

THE SYSTEM Li_3BN_2 AT HIGH PRESSURES AND TEMPERATURES

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ABSTRACT

The system Li_3BN_2 was studied over the pressure and temperature range from 10 to 65 kb and 300-1900°C, respectively. The stability region of a quenchable high pressure modification, $\text{Li}_3\text{BN}_2(\text{W})$, was defined, and the data also suggest the possibility of another nonquenchable high pressure modification. $\text{Li}_3\text{BN}_2(\text{W})$ is the phase which appears to be in equilibrium with borazon (cubic BN) during growth of this phase from the system $\text{Li}_3\text{N-BN}$, and the P-T data obtained on the melting of $\text{Li}_3\text{BN}_2(\text{W})$ are useful for defining the growth conditions for borazon.

Introduction

Within the pressure-temperature space of the system Li-B-N is a volume in which cubic BN (borazon) is stable at high temperatures and pressures (1,2). One of the phases intimately associated with borazon when "quenched" from this system is the "complex" reported by Wentorf (2). One of the results of the present study is that this "complex" is a high pressure form of Li_3BN_2 . This paper is concerned with a study of the P-T conditions for stability of both the one atmosphere and the high pressure modifications of this compound. The results suggest the possibility of a second high pressure polymorph.

Experimental

Starting Compositions

Mixtures were made from Li_3N (Foote Mineral Co.) and BN

(graphite form, 99.9%, Gallard Schlesinger) in 1:1 mole ratio. Quench runs were made both with unreacted mixtures and with the one atmosphere 1:1 compound made by the reaction of the nitrides using the method of Goubeau and Anselment (3). The results were identical with either starting material because Li_3BN_2 forms readily in the high pressure cell during the heating process. Thermal analysis runs were made only with the one atmosphere form of Li_3BN_2 . Those making this compound should be cautioned about the strong exothermic reaction at 650°C associated with the formation of this compound, and the nitride mixture should be heated slowly (about $50^\circ\text{C}/\text{hour}$) through the temperature range $600\text{--}750^\circ\text{C}$.

Cells

All experiments were done in pyrophyllite-tantalum cells as shown in Fig. 1 using the "belt" apparatus (4). The tantalum tube (0.430" x 0.127" OD x 0.116" ID) is simultaneously the container and resistance heater and probably acts as a getter for hydrogen and oxygen from the decomposition of pyrophyllite. No evidence for nitrides or borides of tantalum was found. A flame test on a tantalum heater after a run shows that the lithium contamination, if any, is small.

Since there is a steep temperature gradient in the cell from ends to center, all results were based on material taken from a nearly uniform temperature region 1 to 2 mm high at the center of the cell. The separation of a homogeneous sample presents some problems.

Quench Run Procedure

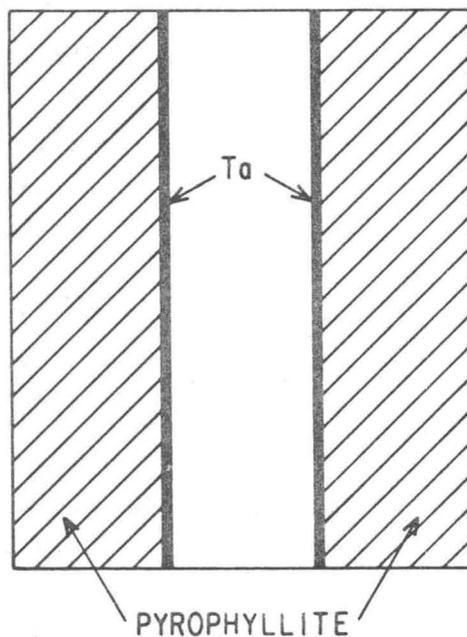
Most of the data on phase changes were obtained by the following procedure. Pressure was applied to the cell to the desired value and then the temperature was raised at a rate of about 400°C per minute. Temperature and pressure were held at the predetermined levels for 10-15 minutes, the power to the cell was switched off, and quenching to room temperature was accomplished in about 30 seconds with the pressure still applied. The pressure was then released.

