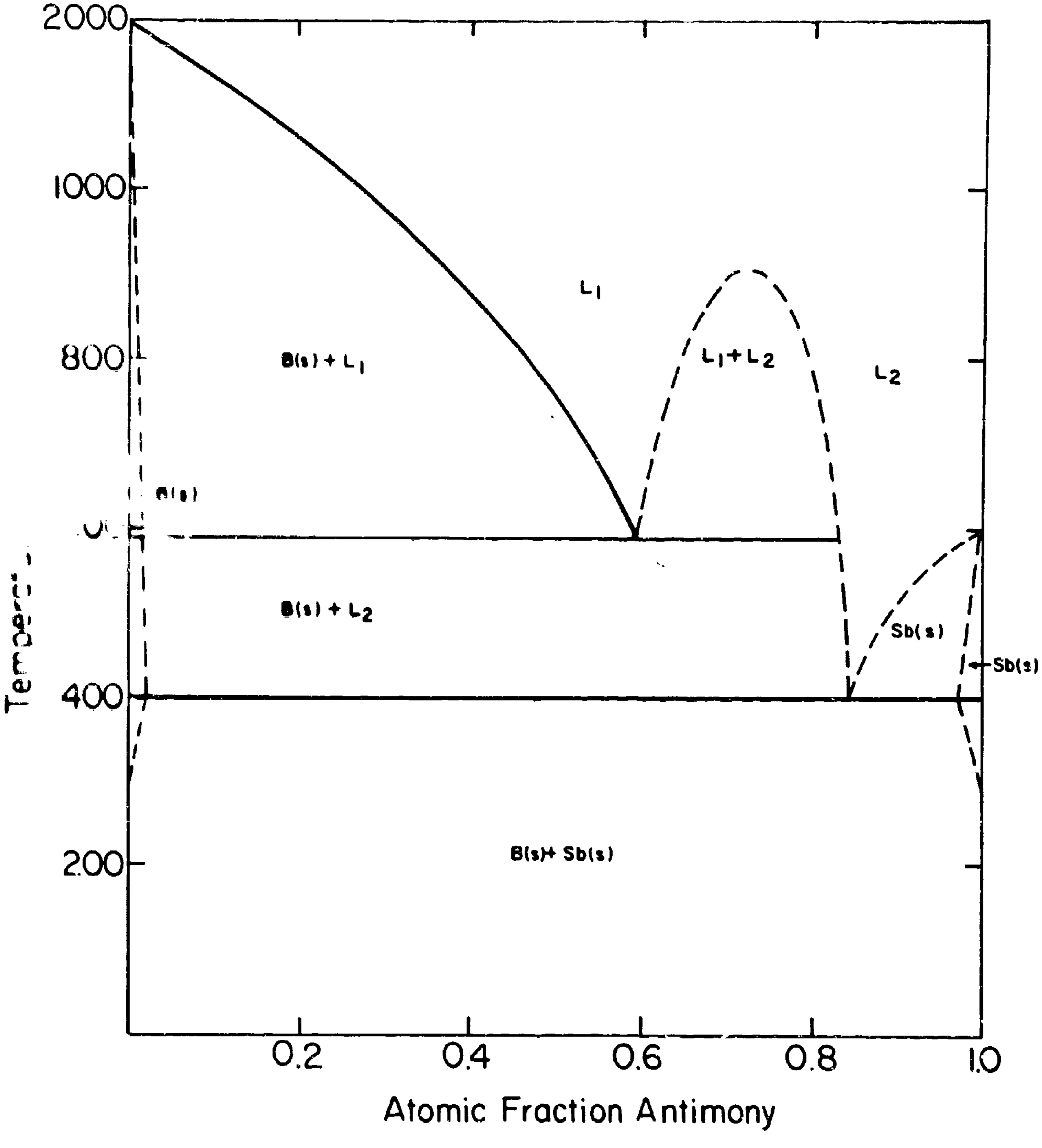

Figure 8 Estimated Phase Relations in B-Sb System at 50 Kilobars.

