AFCRL-68-0109

THERMODYNAMIC STUDY OF SYNTHESIS OF NEW COMPOUND PHASES UNDER HIGH PRESSURE

EDWARD V. CLOUGHERTY AND LARRY KAUFMAN

ManLabs, Inc.
21 Erie Street
Cambridge, Massachusetts 02139

Contract AF 19(628)-5745

Project No.	5620, 4608
Task No.	562005, 460802
Work Unit No.	56200501

FINAL REPORT

1 December 1965 — 30 November 1967

February 1968

Contract Monitor: Harold Posen
Solid State Sciences Laboratory

Prepared for

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
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ABSTRACT

A phenomological analysis and correlation of available volumetric and entropy data was performed for III-V compounds. The results of these procedures were used in the design of high pressure synthesis experiments to attempt to stabilize and retain the compound BSb. Thermodynamic data were calculated for certain III-V compounds for which such data have not been measured. The experimental results for the study of the B-Sb system at 30 and 50 kilobars suggest that a miscibility gap occurs in the liquid phase which prohibits the synthesis of BSb although pressure stabilization of the compound is predicted. An experimental survey of selected chemical stoichiometries which are Group IV element analogues and hence according to Hall and Compton candidate systems for new tetrahedral materials was conducted at 30 and 50 kilobars and elevated temperatures. No new materials were found at the selected stoichiometries but a new pressure stabilized phase, δAl_2S_3 was synthesized. An investigation of ternary systems containing the binary Group IV element analogue combination and a Group IV element showed that tetrahedral structures can be stabilized in this way. Attempts to stabilize the Al_2S stoichiometry with Ge to form Al_2SGe were unsuccessful. A new high pressure stabilized phase with a NaCl cubic structure was produced in the Mo-C-N system.

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A Scientific Report, "Thermodynamic Study of Synthesis of New Compound Phases Under High Pressure", AFCRL-67-0290, was prepared and distributed in February 1967.

I. INTRODUCTION

The study of the program entitled, "Thermodynamic Study of Synthesis of New Compound Phases Under High Pressure", was comprised of three related investigations. The first investigation involved a phenomological analysis and correlation of available volumetric and entropy data which was performed for 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 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 which contributes to the destabilization of the compound BSb. These results have been reported in detail (1).

The second phase of the investigation was concerned with an experimental and phenomological study of binary stoichiometries suggested by Hall and Compton (2) as systems for high pressure synthesis of Group IV element and cross-compound analogues which would be characterized by tetrahedral co-ordination and presumably desirable solid state properties.

Finally, the high pressure synthesis of sodium chloride type transition metal carbide compounds which could have favorable superconducting properties was investigated.

II. HIGH PRESSURE SYNTHESIS CONSIDERATIONS FOR GROUP III-V COMPOUNDS

A. Introduction

The occurrence of tetrahedral structures stable at one atmosphere in Group IV elements and in certain Group III-V compounds, Group IV analogues, is well known. Such compounds show favorable semiconducting properties and are characterized by directional covalent type bonding. Many high pressure synthesis studies have been initialed with the intention of producing new materials with similar structural and, or, bonding features. Such investigations followed the successful high pressure synthesis of diamond from graphite (3) and cubic boron nitride from the layered hexagonal boron nitride (4).

Both thermodynamic and kinetic factors play significant roles in the formation and retention of such new materials. The prediction of the volumetric properties of new materials which are sought in high pressure synthesis studies should be given close attention since thermodynamic stability at high pressure is favored by a negative volume of formation. 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 phase transformation reaction. 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.

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

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

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 for thermodynamic stability it is necessary and sufficient that $\Delta F(T,P)$ 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.

B. Correlation and Prediction of Structural and Thermodynamic Data

1. Structural Considerations

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 Group 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 periodic discontinuity occurred in a system where all other related compounds have one crystal structure, then it is generally 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 (4) 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 (6) 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.

2. 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 tetradedral covalent radii (7) 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

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)		

*Electronegativity differences (7) are tabulated in parenthesis beside each compound.

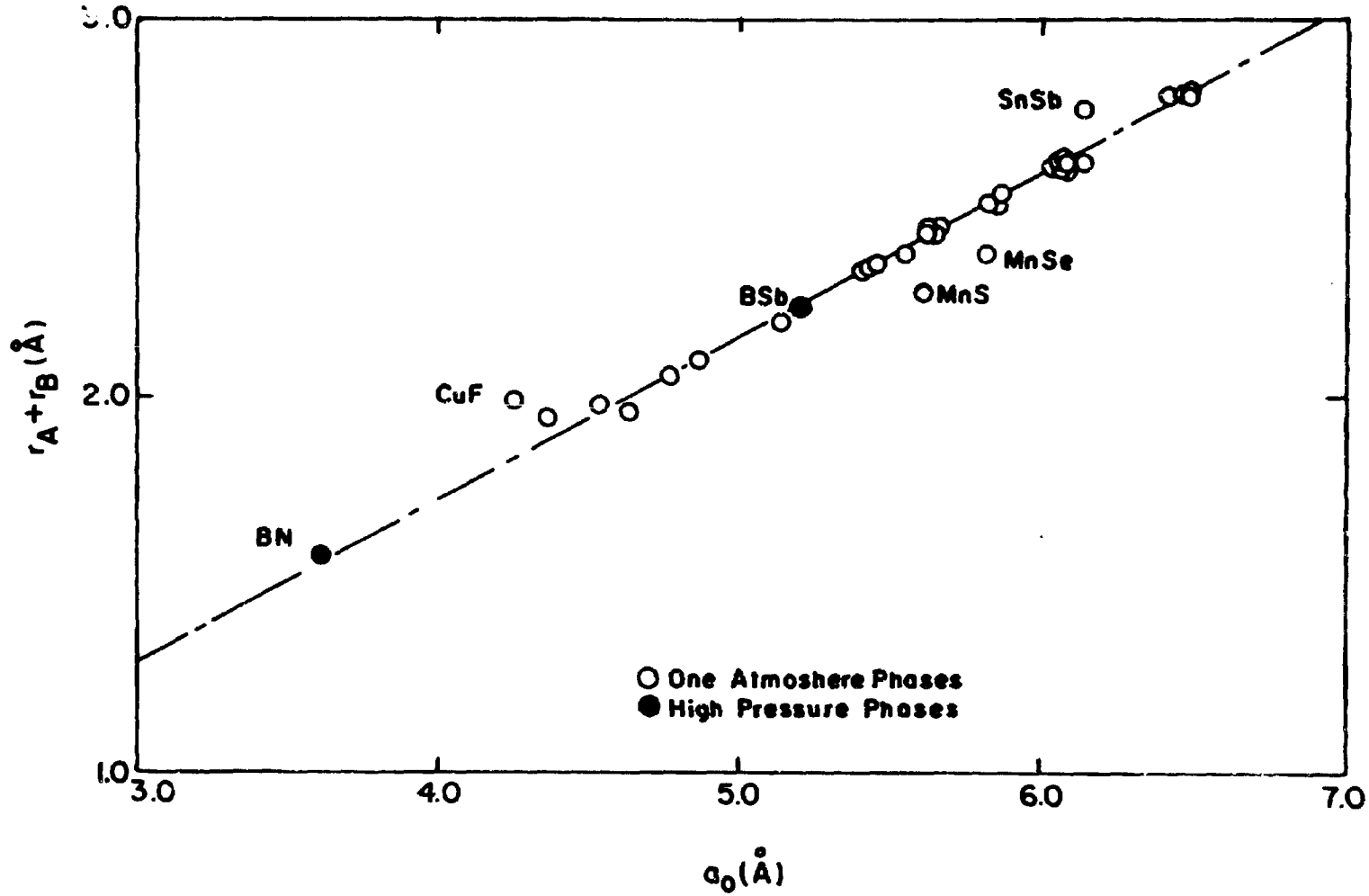


Figure 1. Linear Correlation for the Sum of Pauling's Tetrahedral Covalent Radii with Cubic Lattice Parameter, a_o, for Zinc Blende Structures.