Thermal Analysis Runs

Thermal analysis data were obtained by inserting a Pt-Pt/10-

Rh thermocouple into the one atmosphere form of Li_3BN_2 in the cell and plotting temperature versus time on a recorder and noting the break in the curve. The temperature was increased at a rate of about $200^\circ/\text{min}$ up to 1000°C , $400^\circ/\text{min}$ to 1300°C and $500^\circ/\text{min}$ above 1300°C ; the variable rate is primarily a function of rapid changes in the heater characteristics above 1000°C . Heat effects were observed for the melting of the high pressure phase. The thermal discontinuity upon melting is accompanied by a physical break in the thermocouple since the noble metals react

FIG. 1
Pyrophyllite-Tantalum
Cell for High Pressure
Studies Using the "Belt"
Apparatus



rapidly with the lithium in the melt. The data taken by this technique were reproducible within $\pm 25^\circ\text{C}$ and aided in the interpretation of quench data near the melting curve.

Measurement of Temperature and Pressure

The commonly accepted practice of using a pressure calibration made at room temperature and assuming some validity for this calibration at high temperatures was followed. The cell core, normally occupied by Ta and the sample, was filled with AgCl. Wires of Bi, Ba and Tl were inserted along an axial hole in the AgCl and were used as a part of a bridge circuit to detect the changes in resistance which occur in the materials at 25, 58, and 37 kb, respectively. The plot of these values versus psi on the ram was used to determine pressure.

Temperature measurement was based on the reproducibility of the relationship between temperature and the power requirements of the heater. To determine the watts versus temperature curves for the cell at various pressures, Pt-Pt/10Rh thermocouples were centered in the cell and the graphitic form of BN was packed around the bead. Corrections to the emf as a function of pressure were made (5), and these corrected curves were used in subsequent runs to determine the temperature.

Identification of Phases

The phases in the quenched sample were characterized by both optical and x-ray diffraction techniques. By both methods the two quenchable forms of Li_3BN_2 are easily distinguished. The agreement between our x-ray data for the high pressure form and that of Wentorf's "complex" (2) is sufficiently close to ascertain that the "complex" is in reality the high pressure modification of Li_3BN_2 . (Table 1). This phase is labelled $\text{Li}_3\text{BN}_2(\text{W})$ in Fig. 2. Our x-ray data for the one atmosphere form agree well with those of Goubeau and Anselment (3). (Table 1).

When observed with a petrographic microscope in transmitted light, the one atmosphere form of Li_3BN_2 appears as equant grains with refractive indices greater than 1.700. This phase appears to be biaxial negative with a large 2V. The refractive index of the high pressure form, $\text{Li}_3\text{BN}_2(\text{W})$, is also greater than 1.700, but this phase is uniaxial positive and is easily distinguished by its lath-like or prismatic habit and its parallel extinction. The higher refractive index is along the length of the laths (length slow) as determined with a Berek compensator. These crystals are also pleochroic with the stronger absorption parallel to the lower refractive index; i.e., at right angles to the length of the laths. Both the thermal and mechanical breakdown of this phase appears to take place preferentially along the plane perpendicular to the length of the laths, i.e. it has a preferential parting or weaker bonding perpendicular to the "c" axis. This combination of optical, mechanical, and thermal properties suggests a layer-like structure for $\text{Li}_3\text{BN}_2(\text{W})$.

As a first approximation it is reasonable to assume that the structure of Li_3BN_2 at one atmosphere would be closely related to

TABLE 1

X-Ray Data on Forms of Li_3BN_2

$\text{Li}_3\text{BN}_2(3)$ (1 atm. form)	Li_3BN_2^* (1 atm. form)	Wentorf's phase(2) (quenched from high pressure)	$\text{Li}_3\text{BN}_2(W)^*$ (quenched from high pressure)
$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0
3.81	m	3.73	10
			5.60 m
			3.60 s
3.50	s	3.47	50
		3.27	10
		3.50	mw
		3.34	mw
2.82	vs	2.78	100
		2.67	20
		3.25	w
		3.08	ms
2.63	s	2.63	30
		2.85	w
		2.78	s
2.24	w	2.22	5
		2.67	m
		2.56	mw
2.07	vs	2.07	15
		2.50	mw
		2.35	w
1.93	w	2.05	25
		1.91	5
		2.25	m
		2.15	ms
1.83	vw	2.07	vw
		2.03	m
		2.03	m
1.74	m	1.74	10
		1.96	w
		1.69	5
		1.92	w
1.64	vs	1.64	20
		1.85	mw
		1.73	mw
		1.68	vw
1.55	m	1.55	10
		1.64	m
		1.62	m
1.48	w		
		1.60	m
		1.53	m
1.42	w		
		1.50	vw
1.40	w		
		1.44	w
		1.41	w