$$L = e_p + e_o \tag{23}$$

$$e_o = 23{,}060 \cdot n \cdot (X_B - X_A)^2 \tag{24}$$

$$e_p = (\delta_A^{1/2} - \delta_B^{1/2})^2 \cdot 0.5\,(V_A + V_B) \tag{25}$$

where n is the number of bonds, X_B and X_A are the electronegativities of elements A (Group III) and B (Group V), $\delta_A^{1/2}$ and $\delta_B^{1/2}$ are Hildebrand's solubility parameters for A and B, and V_A and V_B are the gram atomic volumes of A and B. For the III-V compounds n = 4 in the solid state, but Kaufman and Bernstein use n = 5 for many liquid systems. The calculated L parameters are provided in Table 4. The sign and magnitude of the L parameter indicate that immiscibility gaps should occur in the liquid phase for the B-P, B-As, and B-Sb systems. The latter result agrees with the calculations by Wald and Stormont (25) and provides additional support for the previously deduced monotectic system for B-Sb. The formation of stable zinc blende compounds in all of the systems in Table 14 except B-Sb was cited previously. Thus, the presence of the miscibility gap in the liquid phase does not preclude the formation of a stable interelement compound in the solid phase. The calculation of positive valued L-parameters for B-P, B-As and B-Sb indicates that the liquid phase is characterized by a positive volume of formation (28). Hence, the effect of high pressure will be to de-stabilize the free energy term. Accordingly, in viewing the free energy versus composition curves, the effect of pressure will be to lower the free energy values for the zinc blende phase and to raise the free energy values for the liquid phase. The results obtained to date indicate that such pressure stabilization of BSb and de-stabilization of the miscibility gap is not sufficient to make the synthesis of the compound stable.

2 Replacement Synthesis

The initial experiments in this system employed a mixture of B, In and Sb as a starting material. Prefabrication at 100,000 psi produced InSb, Sb and unreacted B, but it was considered desirable to utilize single phase InSb. Accordingly, commercial polycrystalline InSb was purchased and ground to -325 Mesh for these experiments. Experimental details and results are provided in Table 11. Metallographic preparation of the reaction products was difficult, as portions of the surface especially the B tended to be pulled out rather than polished. Microcracks were profuse and overetching was a problem. No indications of a reaction were observed. The earlier observed X-ray diffraction line at 3.02Å was not found, but a new line at 3.91Å was noted. No evidence for the reaction B + InSb → BSb was observed.

3. Substitutional Synthesis

a. B-As-Sb System

Two types of reactions in this system could lead to the formation of BSb. The first reaction is the substitution of Sb for As in BAs to form B(As, Sb). This would depend upon the pressure stabilization of a continuous series of solid solutions in the BAs-BSb pseudobinary. The second type of reaction is a hereogeneous nucleation of BSb by BAs; this mechanism

TABLE 14

CALCULATED LIQUID PHASE INTERACTION PARAMETERS FOR III-V SYSTEMS

System	L (cal/gram atom)
B-P	+106,850
B-As	+ 93,890
B-Sb	+138,000
Al-P	- 37,580
Al-As	- 24,190
Al-Sb	- 31,160
Ga-P	- 41,150
Ga-As	- 28,030
Ga-Sb	- 38,110
In-P	- 17,120
In-As	- 17,670
In-Sb	- 10,360

could be operable since the two compounds probably have a low interface energy due to their chemical and structural similarities.

The results presented herein indicate that some uncertainty exists regarding the stability of BAs. Although this compound was readily formed as the principal phase in Experiment Nos. 20 and 23, it has been difficult to repeat the synthesis under similar conditions. This had been attributed to the use of mixtures of higher Sb:As ratios and the formation of As/Sb solid solution. Attempts to prepare BAs from B + As mixtures have also failed. Experiment Nos. 20 and 57 employed the same reaction conditions, but the arsenic was obtained from two different sources. The experimental conditions and the characterization results are provided in Table 12.