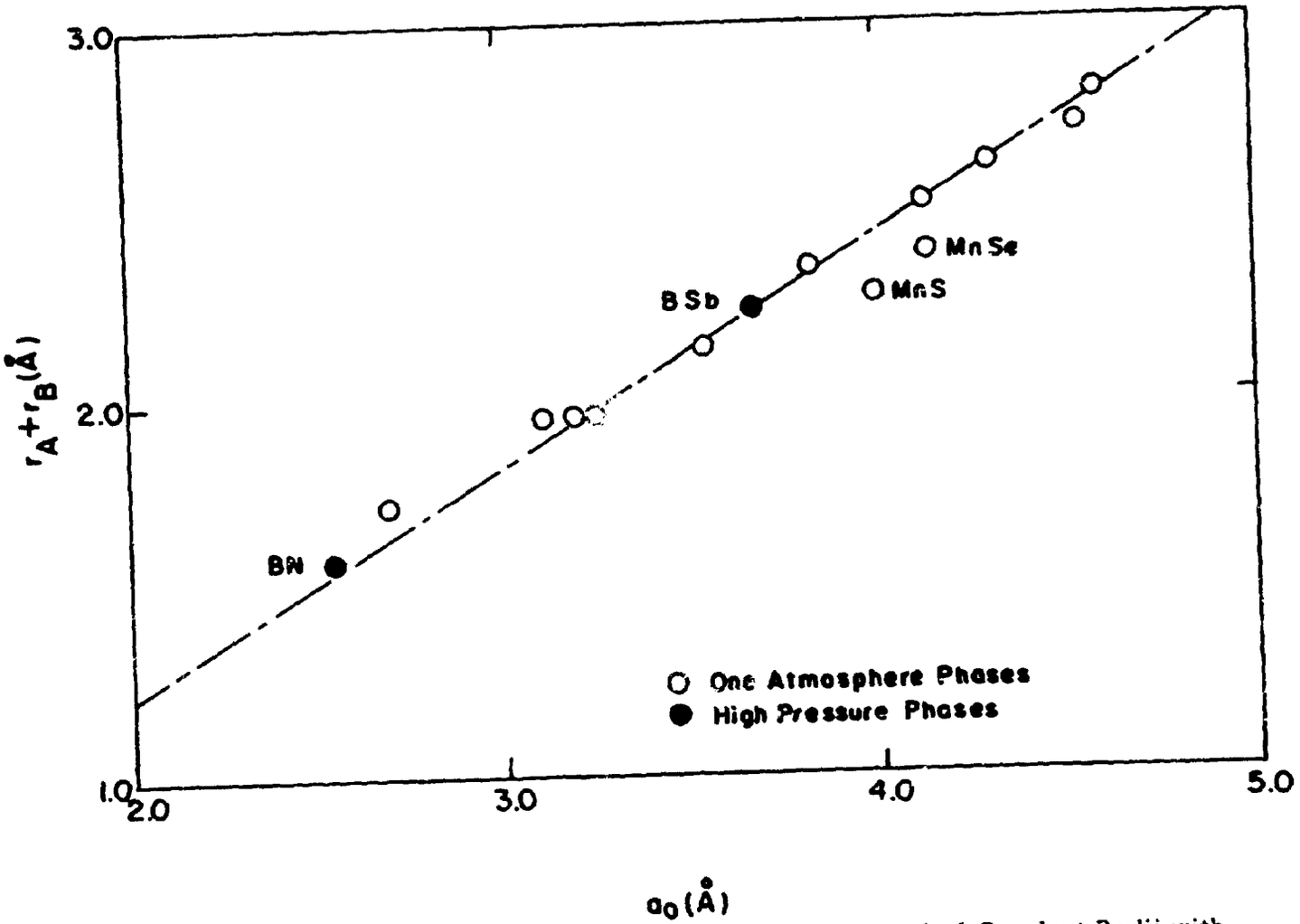


Figure 2. Linear Correlation for the Sum of Pauling's Tetrahedral Covalent Radii with Hexagonal Lattice Parameter, a_o, for Wurtzite Structures.

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 $(e.v.)^{1/2}$ 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 known that Bundy and Wentorf (5) have prepared both forms. The measured volumes are: $V^{\delta}_{BN} = 3.563$ cm^3/g.atom and $V^{\omega}_{BN} = 3.65$ cm^3/g.atom.

The calculated volume changes presented in Table 3 for AlN, GaN and InN are different than those obtained from earlier results (8). 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

TABLE 2

VOLUMETRIC PROPERTIES OF III-V COMPOUNDS AT 298°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 (9) 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

correlation for the zinc blende structure; eleven (11) data points were used for the correlation for the wurtzite structures. The linear correlations developed in this program can be expressed analytically as:

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

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

where

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

The previous results (5) gave:

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

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

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 synthesis experiments should be performed for GaN. The results for InN predict a pressure enhancement of the zinc blende structure in agreement with previous findings (8).

3. 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 (10,11) 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)

$$S^{\delta}_{AB} = 1/2\, S^{\delta}_{A} + 1/2\, S^{\delta}_{B} \tag{13}$$

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

$$S^{\delta}_{InSb} = 10.30 \text{ e.u./g.atom} \tag{14}$$

$$S^{\delta}_{Sn} = 10.55 \text{ e.u./g.atom} \tag{15}$$

$$S^{\delta}_{GaAs} = 7.67 \text{ e.u./g.atom} \tag{16}$$

$$S^{\delta}_{Ge} = 7.46 \text{ e.u./g.atom} \tag{17}$$

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:

$$S^{\delta}_{In} = S^{\delta}_{Sb} = S^{\delta}_{Sn} = 10.55 \text{ e.u./g.atom} \quad (18)$$

$$S^{\delta}_{Ga} = S^{\delta}_{As} = S^{\delta}_{Ge} = 7.46 \text{ e.u./g.atom} \quad (19)$$

$$S^{\delta}_{Al} = S^{\delta}_{P} = S^{\delta}_{Si} = 4.44 \text{ e.u./g.atom} \quad (20)$$

$$S^{\delta}_{B} = S^{\delta}_{N} = S^{\delta}_{C} = 0.58 \text{ e.u./g.atom} \quad (21)$$

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 4 provide a comparison of calculated and experimentally observed entropy values.

The calculated entropy values for the remaining III-V compounds are provided in Table 5; the parenthetically enclosed compounds are of interest as regards high pressure synthesis. The results in Table 5 can be used to calculate the entropy change for the elemental synthesis of BSB(δ). The calculated results summarized in Table 6 were obtained using S[298] = 1.42 e.u./g.atom for B (12), 10.92 e.u./g.atom for Sb (13) and 1.84 e.u./g.atom for γ BN (14).

TABLE 4

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

Compound	S^{δ}[.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	7.57

TABLE 5

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 6

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 for BSb(δ) indicated 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 7. 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.

4. Correlation and Prediction of Enthalpy Data

Enthalpy correlations have been developed for various types of compounds. Kubaschewski (15) derived an expression for metallic compounds in which the increase in effective co-ordination number in the compound relative to

TABLE 7

CALCULATED* AND OBSERVED ENTROPY OF FORMATION

OF ZINC BLENDE III-V COMPOUNDS AT 298°K

Compound	S^{δ}_{AB}	$1/2\,(S_A + S_B)$	ΔS_f
	cal/°K g. atom	cal/°K g. atom	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)

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

the elements is combined with thermal properties of the elements. Pauling (7) developed expressions relating electronegativity differences to the heat of formation of a variety of compounds. Other authors, for example, Robinson and Bever (16) 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 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 (15) would not be directly applicable. The antimonides of aluminum, gallium and indium are characterized by positive volumes of formation and small (less than -8 kilocalories per gram atom) heats of formation. Pauling procedure for calculating the enthalpy of formation (7) 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 (16) 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 enthalpy data are 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^6 will be negative and that high pressure should further enhance the stability of the compound. Although it is necessary for ΔV^f_{AB} to be negative, it is necessary and sufficient that the free energy versus composition curve be a minimum relative to all other phases and combination of phases at the equiatomic composition.

C. Attempted Synthesis of BSb

1. Experimental Procedure

High pressure synthesis experiments are performed in an MIA (17) 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 (17) 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 (18, 19) to fabricate dense solid mixtures of reactant powders which could be characterized by metallographic procedures prior to and after a high pressure synthesis experiment.

