III. EXPERIMENTAL INVESTIGATIONS

A. TRANSFORMATION OF PREVIOUSLY KNOWN HIGH-PRESSURE PHASES

1. Cubic BN

Another new material which has been synthesized since the advent of man-made diamonds is the cubic form of boron nitride.

Boron nitride, isoelectronic with carbon, is known to exist in two modifications.[17] The hexagonal modification which has many properties similar to those of graphite is well known. A metastable modification is cubic and has the sphalerite structure of the diamond and many of the properties of the diamond including high hardness. At high pressure and temperature, this modification becomes stable relative to the hexagonal modification. The transformation is slow, however, except in the presence of some catalyst. The best catalyst appears to be Li_3N.

Lithium nitride was prepared by reacting metallic lithium with ammonia gas or dry nitrogen according to the following schemes:

$$3\ Li + NH_3 \rightarrow Li_3N + 1\text{-}1/2\ H_2$$

or

$$3\ Li + 1/2N_2 \rightarrow Li_3N$$

Both of these reactions go readily at moderate temperature, and both reactions were used to prepare catalyst for these runs. It was observed, however, that the material prepared by the second reaction was more stable in air atmosphere and did not appear to react as rapidly with the moisture in the air. Only this second material was used for the synthesis runs.

Samples were prepared by packing a layer of powdered hexagonal boron nitride in a graphite heater tube (rather than nickel which is attacked by the lithium nitride) sprinkling in crushed lithium nitride, adding another layer of boron nitride, packing and adding catalyst and repeating about five times. Molybdenum end discs closed the system. The sample was placed in the die with the usual pyrophyllite insulator.

Since these samples were not prepressed, the packed density was relatively low. This gave a large compression ratio at synthesis pressures which would have resulted in thermocouple failure, and thermocouples were therefore not installed. The temperature of reaction was not measured, but was estimated from the power input.

Five runs are summarized in Table III. After run No. 3, at an estimated pressure of 7×10^5 psi, examination of the sample revealed amber colored crystals which resembled boron cubic nitride. These crystals were too small to isolate for X-ray diffraction.

TABLE III

CUBIC BORON NITRIDE PREPARATIONS

Run No.	Pressure (psi)	Power (watts)	Results
1	7×10^5	No heat	Die cracked
2	7×10^5	1028	Too low temperature
3	7×10^5	1428	Amber colored crystals formed
4	7×10^5	1506	No change in hex BN
5	7×10^5	No heat	Die cracked