The main product in the B-As-Sb synthesis experiments has been the As/Sb solid solution. The experiments for $B_{0.5}As_{0.2}Sb_{0.3}$ at 50 kilobars for 45 minutes (see Table 12) indicate the following: (1) below 500°C, As and Sb do not form a solid solution, (2) at 570°C (Experiment No. 39) two As/Sb solid solutions are formed indicating the possibility of a pressure stabilization of a miscibility gap, possibly by kinetic factors and (3) at 700°C a single phase solid solution is formed indicating that the critical temperature for the miscibility gap is between 570° and 700°C. The published (10) lattice parameters for the hexagonal $As_{0.4}Sb_{0.6}$ are $a_o = 4.08\text{Å}$ and $c_o = 11.02\text{Å}$ with a c/a ratio of 2.70. The diffraction lines observed in the sample heated at 570°C at 50 kilobars for 45 minutes (Experiment No. 39) correspond to parameters $a_o = 4.12\text{Å}$ $c_o = 10.93\text{Å}$, $c/a = 2.654$ for one phase (presumably the Sb-rich) and $a_o = 4.03\text{Å}$, $c_o = 10.85\text{Å}$, $c/a = 2.694$ for the other phase (presumably As-rich). Microstructural features of the reaction products of two stoichiometries employed shown in Figures 9a and 9b suggest the possibility of the production of precipitates by dissolution of antimony rich solutions as previously shown in the B-Sb system.

b. B-Al-Sb System

The rational for the experiments in the B-Al-Sb system is the same as for the B-As-Sb. The experimental conditions employed and the results obtained are provided in Table 13. All prefabrication experiments produced a 4-phase microstructure consisting of B, Al, Sb and AlSb. A typical microstructure shown in Figure 10 reveals that the AlSb precipitates from a solution of aluminum in antimony. The dark grey phase is aluminum antimonide, the speckled white is aluminum, the white structure is antimony, and the light grey grains (out of focus) are boron.

Electron beam microanalysis detected only boron in the light grey phase; boron was not detected in any other phase. The AlSb is initially a grey color, but turns brown upon exposure to air. Electron microanalysis showed a high oxygen concentration of the surface of an AlSb specimen which had developed the brown surface coloration. Further decompostion of these specimens proceeds with exposure to air, and the sample eventually (in a few days) loses its integrity. As disintegration proceeds, whole pieces of the specimen fall off, and substantial amounts of a black powder form. This powder product of advanced decomposition was found to contain large amounts of B, Al and Sb, as determined by emission spectroscopy. Similar behavior was observed for two specimens produced from the same original

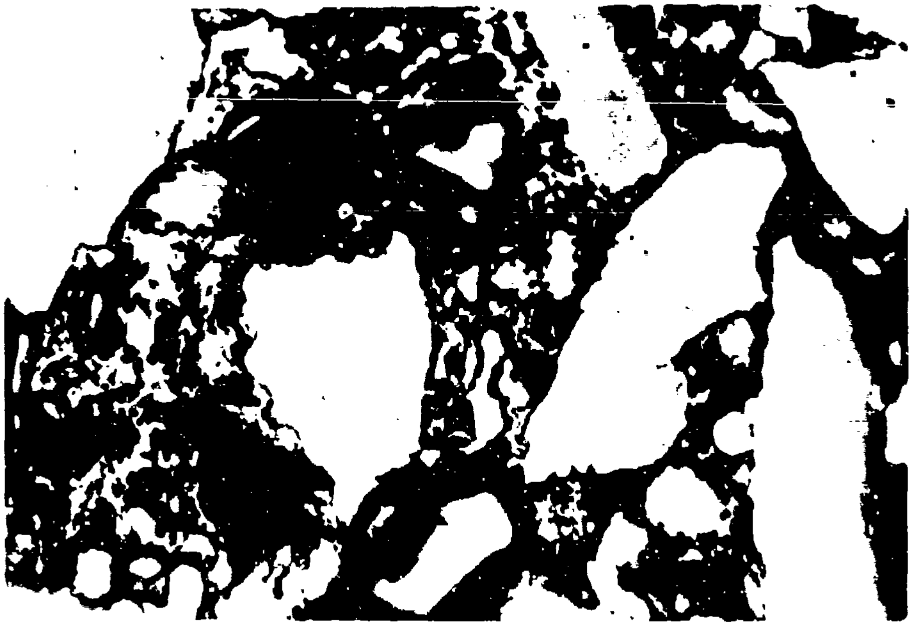
Plate 8244

Unetched 1000X

Note: White phase is Sb; grey, As/Sb solid solution; black, As; and blurred grey, B.

Figure 9a. Reaction Product Experiment No. 35, 0.5B + 0.2As + 0.3Sb.


Plate 8262

Unetched 630X

Note: Dissolution of Sb grains; phase identification same as above.

Figure 9b. Reaction Product Experiment No. 41, 0.5B + 0.3As + 0.2Sb.