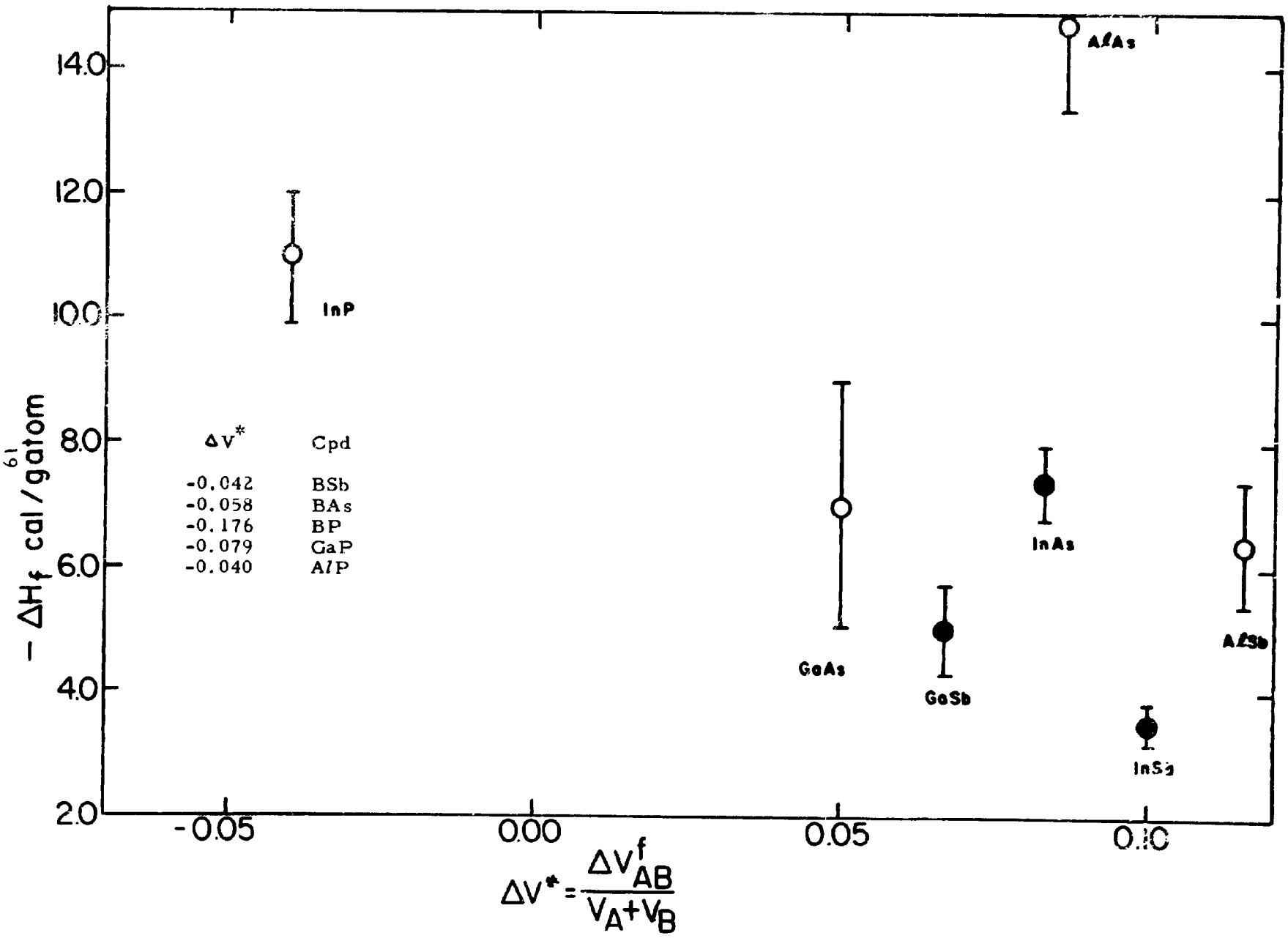


Figure 3. Volumetric Correlation of Enthalpy of Formation for III-V Compounds.

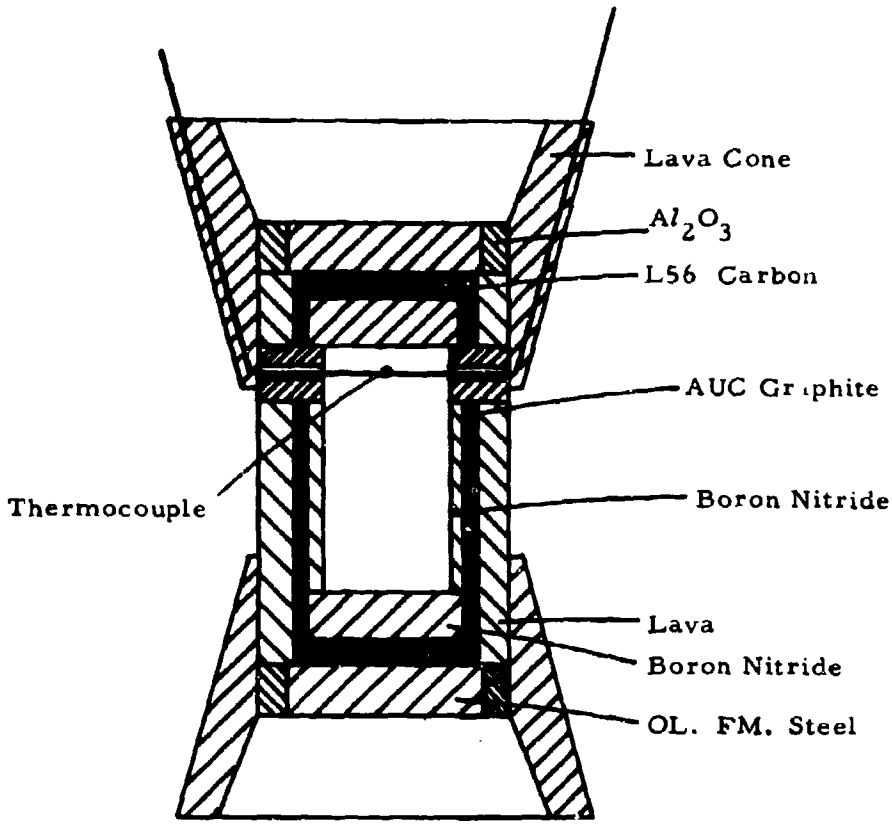


Figure 4. High Pressure (MIA) Synthesis Apparatus.

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 materials when one material has a much 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.

2. Description of Experiments

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:

Elemental Synthesis:

$$0.5B + 0.5Sb \rightarrow B_{0.5}Sb_{0.5}$$

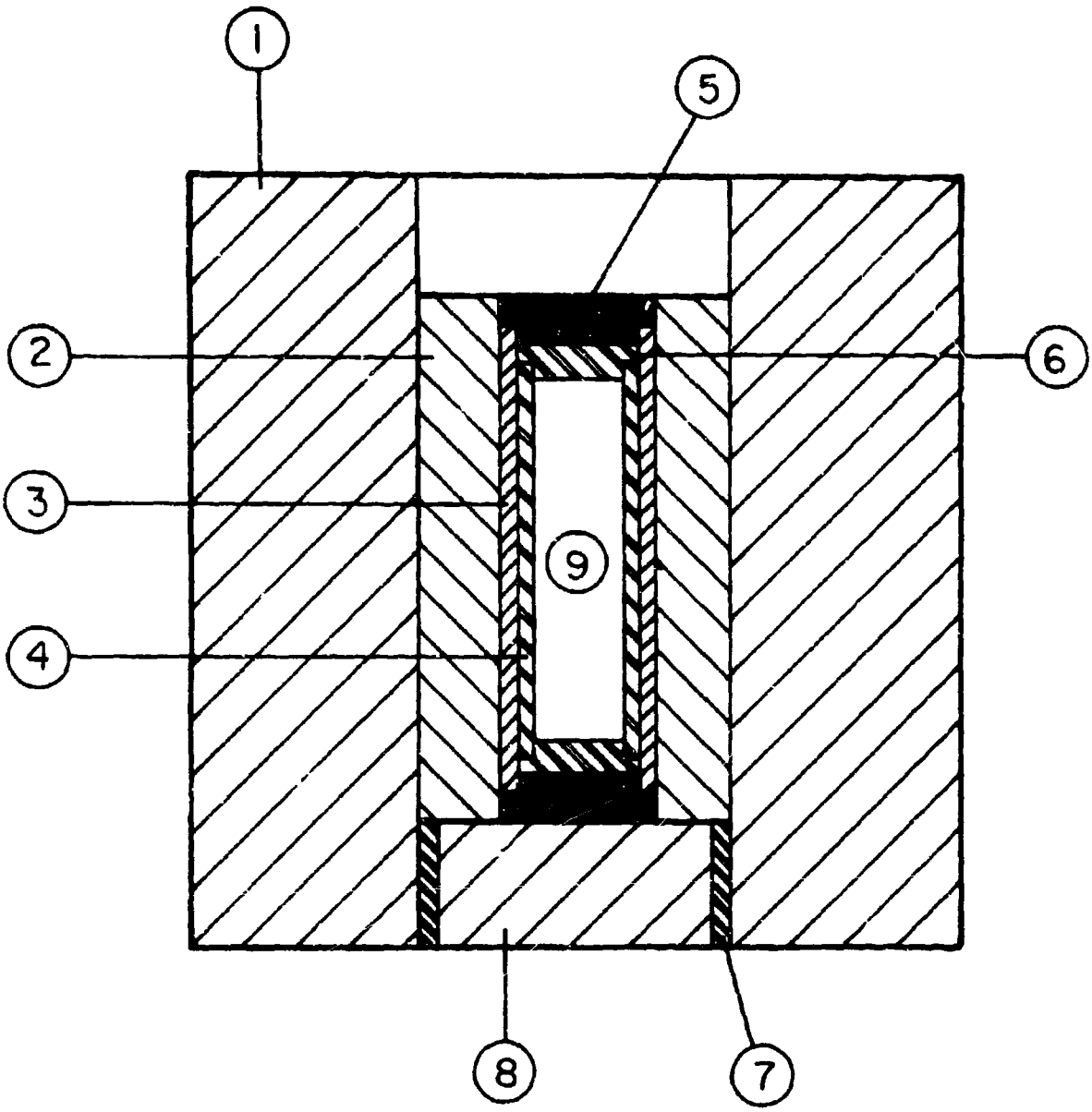
Substitutional Synthesis:

$$0.5B + (0.5-x)As + xSb \rightarrow B_{0.5}As_{0.5-x}Sb_x$$

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

Replacement Synthesis:

$$0.5B + In_{0.5}Sb_{0.5} \rightarrow B_{0.5}Sb_{0.5} + 0.5In$$



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.

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 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 8.

The conditions employed for the experiments performed are provided in Tables 9 through 12. 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.

a. Elemental Synthesis

Elemental synthesis results presented in Table 9 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

TABLE 8

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)

* 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 9

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 10

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 11

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 12

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

Exp. No.	Mixture No.*	Atomic Ratio Al:L	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

* 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.

