

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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