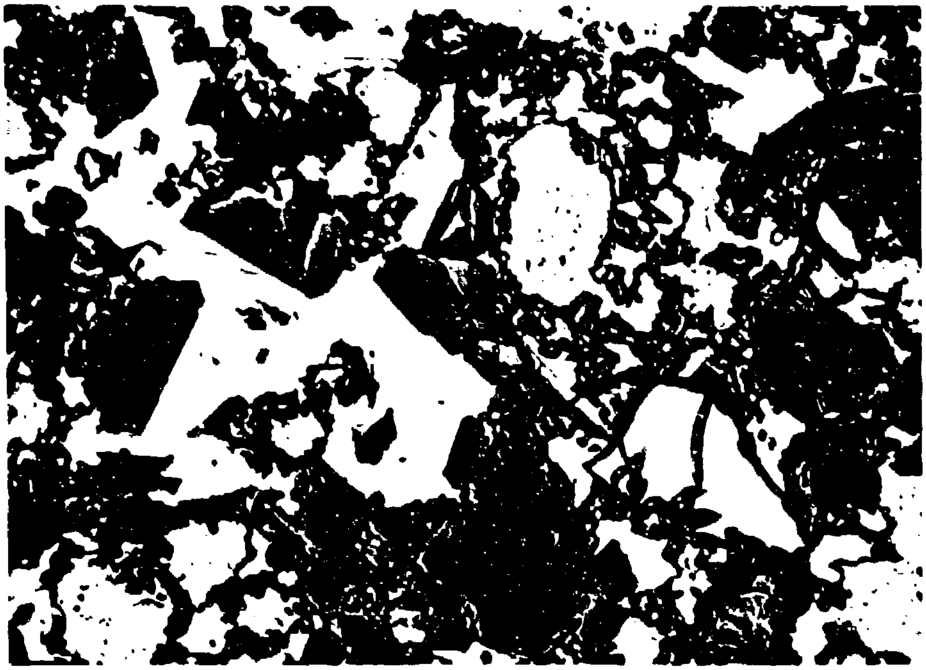

Plate 8334

Unetched

500X

Figure 10. Product of Prefabrication Experiment No. 45 0.2B + 0.8Al + 1.0Sb.

powder by vacuum melting at 1000°C. These specimens were in all respects similar to the HPHP specimens, except that a certain amount of boron segregation occurred at the top of the samples, presumably by simple floating.

Equiatomic amounts of aluminum and antimony with no boron additive were hot pressed in Experiment Nos. 52 and 53. These samples differed little from the specimens containing boron. Room temperature oxidation was also noted in these samples, but no large scale decomposition occurred. This difference could be due to the presence of boron in the AlSb lattice.

The two high pressure runs, Experiment Nos. 55 and 56, produced more complicated diffraction patterns, but the expected lines for BSb (d = 2.99, 2.58, 1.82) did not appear.

The results obtained for both the substitutional and the replacement synthesis experiments show that analytical experimental design considerations would be extremely difficult. The introduction of the third element did not provide results from which experimental direction for the BSb synthesis problem.

C. Synthesis Considerations for Nitrides of Aluminum, Gallium and Indium

1. Introduction

In the development of the volumetric correlation functions it was noted that the refined method for predicting the lattice parameter for AlN(δ) lead to positive $\Delta V^{\omega\to\delta}$ for this compound. Hence, synthesis experiments were not performed directly for AlN, but in the examination of the possibility of producing coarse grained AlN by subjecting polycrystalline material to condit s for grain growth under pressure, it was observed that AlN diffuses exter ly into BN. The diffusion is clearly shown by metallographic inspection and [illegible] changes in the microhardness of the BN.

Preliminary high pressure experiments were performed for GaN and InN. Considerable difficulty was encountered in preparing dense solid starting materials by high pressure hot pressing (22, 23). The available results do not show evidence of new compound formation.