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 (20) 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 (21). The latter based their prediction on calculations employing Hildebrands rule (22) 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 (23) which is analogous to that developed by Hildebrand (22) was used to estimate the interaction parameter, L, for the liquid phase. According to this method L is defined as:

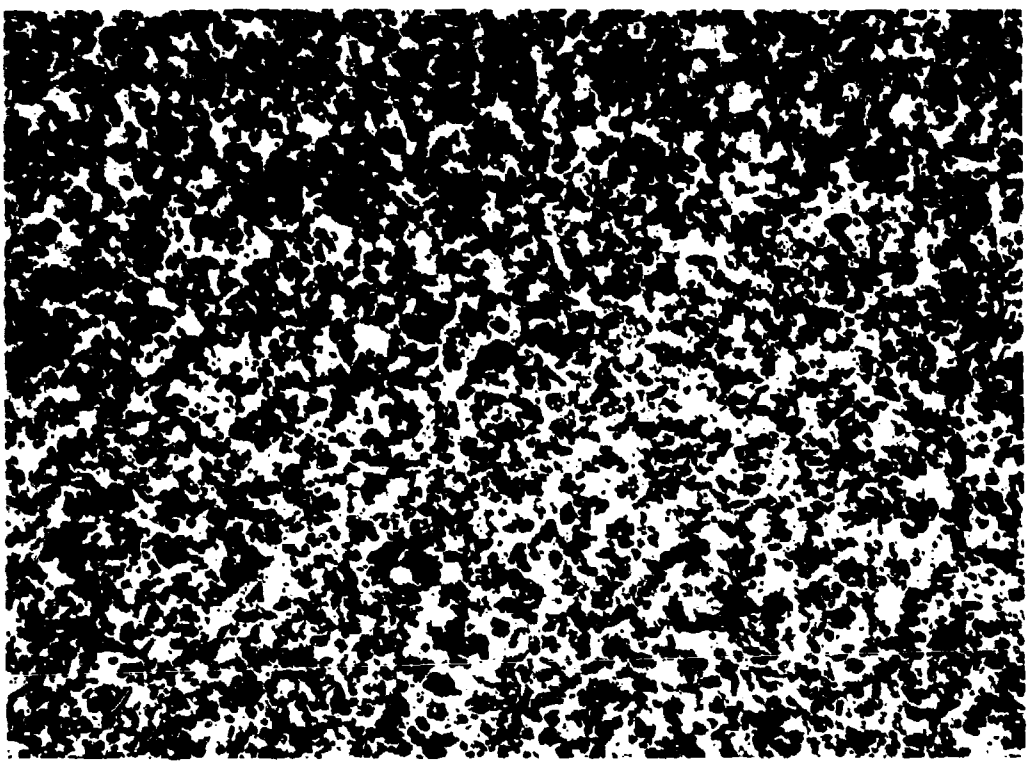


Figure 6. High Pressure Hot Pressed Mixture of Boron and Antimony.

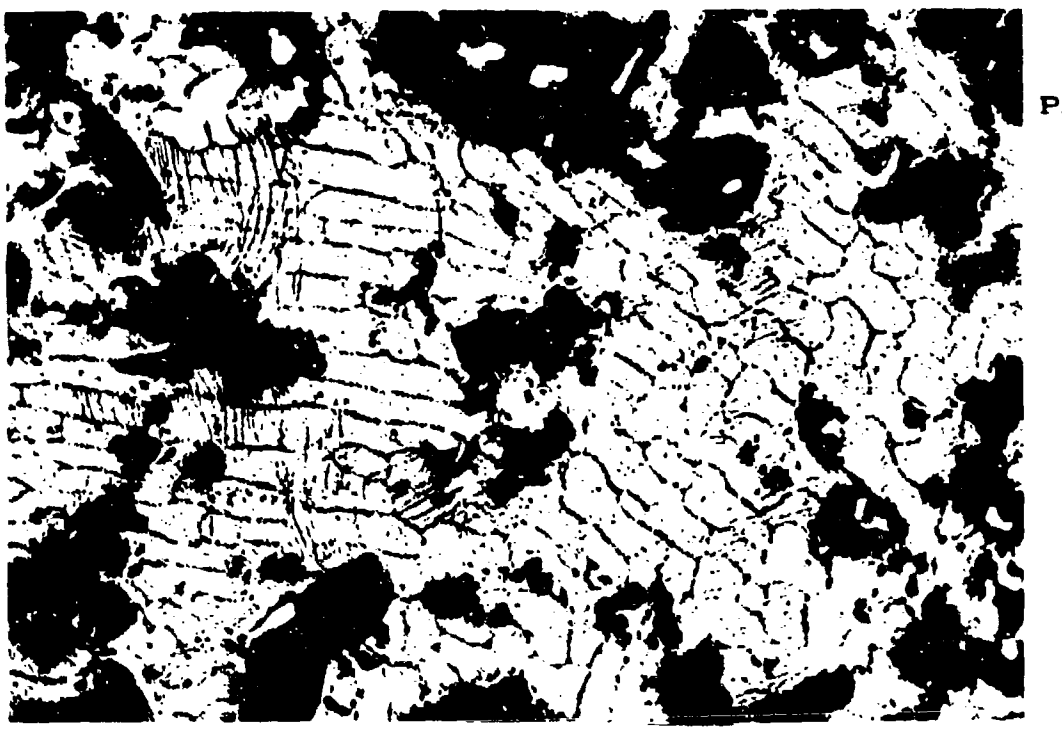


Plate 8328

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.

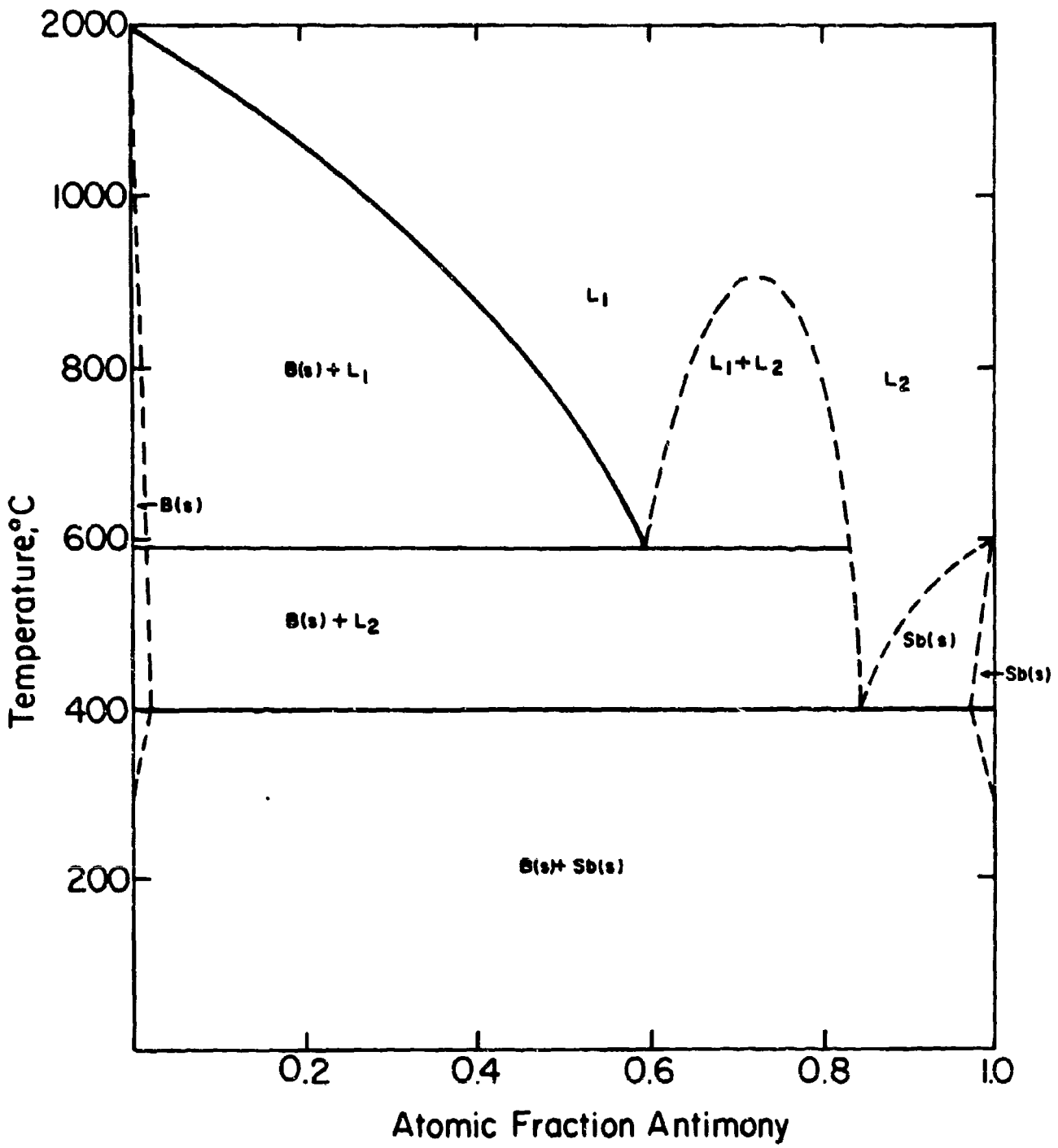


Figure 8. Estimated Phase Relations in B-Sb System at 50 Kilobars.

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

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

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

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 13. 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 (21) 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 13 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 (24). Hence, the effect of high pressure will be to destabilize 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 destablization of the miscibility gapare not sufficient to effect synthesis of the compound.

b. 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

TABLE 13

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

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 10. 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.

c. Substitutional Synthesis

(1) 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 pseudo binary. The second type of reaction is a heterogeneous nucleation of BSb by BAs; this mechanism 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 11.

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 11) 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 (9) 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.

(2) 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 12. 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 gray phase is aluminum antimonide, the speckled white is aluminum, the white structure is antimony and the light gray grains (out of focus) are boron.