* X-ray results from present study; data taken on GE x-ray diffractometer with $\text{CrK}\alpha$ radiation; s=strong; m=medium; w=weak; v=very. Additional weak lines at smaller d-spacings are found in published data from references (2) and (3).

that of Li_3AlN_2 and the other members of an isomorphous series (6) formed by substitutions for Al^{3+} and for N^{3-} . Since the structures of these compounds are based on an anti- CaF_2 lattice (i.e., N^{3-} in Ca^{2+} sites), compression along $\langle 111 \rangle$ could result in a layer lattice of hexagonal symmetry with layers of close-packed N^{3-} ions perpendicular to the hexagonal "c" axis.

The lath-like morphology of this form is best developed between 1000°C and 1400°C above 40 kb. Quenched runs from the liquid region above the melting curve of the high pressure form are characterized by fine-grained clusters of equant crystals, and the x-ray patterns differ somewhat in peak intensity from those of crystals quenched from the stability region of the phase. These differences appear to be related to a more random orientation obtained when preparing an x-ray slide with the material quenched from the liquid.

$\text{Li}_3\text{BN}_2(\text{W})$ is also markedly less soluble in water at room temperature than the low pressure form.

Results and Discussion

General

Our interpretation of the results is summarized in the P-T representation of Fig. 2 in which a large area of stability of $\text{Li}_3\text{BN}_2(\text{W})$ exists. Some aspects of this interpretation need amplification.

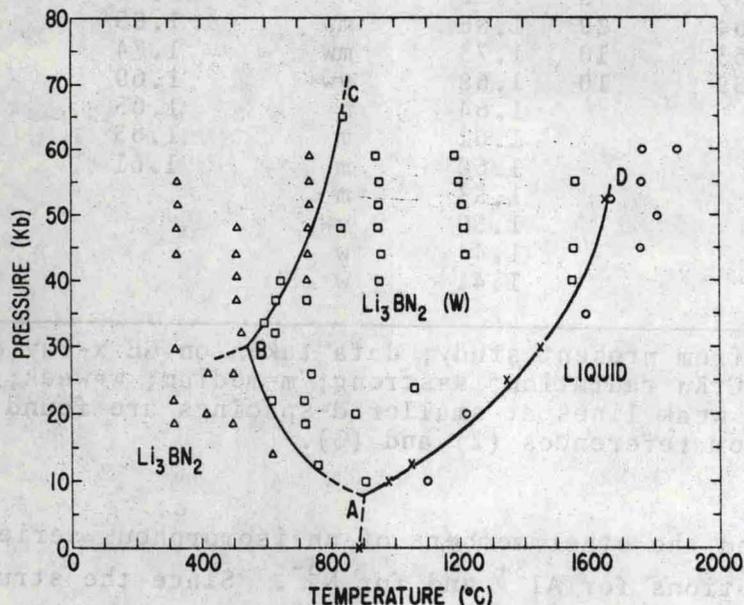


FIG. 2
P-T Diagram for the
System Li_3BN_2
Quench data indicated by Δ, \square, \circ ;
thermal analysis
data by \times

A clean separation of a homogeneous sample from the center of a cell in which a temperature gradient existed was sometimes difficult to obtain. Particularly near the P-T conditions where

a phase transformation is occurring, the sample that is examined may contain more than one phase. Since all starting mixtures were either the one atmosphere form of Li_3BN_2 or equimolar ratios of Li_3N and BN , any appearance of the $\text{Li}_3\text{BN}_2(\text{W})$ phase was interpreted as indicating its stability region had been reached. In this way the boundaries, AB and BC were established even though more than one phase may have been present in the sample that was examined. It is felt that the mixture is as much due to the gradient effects as it is to kinetic considerations.