2. Aluminum Nitride

High pressure hot pressing experiments were carried out for polycrystalline AlN to ascertain the possibility of employing high pressure to extend the temperature range in which this material can be heated without producing significant compositional changes by preferential loss of nitrogen. The microstructural features of the as received AlN are shown in Figure 11. Conditions employed for the high pressure hot pressing experiments and for subsequent high pressure diffusion experiments are summarized in Table 15. The hot pressing experiments did not show any significant evidence for grain growth, but the morphology of the grains appeared to change at the outer edge of the sample, Figure 12. Detailed examination of the AlN/BN interface showed definite indications of diffusion phenomena. A series of high pressure

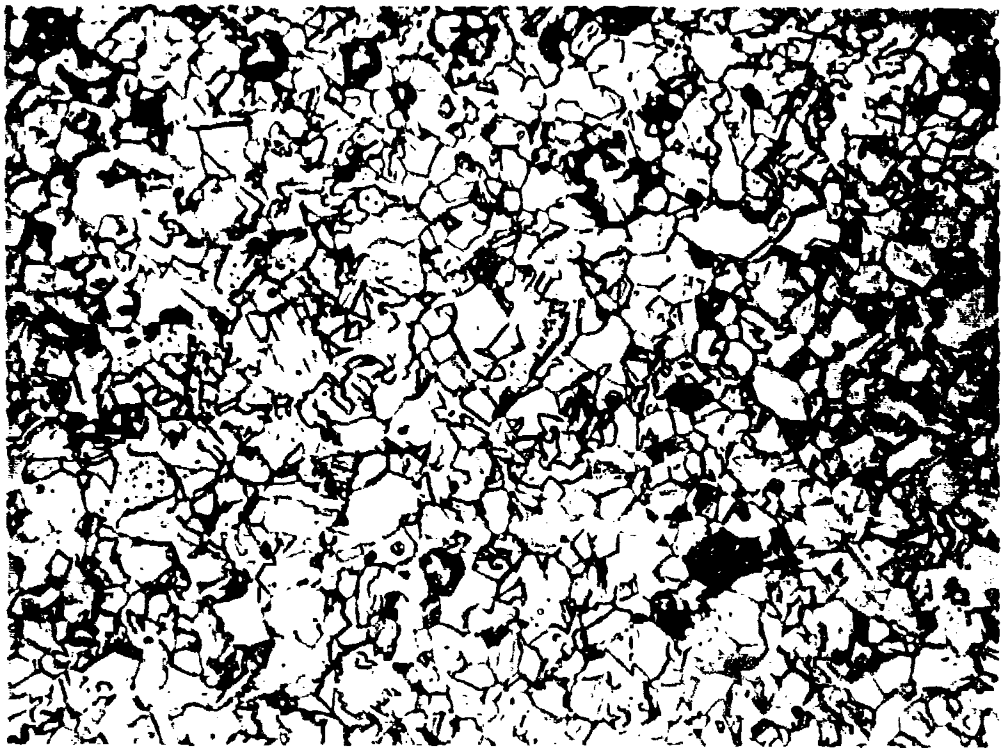

Plate No. 4461

Etched 1000X

Etchant: Boiling ten per cent aqueous $KHSO_4$ (2 - 4 hours).

Figure 11. Microstructural Features of As Received Polycrystalline Aluminum Nitride.

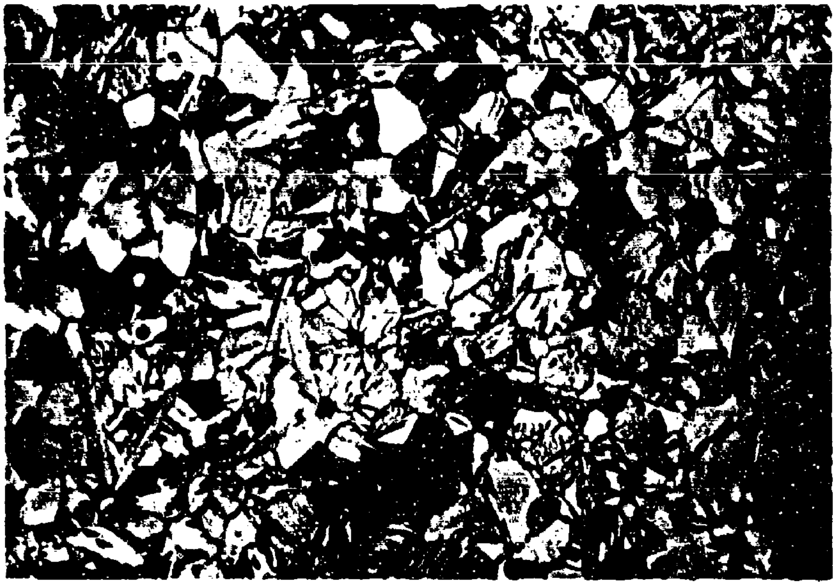

Plate No. 4399

Etched Interior Area 1000X

Plate No. 4400

Etched 1000X

Etchant: Boiling ten per cent aqueous $KHSO_4$ (2 - 4 hours).