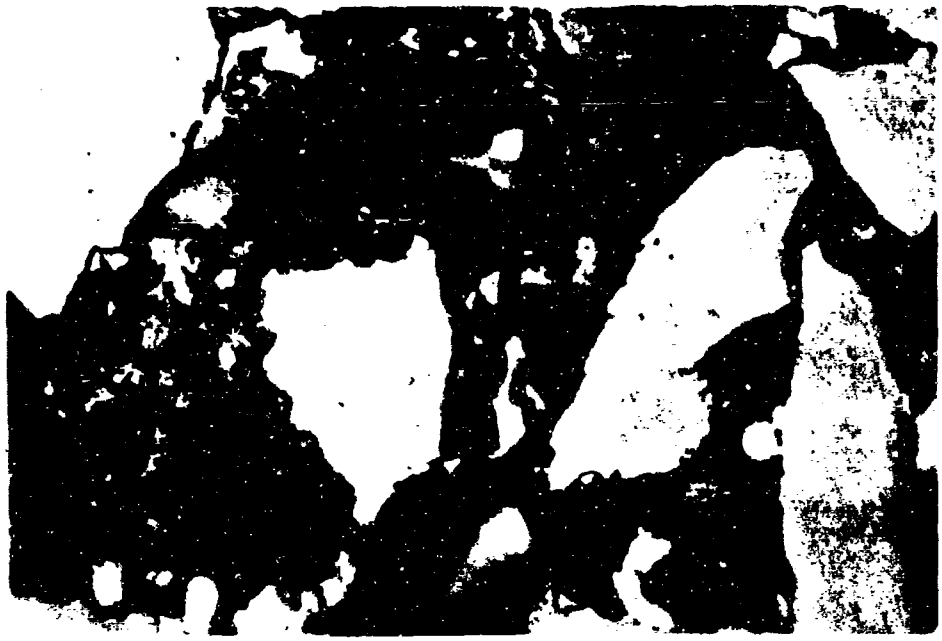


Plate 8244

Unetched 1000X

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

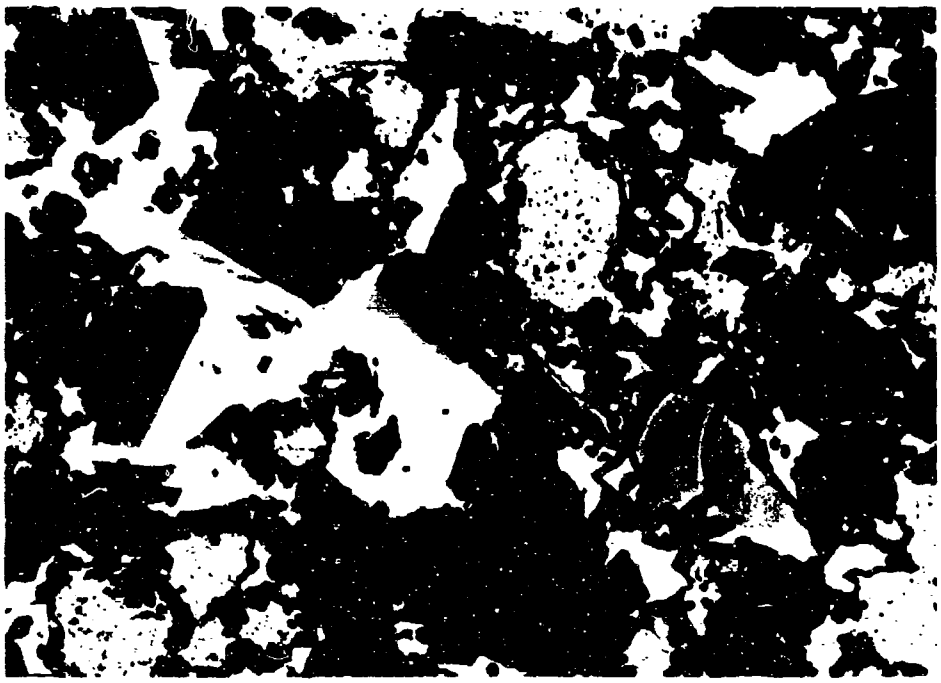


Plate 8334

Unetched 500X

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

Electron beam microanalysis detected only boron in the light gray phase; boron was not detected in any other phase. The AlSb is initially a gray 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 decomposition 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 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 No.'s 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 No.'s 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 are extremely difficult to interpret. The introduction of the third element did not provide results from which experimental direction for the BSb synthesis could be approached.

D. Summary

A phenemological analysis and a correlation of available volumetric and entropy property data were performed for III-V compounds. The volumetric analysis was a refinement of earlier reported (8) results; the entropy analysis was performed for Group IV elements as well as for the isoelectronic III-V compounds. 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.

The analyses and correlations were used as a basis for experimental studies in the B-Sb system. These procedures provided reliable prediction of volumetric and entropy data and crystal structure of BSb, a Group IV analogue, which is not stable at one atmosphere. The predicted thermodynamic data showed that high pressure should enhance the synthesis of this compound and that very high temperatures should be avoided as a negative entropy of formation was predicted. Predictions of enthalpy data were semiquantitative at best, however, a negative enthalpy of formation of BSb is anticipated. Attempted synthesis of BSb was unsuccessful; the available results suggest that synthesis was not achieved because of a miscibility gap in the liquid phase in the B-Sb system at high pressures above 600°C. Experiments are not feasible in the solid state at lower temperatures.

The correlations were also used to predict the values of the entropy at 298°K for several known III-V compounds and the high pressure polymorph, BN (diamond cubic form). The results of the volumetric and entropy property correlations were used 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. The comparison of the calculated value with the experimentally observed value for the "catalyzed" transformation (5) was satisfactory.

III. HIGH PRESSURE SYNTHESIS OF GROUP IV ANALOGUES

A. Introduction

Hall (25) and Hall and Compton (2) have delineated a series of stoichiometric ratios of binary systems which are iso-lectronic to a Group IV element; that is, the average number of bonding electrons per atom is four. Hall and Compton suggest that such systems should be examined in high pressure studies designed to synthesize new tetrahedral materials which could have desirable solid state properties. The examination of such systems is a logical extension of the high pressure synthesis studies of III-V compounds.

B. Selection of Systems of High Pressure Synthesis

The Group IV analogues are conveniently classified as isoelectronic two-atom analogues of carbon with principal quantum number of n = 2 as shown in Table 14. Similarly, the two atom analogues of silicon, n = 3 and the so-called Group IV cross compounds comprised of elements with n = 2 and n = 3 of appropriate stoichiometry to give an arithmetic average of four bonding electrons per atom are provided in Tables 15 and 16. Electronegativity differences are included in parentheses beside each stoichiometry in Tables 14 through 16, which are reproduced with little change from the original tabulations by Hall and Compton (2).

TABLE 14

ISOELECTRONIC TWO-ATOM CARBON ANALOGUES

(Elements n = 2)

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)

TABLE 15

ISOELECTRONIC TWO ATOM SILICON ANALOGUES

(Elements n = 3)

Symmetrical	Unsymmetrical	
AlP (0.6)	Al_2S (1.0)	Al_3Cl (1.5)
MgS (1.3)	MgP_2 (0.9)	Mg_3Cl_2 (1.8)
NaCl (2.1)	NaP_3 (1.3)	Na_2S_3 (1.6)

TABLE 16

CROSS ELEMENT PSEUDO GROUP IV ANALOGUES

(Elements n = 2 and n = 3)

Symmetrical		Unsymmetrical	
LiCl (2.0)	NaF (3.1)	Li_2S_3 (1.5)	Na_2O_3 (2.6)
BeS (1.0)	MgO (2.3)	LiP_3 (1.1)	NaN_3 (2.1)
BP (0.1)	AlN (1.5)	Be_3Cl_2 (1.5)	Mg_3F_2 (2.8)
CSi (0.7)	SiC (0.7)	BeP_2 (0.6)	MgN_2 (1.8)
		Be_3Cl (1.0)	Al_3F (2.5)
		B_2S (0.5)	Al_2O (3.0)

Examination of the crystal structures of the symmetrical combinations in Tables 14 through 16 revealed that the underlined compounds are stable at one atmosphere in either a cubic zinc blende, B-3, or a hexagonal wurtzite B-4 structure both of which have tetrahedral co-ordination. High pressure synthesis has produced BN in both the zinc blende (4) and the wurtzite (5) structures. Sodium azide is the only

unsymmetrical combination that is stable in a tetrahedral structure, wurtzite, at one atmosphere.

Both practical and theoretical reasoning were employed in order to select a limited number of systems for high pressure synthesis studies. Systems which contain dense structures such as cubic B-1 and B-2, stable at one atmosphere in the tabulated stoichiometries were excluded in the bases on unfavorable pressure effects; that is, the volume change for the particular system would be positive. Hence, LiF, NaCl, LiCl, NaF, MgO and MgS were eliminated. It is important to note that the B-3 and B-4 structures which have been the objects of many high pressure synthesis studies have tetrahedral co-ordination while the cubic B-1 and B-2 structures have hexahedral and octahedral co-ordination, respectively. The latter have higher densities. Examination of Tables 14 through 16 reveals that all the symmetrical combinations are either stable or metastable at one atmosphere in a tetrahedral structure or stable at one atmosphere in a structure more dense than a tetrahedral structure.