In general the reversibility of the reactions indicated by the univariant lines was not established. No conversion of the $\text{Li}_3\text{BN}_2(\text{W})$ phase to the one atmosphere form was found when the former was held at 550°C and 55kb for 30 minutes. Partial conversion was found when the high pressure form was heated at 700°C in nitrogen at one atmosphere for 5 hours.

Possibility of a Second High Pressure Form of Li_3BN_2

The phase quenched from the P-T area on the low temperature side of the AB and BC boundaries was always the low pressure form of Li_3BN_2 . We interpret the discontinuous nature of this boundary to mean the existence of yet another high pressure form. If this is true, the phase transformation between it and the normal one atmosphere form must be of the displacive type involving only small structural changes that cannot be quenched under the conditions used. There is no observable difference between products quenched from above and below the discontinuity as determined from petrographic examination. The reality of this phase change will have to be explored using high pressure x-ray techniques. There was no obvious change noticed optically in a single experiment in which the one atmosphere form was pressed between two diamond anvils at room temperature to the limit of a diamond anvil apparatus (7).

The structure of Li_3AlN_2 also provides a basis for considering a reversible phase transformation. In that structure the Li and Al ions are arranged on small cubes equivalent to the arrangement of F^{2-} ions in the CaF_2 lattice (6). In Li_3AlN_2 these cubes are distorted, and a possible structural explanation for a reversible transformation may lie in a simple change in the form of the arrangement of the Li and B ions in Li_3BN_2 .

Melting Curve AD

The melting curve of $\text{Li}_3\text{BN}_2(\text{W})$ was better defined by the thermal analysis data than by quench runs because of difficulties with temperature control when a conducting melt forms. There is also some tendency toward decomposition of the high pressure phase when melted as indicated by the formation of a few percent BN (graphite form). We do not think this is true incongruent melting. It seems more likely to be caused by a small amount of decomposition caused by a slight loss of Li from the cell via reaction with the heater or by leakage through to other parts of the cell out of the reaction region.

Relation to the System Li_3BN_2 -BN

When $\text{Li}_3\text{BN}_2(\text{W})$ was held in the P-T range where borazon is stable, borazon did not form and it was found only when excess BN (graphitic form) was added. This behavior and the fact that $\text{Li}_3\text{BN}_2(\text{W})$ appears to be in equilibrium with borazon from melts with excess BN suggest that a eutectic relationship may exist between these two phases. With this assumption the data available from the melting curve of the $\text{Li}_3\text{BN}_2(\text{W})$ phase can be combined with data on the change in the cubic-hexagonal inversion temperature of BN as a function of pressure (8,9) and schematic isobaric sections can be constructed for the Li_3BN_2 -BN system at high pressure.

Summary

The P-T stability region of a high pressure polymorph of Li_3BN_2 has been defined. This phase does not form borazon but appears to be in equilibrium with borazon at high pressure and temperature when BN is present in excess over the 1:1 ratio in the system Li_3N -BN.

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References

1. R. H. Wentorf, Jr., U. S. Patent 2,947,617, August 2, 1960, assigned to General Electric Company.
2. R. H. Wentorf, Jr., J. Chem. Phys. 34, 809 (1961).
3. J. Goubeau and W. Anselment, Z. anorg. Chem. 310, 249 (1961).
4. H. T. Hall, Rev. Sci. Instr. 31, 125 (1960).
5. R. E. Hanneman, H. M. Strong and F. P. Bundy, GE R&D Center Report No. 68-C-367, December (1968).
6. R. Juza, K. Langer and K. von Benda, Angew. Chem. internat. Edit. 7, 360 (1968).
7. C. E. Weir, E. R. Lippincott, A. VanValkenburg and E. N. Bunting, J. Res. Nat. Bur. Stds. 63A, 55 (1959).
8. F. P. Bundy and R. H. Wentorf, Jr., J. Chem. Phys. 38, 1144 (1963).
9. K. Kudaka, H. Konno, ^{and} T. Matoba, ~~and~~ Kogyo Kagaku Zasshi, J. Chem. Soc. Japan, Industrial Chemistry Section 69, 365 (1966).