Figure 12. Microstructural Features of High Pressure Hot Pressed Aluminum Nitride, Experiment No. 92.

diffusion experiments were performed to further examine the high pressure hot pressing results. The results are summarized in Table 15 and metallographic evidence for diffusion and an apparent reaction are provided in Figure 13. Microhardness traverses across the interface, Figure 13, show a substantial increase in the hardness of boron nitride. Further, the morphology of the boron nitride has changed as evidenced in the appearance of grain boundaries in the as polished condition and the production of flake-type precipitate. Examination of the interface area by electron microprobe techniques showed clear evidence for diffusion of aluminum (and presumably nitrogen) into the boron nitride regions which showed the increase in hardness. Examination of the flake-type precipitates by this method showed the absence of aluminum. Results of X-ray diffraction experiments on the samples did not reveal any new phases, but it is difficult to separate the sample areas and all samples examined showed AlN and/or BN (one atmosphere form). The results indicate that the diffusion and reaction are enhanced by high temperature and high pressure, although the latter will not enhance grain growth.

The AlN/BN diffusion reaction experiments are continuing.

3. Gallium Nitride and Indium Nitride

Considerable experimental difficulty has been encountered in the preparation of dense, characterizable solid samples of GaN and InN. The volumetric correlations developed in this program indicate a possible pressure enhancement of the zinc blende over the wurtzite phase for these two compounds.

The synthesis experiments for these materials are continuing An attempt will be made to make in situ resistance measurements during synthesis experiments.

TABLE 15

HOT PRESSING AND HIGH PRESSURE DIFFUSION EXPERIMENTS FOR ALUMINUM NITRIDE

Experiment No.	Temperature °C	Time min.	Pressure	Remarks
Hot Pressing:				
89A	1820	45	169,000 psi	No grain growth
92	2000	10	185,000 psi	Apparent reaction at outside edge of sample
93	1860	10	219,000 psi	No grain growth
94	1900	20	175,000 psi	No grain growth
95	2060	10	187,000 psi	No grain growth but extensive diffusion
98	2060	10	231,000 psi	Slight indication of grain growth (extensive diffusion)
High Pressure Diffusion:				
106	1800-2000	11	50 kilobars	Figure 16
108	1800-2000	8	50 kilobars	Extensive diffusion
122	1800-2000	1	50 kilobars	Extensive diffusion
126	1600-1800	10	50 kilobars	-----
128	1400-1600	10	50 kilobars	Extensive diffusion, no grain growth

Plate No. 4508

As Polished 400X

Plate No. 4510

As Polished 650X

Figure 13. Microstructural Features of Boron Nitride Aluminum Nitride Diffusion Zone, Experiment No. 106.

IV. FUTURE PLANS

Experimental synthesis procedures will be limited for the most part to binary systems to attempt to synthesize new compound phases. The systems selected for study will be based on an extension of the analytical methods developed in this program. The system of compounds suggested by Hall and Compton (11) will be examined. The synthesis experiments in the Ga-N and In-N will be initiated. The AlN/BN diffusion will be further examined and a very limited number of very high pressure experiments will be performed by the B-Sb system.

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13. ABSTRACT

A phenomological analysis and correlation of available volumetric and entropy data was performed for the III-V compounds. The results of these procedures were used to predict the volumetric properties of the known high pressure forms of BN and the unknown forms of BSb. In addition, values for compound entropy and the entropy of formation were predicted for the above compounds, BN and BSb, and for several known III-V compounds for which such data are presently lacking. The value for the P-T coefficient, $dP/dT = \Delta S/\Delta V$, was also calculated (from the predicted quantities) for the BN transformations and for the synthesis of BSb from the elements. An experimental program was carried out to attempt to synthesize a new compound BSb. The results obtained suggest that the B-Sb system at 50 kilobars is characterized by a miscibility gap in the liquid phase. High pressure experiments were also carried out for AlN; the results obtained show that solid aluminum nitride and solid boron nitride react by a diffusion process which produces marked changes in the microhardness and morphology of the boron nitride.

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