Consideration of some practical limitations on experimentation for the unsymmetrical combinations lead to the elimination of beryllium containing mixtures on the basis of toxicity considerations. Mixtures containing lithium and to a lesser extend sodium were not investigated as experimental difficulties were anticipated from their hydroscopic properties. Such a limitation is imposed by the nature of currently employed experimental procedures for high pressure reactions as detailed in a subsequent section of this report. Equipment restrictions also impose an elimination of systems requiring gaseous reactants. Accordingly, the high pressure synthesis of B_3F, B_3Cl and MgN_2 can not be readily studied.

Electronegativity differences also contribute to the stability of tetrahedral structures as was shown in the previous analysis for Group III-V compounds. Low values of electronegativity difference of

$\Delta X(e.v.^{1/2}) \leq 1$, characterize the B-3 structure; ΔX values of 0.7 to 1.5 $e.v.^{1/2}$ are generally found for the B-4 structure. The largest value observed for a B-4 structure was 2.0 $e.v.^{1/2}$ for BeO.

The systems chosen for high pressure synthesis screening experiments and the reactions employed are provided in Table 17. Tetrahedral ternary phases which are stable at one atmosphere and have the same stoichiometry as the synthesis system, but which in addition contain a Group IV element are also tabulated when such structures are known. Hereafter, the Group IV element in such compounds is called a tetrahedral promoting agent. The existence of such compounds appears to lend some support to the choice of the indicated binary systems for high pressure synthesis of new materials with a tetrahedral structure. Systems in the unsymmetrical combinations not investigated herein include B_2O, in which Hall and Compton (2) have found some evidence for a new material, B_2S which is analogous to B_2O and Al_3Cl which would require experimentation with hydroscopic $AlCl_3$.

It was not feasible to extend the volumetric predictions developed in the high pressure study of Group III-V compounds (1), prior to the initiation of high pressure experiments in these systems. Such a procedure would involve assumptions regarding ordering or random arrangements for the tetrahedral co-ordinations for which the original stoichiometries were selected. It was also considered prudent to perform a limited number of high pressure experiments and examine the results prior to the development of new correlations and prediction techniques. The initial screening experiments were performed at 875°C for 10 minutes in a two series, one at 30 kilobars and a second at 50 kilobars. All reactions were rapidly quenched to room temperature at the indicated pressure to enhance the retention of metastable materials to one atmosphere and ambient temperature. The reaction products were examined by X-ray diffraction for phase identification; metallographic procedures were also employed where feasible.

TABLE 17

GROUP IV ANALOGUE SYSTEMS SELECTED FOR HIGH PRESSURE SYNTHESIS SCREENING AND TERNARY TETRAHEDRAL

Reactants	Product Sought	ΔX, e.v.$^{1/2}$	Ternary Tetrahedral Phase
2 Al + S	Al_2S	1.0	unknown
$MgCl_2$ + 2 Mg	Mg_3Cl_2	1.8	unknown
AlF_3 + 8 Al	Al_3F	2.5	unknown
Al_2O_3 + 4 Al	Al_2O	3.0	Al_2CO (26, 27)
Al + P	AlP	0.6	unknown
Mg + 2 P	MgP_2	0.9	$MgGeP_2$ (28)
MgF_2 + 2 Mg	Mg_3F_2	2.8	unknown

C. Experimental

The high pressure synthesis cell and die assembly which is capable of transferring pressures from 10 to 90 kilobars at temperatures up to 2000°C on specimen diameters of 0.10 inch by 0.40 inch high is described in the previous section. Container materials provide a major limitation in high pressure reaction chemistry. Boron nitride provides excellent protection from the graphite furnaces and is generally inert to most reactants to quite high temperatures. Results cited below will provide evidence for reactions of molten aluminum with boron nitride above 1200°C. Vacuum encapsulation procedures employing metal containers such as stainless steel for intermediate temperatures and molybdenum or tantalum for elevated temperatures have been successfully employed for high pressure hot pressing procedures which require outgassing of refractory metal powders prior to consolidation at pressures in the range 7 to 30 kilobars (29,30). Such a technique has not been used for synthesis studies, but its introduction would extend the types of materials which could be used and would minimize contamination problems. Introduction of gaseous reactants remains a difficult task for the general types of high pressure equipment which are currently in operation.

D. Results

The results of the initial high pressure screening reactions are provided in Table 18. Examination of these results suggested the need for additional experiments for certain systems. It is convenient to discuss the individual systems in the light of the initial and any subsequent high pressure results.

System: $2Al + S = Al_2S$

Three phases designated α-, β- and γ-Al_2S_3 were previously known to be stable at one atmosphere in the Al-S binary system (9). In addition, a denser, cubic phase of the same stoichiometry with approximately two atom per cent arsenic in substitutional solid solutions on the aluminum lattice sites was also known (9,31).

TABLE 18

HIGH PRESSURE SCREENING EXPERIMENTS ON SELECTED GROUP IV ANALOGUE SYSTEMS (875°C - 10 MINUTES - 30 KILOBARS AND 50 KILOBARS)

Exp. No.	System	Pressure (kilobars)	Identified Products	Remarks
152	$2Al + S$	30	Al, δAl_2S_3 (note 1)	New Al_2S_3 Phase
148	$2Al + S$	50	Al, δAl_2S_3	New Al_2S_3 Phase
138	$MgCl_2 + 2Mg$	30	Mg, $MgClO_4 \cdot 6H_2O$	Oxygen Contamination
150A	$MgCl_2 + 2Mg$	50	$MgCl_2$, MgO	Oxygen Contamination
134	$AlF_3 + 8Al$	30	AlF_3, Al	No Reaction
145	$AlF_3 + 8Al$	50	AlF_3, Al	No Reaction
135	$\alpha Al_2O_3 + 4Al$	30	αAl_2O_3, Al	No Reaction
147	$\alpha Al_2O_3 + 4Al$	50	αAl_2O_3, Al	No Reaction
153	Al + P (red)	30	Al, P_{Red}, trace Al_2O_3	No Reaction, Slight Contamination
146	Al + P (red)	50	Al, P_{Red}, trace Al_2O_3	No Reaction, Slight Contamination
136	$Mg + 2P$	30	MgO	Oxygen Contamination
154	$Mg + 2P$	50	MgO, P	Oxygen Contamination
137	$MgF_2 + 2Mg$	30	MgF_2, Mg	No Reaction
149	$MgF_2 + 2Mg$	50	MgF_2, Mg	No Reaction

Note 1 - The high pressure phase is designated, δAl_2S_3.

The product of the initial screening experiments contained unreacted aluminum and a compound of the same d-spacings of the As stabilized Al_2S_3; this high pressure stabilized phase was designated δ-Al_2S_3. The latter was subsequently prepared at 875°C and 30 kilobars for 10 minutes from $4Al + \alpha Al_2S_3$, αAl_2S_3 and $3Al + 2S$. Products from the Al_2S stoichiometry were generally gray and two phases were distinctly observed in polished metallographic sections. The color of δ-Al_2S_3 varied from reddish brown to pale yellow. The latter color was only observed for the product produced from the $3Al + 2S$. The compound is of course susceptible to hydrolysis to H_2S, but the orange color persists in material stored in a desiccator and the X-ray pattern is unchanged after two weeks. Synthesis reactions at 1000° and 1200°C at 30 kilobars also produced δ-Al_2S_3. The metastability of the high pressure polymorph, δ-Al_2S_3 was shown by the reversion of δ-Al_2S_3 to α-Al_2S_3 after heating in a sealed glass tube at 875°C for 30 minutes and cooling to ambient temperature.

Thus, the pressure stabilization of δ-Al_2S_3 renders the high pressure synthesis of a tetrahedral structure at the Al_2S stoichiometry more difficult. Ternary systems containing Al_2S and a tetrahedral promoting agent are unknown.

System: $MgCl_2 + 2\ Mg = Mg_3Cl_2$

Oxygen contamination resulting in the formation of MgO prohibited a complete examination of this system with the present equipment. Magnesium metal is particularly sensitive to contamination from entrapped oxygen gas. No further experiments were performed for this system.

System: $AlF_3 + 8\ Al = Al_3F$

No reactions were observed in the screening experiments at 30 and 50 kilobars. Subsequent synthesis attempts at 50 kilobars employing increased temperatures of 1200° and 1500°C lead to the apparent synthesis of a needle-like precipitate which proved to be a reaction product of the boron nitride container material. The AlF_3

starting material persisted unchanged after the reactions at 1200° and 1500°C. No other experiments were performed.

System: $Al_2O_3 + 4\,Al = Al_2O$

No reactions were observed in the screening experiments at 30 and 50 kilobars. The high temperature reaction of aluminum with the boron nitride liner found in the Al_3F system precluded the use of higher reaction temperatures in the present system. A ternary phase, Al_2CO, is reported (26, 27) stable at one atmosphere in a tetrahedral structure hence, the ternary stoichiometry was selected for study to ascertain the feasibility of preparing the known compound (Al_2CO) prior to any further synthesis experiments with the Al_2O stoichiometry. A discussion of the results of high pressure reactions involving Al_2CO and analogous ternary compositions is provided below.

System: $Al + P = AlP$

The Group III-V compound, AlP, is stable at one atmosphere in a zinc blende, B-3, structure. The volumetric calculations performed in the previous section showed that several of these stable compounds were characterized by positive volumes of formation (1). A negative volume of formation of -1.34 cm^3/g.atom was tabulated for the reaction:

$$Al + P_{white} \rightarrow AlP$$

but red phosphorous was used as a reactant in the present study and the pressure stabilization of black phosphorous is well known (32). The results of the screening experiments demonstrated that the AlP compound could not be prepared at 875°C and 30 kilobars. Calculation of the volume of formation employing red and black phosphorous afforded $\Delta V_f(AlP)$ as + 0.59 cm^3/g.atom and +1.42 cm^3/g.atom, respectively, in agreement with the observed pressure destabilization of the compound AlP which is stable at one atmosphere. No further experiments were performed for this system.

System: $Mg + 2P = MgP_2$

Oxidation of magnesium to MgO was the principal reaction observed; the pressure stabilization of the more dense forms of phosphorous would also lead to destabilization of any compounds in this system. No other experiments were performed.

System: $2\ Mg + MgF_2 = Mg_3F_2$

No reactions were observed in the 875°C screening experiments. The previously encountered oxidation of magnesium by entrapped oxygen was not observed, but the anticipation of this undesireable side reaction precluded the examination of this system at higher temperaturer. Accordingly, no additional experiments were performed.

The combined results above demonstrate that many experimental problems as well as theoretical limitations must be considered in the use of the Group IV analogue approach as a basis for planning high pressure synthesis experiments. The limitations imposed by gaseous contaminants can be minimized by employing a rigorous degassing procedure followed by vacuum encapsulation in a suitable metallic container. The pressure stabilization of reactants such as phosphorous or of undesireable products such as δ-Al_2S_3 can not be avoided, but can be anticipated in certain cases.

In order to complement the experimental screening of the originally selected binary stoichiometries, a limited number of experiments were performed with ternary systems composed of a binary Group IV stoichiometry and a tetrahedral promoting agent, namely, carbon, silicon or germanium. The known ternary phases which contain the Group IV stoichiometric ratios shown in Table 14 through 16 are $MgGeP_2$, B_6SiN_2 (33) and Al_2CO. The volumetric prediction technique developed for Group III-V compounds (1) was used to calculate lattice parameters for these compounds by assuming a random mixing of carbon and oxygen in Al_2CO on the S

sites of ZnS in the wurtzite structure, similarly beryllium and silicon in $BeSiN_2$ and magnesium and silicon in $MgSiN_2$ on the Zn sites. Effective electronegativity differences were calculated by assuming

$$\Delta X\ (MgGeP_2) = \frac{2X_P - X_{Ge} - X_{Mg}}{2}$$

The combined results are provided in Table 19. It is significant to note that the relative stability of the zinc blende structure to the wurtzite structure for the ternary phases is favored by lower electronegativity differences, essentially $\Delta X \leq 1.0$ e.v.$^{1/2}$ as was also noted in the previous section for binary III-V compounds. The introduction of the tetrahedral promoting agent reduces the effective electronegativity difference of the stable ternary compounds as compared to the proposed binary stoichiometries. The agreement of the calculated and observed volumetric properties of the ternary tetrahedral structures provides additional confidence to the use of such techniques in systematic inorganic synthesis studies.

The ternary system chosen for high pressure synthesis studies include both isoelectronic and cross element pseudo Group IV analogues. The structural features of the former would differ from the latter as the tetrahedral promoting agent would have to form a pseudo solid solution with the binary ordered compound as opposed to the above model for Al_2CO which would be representative of the cross element pseudo Group IV analogues. The reactants and the experimental conditions and results are summarized in Table 20. A partial success was found in the synthesis of Al_2CO. Oxygen contamination leading to undesireable side reactions remains a problem for mixtures containing magnesium metal. The pressure stabilization of an undesireable product, δ-Al_2S_3, imposes limitations on the pressure synthesis of Al_2GeS. The introduction of the tetrahedral promoting germanium lowers the effective electronegativity difference from 1.0 e.v.$^{1/2}$ for Al_2S to 0.7 e.v.$^{1/2}$, thus providing increased relative stability of the proposed tetrahedral structure,

TABLE 19

STRUCTURAL FEATURES OF BINARY AND TERNARY GROUP IV ELEMENT ANALOGUES

Group IV Analogue			Structural Data for Ternary Analogue			
Binary	ΔX $(e.v.)^{1/2}$	Ternary	ΔX $(e.v.)^{1/2}$	Structure	Calculated	Observed
MgP_2	0.9	$MgGeP_2$	0.6	Zinc Blende	a_o=5.57	a_o=5.65 (28)
BeN_2	1.5	$BeSiN_2$	1.35	Wurtzite	a_o=2.93 c_o=4.75	
Al_2O	3.0	Al_2CO	1.50	Wurtzite	a_o=3.21 c_o=5.20	a_o=3.19 (33) c_o=5.09 (26,27)

TABLE 20

HIGH PRESSURE SYNTHESES FOR TERNARY GROUP IV ANALOGUES

Exp. No.	Reactants	Desired Product	Conditions			Identified Products	Remarks
			Temp. °C	Pressure kilobars	Time (min)		
182	$Al_2O_3 + 4Al + 3C$	Al_2CO	1600	30	10	$C, \alpha\text{-}Al_2O_3, Al_2CO$	Partially Successful
190	$Mg + Ge + P_2$	$MgGeP_2$	875	30	10	$MgGeO_3$, MgO	Oxidation
189	$2Al + Ge + S$	Al_2GeS	875	30	10	$\delta\text{-}Al_2S_3$, Al, Ge	No Reaction with Ge, Pressure Stabilized $\delta\text{-}Al_2S_3$ Formed
183	BN + Si	BSiN	1800	30	10	BN, Si	No Reaction
184	AlN + Si	AlSiN	1800	30	10	Si, $\beta\text{-}Si_3N_4$	Side Reaction
188	Mg + Ge + S	MgGeS	875	30	10	Ge, GeS, MgS	Side Reactions

but apparently pressure stabilization of δ-Al_2S_3 remains as controlling factor. Reactions employing a tetrahedral promoting element and an isolectronic Group IV analogue have been attempted in many high pressure synthesis experiments; the available results did not provide any indication of successful synthesis. Cursory examination of the results and discussions presented herein suggest that quite different mechanisms may be involved in the apparent stabilization of tetrahedral structures for cross element pseudo Group IV analogues than for isoelectronic Group IV analogues.

E. Summary

An experimental screening program was performed for several binary systems selected for high pressure synthesis on the basis of guidelines set forth by Hall and Compton who described a series of stoichiometries which are Group IV analogues and which should be favorable for the formation of tetrahedral structures. The examination of these binary stoichiometries lead to the rejection of several systems on the basis of known denser structures of the same stoichiometry. High pressure synthesis studies were not feasible in other systems as the presently available experimental techniques are not generally suitable for handling gaseous or extremely environment sensitive reactants. Examination of a selected number of binary systems did not provide any evidence of new materials synthesized at selected stoichiometries. A new high pressure polymorph was produced from a variety of reactant combinations containing aluminum and sulfur by reactions at 875°C for 10 minutes at 30 kilobars. The new material has a cubic structure and is designated δ-Al_2S_3 to distinguish this phase from α-, β- and γ-Al_2S_3 which are less dense and stable at one atmosphere. The experimental results showed that pressure stabilization of reactants, e.g. elemental phosphorous, and of products at different stoichiometries, e.g., δ-Al_2S_3 from Al_2S, and pressure destabilization of products, e.g., AlP are significant factors which should also be considered in the design of high pressure synthesis experiments.

A limited investigation of the role of tetrahedral promoting agents such as carbon, silicon and germanium in stabilizing the binary stoichiometries which are Group IV analogues showed that such elements do lower the effective electronegativity differences. Three of the binary Group IV analogue stoichiometries are found in ternary Group IV analogues which are tetrahedral. An attempt to stabilize Al_2S with Al_2Ge using high pressure reaction conditions was unsuccessful; the high pressure phase δ-Al_2S_3 was again formed.

IV. HIGH PRESSURE SYNTHESIS OF TRANSITION METAL CARBIDE COMPOUNDS

A. Introduction

One approach to the selection of suitable systems for high pressure synthesis studies is based upon the appearance of structural discontinuities in periodically related compounds. Boron nitride and boron antimonide represent structural discontinuities in the compounds which are formed by the elements of Groups III and V. All other III-V binary compounds are stable at one atmosphere in a tetrahedral structure either zinc blend, B-3 or wurtzite, B-4. This type of system selection has been previously discussed (1, 17). In particular, the occurrence of the discontinuity of the NaCl, B-1 structure in monocarbides, of the transition Group VI elements: Cr, Mo and W (9) relative to the monocarbides of Group IV: Ti, Zr and Hf and Group V: V, Nb and Ta lead to the choice of the Mo-C and W-C systems for earlier high pressure synthesis (17). The high pressure form of cubic molybdenum carbide, α Mo $C_{0.67+x}$ where $x \sim 0.1$ (17) probably has the same superconducting properties as cubic Mo $C_{0.67}$ ($T_c = 12.2^{\circ}K$) prepared by Toth, et al. (34). A stoichiometric cubic Mo $C_{1.0}$ has a reported (34) $T_c = 14.3^{\circ}K$. The complex hexagonal Mo $C_{0.67}$ has a reported (34) $T_c = 9.9^{\circ}K$. Earlier unpublished results (35) showed that the superconducting transition temperature of the high pressure phase is approximately $2^{\circ}K$ higher than that observed for the complex hexagonal Mo $C_{0.67}$.

Measurements of superconducting temperatures have been performed for many compositions of NaCl structures and β-W structures. Materials with these structures have the highest reported T_c values. Ternary and higher order alloys of these two structures display opposite behavior as regards superconducting

properties. Some ternary and higher order solid solutions of the NaCl structure display higher T_c than the binary constituents, e.g., nitrides of niobium have T_c value reported between 14.7° and 16.0°K while Nb $C_{0.3}$ $N_{0.7}$ remains superconducting up to 17.8° (36). The ternary alloys of β-W structures show the opposite effect. Extensive experimental investigation (37) of the superconducting properties of the NbN-NbC pseudo binary verified the earlier findings (36). The measured T_c for cubic NbC was 11.5°K.

A high pressure synthesis study was initiated in the Mo-C-N ternary to attempt to stabilize a NaCl, cubic phase material. The superconducting properties of the Nb-N-C system and of cubic Mo $C_{0.67}$ and Mo $C_{1.0}$ suggest that such a ternary phase material would have a superconducting transition temperature above 14°K.

B. Experimental

Starting materials used for these experiments are described in Table 21. Attempts to purchase stoichiometric Mo C and Mo N were unsuccessful. Oxygen, a common impurity in refractory metal compounds such as carbides, borides and nitrides, has been found to affect superconducting properties (37).

A series of high pressure experiments were performed with two Mo C_x stoichiometries to confirm previously established conditions for pressure stabilization of α-Mo $C_{0.7}$ (17). Subsequently, experiments were performed with Mo-N-C stoichiometries to define the conditions required for pressure stabilization of a single phase, NaCl cubic structure. X-ray diffraction and metallographic analysis were used to identify products. Reactions were carried out in the same system used in the other previous synthesis studies. The experimental conditions employed and the product characterization data are provided in Table 22.

TABLE 21

STARTING MATERIALS FOR HIGH PRESSURE SYNTHESIS IN Mo-C-N SYSTEM

Material	Source	Phases Identified* / Particle Size	Chemistry
Mo_2C	Cerac Inc.	αMo_2C / 5μ	O, 0.51; C, 5.9
C	Mallinckrodt (Reagent)	Graphite / -325 mesh	
Mo_2N	Cerac Inc.	Mo, Mo_2N / -325 Mesh	N, 4.0; O, 0.67; Mo, 95.7

*X-ray phase identification results based upon data in Reference 9.

TABLE 22

HIGH PRESSURE SYNTHESIS OF COMPOUNDS IN THE Mo-C AND Mo-C-N SYSTEMS

(all reactions quenched under pressure from temperature after 10 minutes)

Exp. No.	Reactants	Conditions Temp. °C	Conditions Press. k.bars	Product Characterization: Identified Phases	Product Characterization: Metallographic Features: As Polished	Product Characterization: Metallographic Features: Etched
141	Mo_2C+C	1800	30	$\alpha MoC, \gamma' MoC$	small amount of second phase in continuous matrix	apparent deformation twinning in matrix phase
160	Mo_2C+C	2000	30	$\alpha MoC_{0.7}, \eta MoC_{0.67}$	graphite plus single phase matrix	apparent deformation twinning in two-thirds of the matrix grains
158	Mo_2C+0.6C	2000	30	$\alpha MoC_{0.7}$, C	single phase with graphite at grain boundaries	apparent deformation twinning in one-half of the grains
159	Mo_2N+C	2000	30	$\delta MoN, \alpha Mo(C,N)_{0.7}$	platelet phase in continuous matrix phase	slip lines observed
167	Mo_2N+C	2000	50	$\delta MoN, \alpha Mo(C,N)_{0.7}$	platelet phase in continuous matrix phase	slip lines observed
165	Mo_2N+C	1800	30	$\delta MoN, \alpha Mo(C,N)_{0.7}$	platelet phase in continuous matrix phase	slip lines observed
166	Mo_2N+C	1800	50	$\delta MoN, \alpha Mo(C,N)_{0.7}$	platelet phase in continuous matrix phase and a segregated single phase area	some slip lines observed

TABLE 22 (CONT)

HIGH PRESSURE SYNTHESIS OF COMPOUNDS IN THE Mo-C AND Mo-C-N SYSTEMS

(all reactions quenched under pressure from temperature after 10 minutes)

Exp. No.	Reactants	Temp. °C	Conditions Press. k.bars	Product Characterization: Identified Phases	Metallographic Features: As Polished	Metallographic Features: Etched
170	Mo_2N+0.6C	2000	30	$\alpha Mo(C,N)_{0.7}$ *	single phase	only grain boundaries visible - no twinning - no slip lines
171	Mo_2N+0.6C	2000	50	$\alpha Mo(C,N)_{0.7}$ *	single phase matrix with gray phase at grain boundaries	only grain boundaries visible
168	Mo_2N+0.6C	1800	30	$\alpha Mo(C,N)_{0.7}$ *	single phase	slip lines observed
169	Mo_2N+0.6C	1800	50	$\alpha Mo(C,N)_{0.7}$ *	single phase	grain growth observed-grain markings noted but neither twinning nor slip lines found
226	Mo_2N+0.6C	1750	30	$\alpha Mo(C,N)_{0.7}$ * δMoN	difficult to polish	
227	Mo_2N+0.6C	1750	50	$\alpha Mo(C,N)_{0.7}$ * δMoN	difficult to polish	
228	Mo_2N+0.6C	1700	30	$\alpha Mo(C,N)_{0.7}$ * δMoN	two phase	slip lines observed
229	Mo_2N+0.6C	1600	50	$\alpha Mo(C,N)_{0.7}$ (multiple line splitting) Mo_2C	single phase	

*X-ray line splitting of cubic reflections observed for phases marked with an asterisk.

C. Discussion of Results

The experiments in the Mo-C binary system showed that compositions deficient in carbon relative to $MoC_{1.0}$ were necessary to produce single phase α-$MoC_{0.7}$ in agreement with earlier work (17). Etching of the cubic matrix phase produced extensive deformation twinning.

The first series of experiments in the Mo-C-N ternary were performed with the reactants in molar amounts corresponding to Mo_2N+C. The presence of free molybdenum in the Mo_2N starting material indicates that the Mo_2N+C mixture is slightly deficient in carbon and nitrogen relative to $Mo(N+C)_{1.0}$. Experiments at 30 and 50 kilobars with temperatures of 1800° and 2000°C produced two phases mixtures containing a cubic phase designated $\alpha Mo(C,N)_{0.7}$ and a hexagonal phase δMoN. The latter may also contain some carbon; the former is a pressure stabilized phase which had not previously been prepared. Etching of these structures produced extensive slip plane formation.

Reduction of the amount of carbon to the nominal Mo_2N+0.6C effected a successful synthesis of single phase cubic $\alpha Mo(C,N)$ at 1800° and 2000°C for 30 and 50 kilobars for 10 minutes. X-ray evidence of line splitting for cubic reflections suggest the possibility of incomplete chemical reaction due to the short reaction times and high pressures inhibiting diffusional processes. Reduction of the temperature to 1750°C produced two phase structures. One additional experiment was performed using the Mo_2N starting material employing conditions of 1800°C and 30 kilobars for 10 minutes. X-ray results showed γ-Mo_2N and Mo unchanged from the starting material. Hence, the carbon is necessary to adjust the stoichiometry and stabilize the cubic carbonitride.

The results obtained thus far demonstrate new cubic phase materials can be pressure stabilized and retained at ambient conditions. The oxygen content

of the starting materials was found to increase by about one per cent in the high pressure treatment. The feasibility of preparing the cubic structures in the Mo-N-C system has been demonstrated, but optimized material for superconducting property evaluations was not prepared. Application of the more vigorous degassing procedures cited in the previous section would produce material with minimal oxygen contamination.

D. Summary

A new high pressure stabilized phase was produced in the Mo-C-N system at 1800° and 2000°C and 30 and 50 kilobars and retained at ambient conditions. The new material has a NaCl, B-1 cubic structure and is deficient in carbon and nitrogen relative to a stoichiometric compound, $Mo(C,N)_{1.0}$. Refinement of experimental procedures employed in this study to include rigorous degassing procedures should produce materials with superconducting temperatures above 14°K.

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13 ABSTRACT

A phenomological analysis and correlation of available volumetric and entropy data was performed for III-V compounds. The results of these procedures were used in the design of high pressure synthesis experiments to attempt to stabilize and retain the compound BSb. Thermodynamic data were calculated for certain III-V compounds for which such data have not been measured. The experimental results for the study of the B-Sb system at 30 and 50 kilobars suggest that a miscibility gap occurs in the liquid phase which prohibits the synthesis of BSb although pressure stabilization of the compound is predicted. An experimental survey of selected chemical stoichiometries which are Group IV element analogues and hence according to Hall and Compton candidate systems for new tetrahedral materials was conducted at 30 and 50 kilobars and elevated temperatures. No new materials were found at the selected stoichiometries but a new pressure stabilized phase, αAl_2S_3 was synthesized. An investigation of ternary systems containing the binary Group IV element analogue combination and a Group IV element showed that tetrahedral structures can be stabilized in this way. Attempts to stabilize the Al_2S_3 stoichiometry with Ge to form Al_2SGe were unsuccessful. A new high pressure stabilized phase with a NaCl cubic structure was produced in the Mo-C-N system.

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