Supporting Information

Phase diagram analysis of high-pressure/high-temperature polymorphs of ammonia borane

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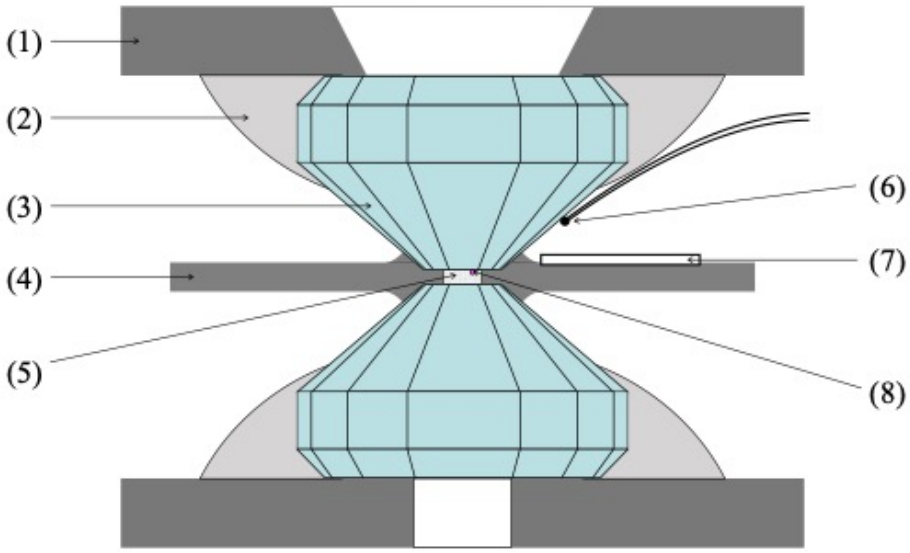
1. Configuration of the DAC and the external heating system

(a) Around the sample chamber



(b) Mao-Bell DAC and the band heater

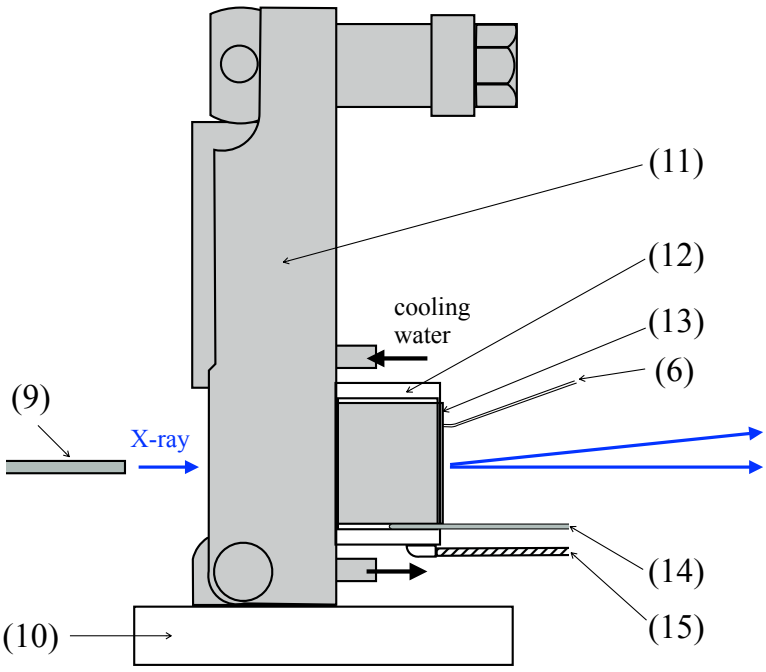
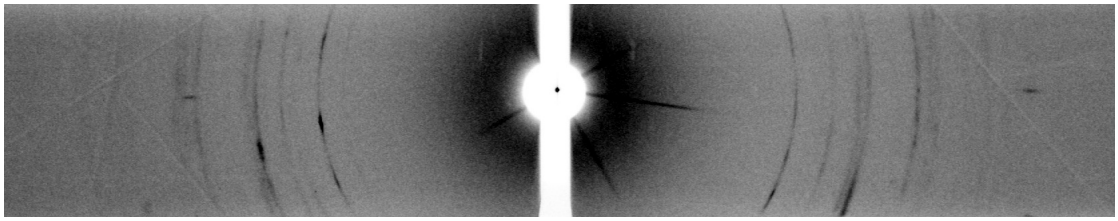


Figure S1. Schematic drawing of the configuration of the DAC and the external heating system. (1) WC-Co backing plate, (2) cement, (3) diamond anvil, (4) gasket, (5) sample

chamber, (6) ceramic coated K-type thermocouple for sample temperature measurement, (7) mica insulator, (8) ruby ball, (9) collimator, (10) ZrO_2 seat, (11) DAC lever-arm, (12) band heater, (13) Mao-Bell DAC, (14) sheathed K-type thermocouple for temperature control, (15) heater cable.

2. Examples of two-dimensional (2D) X-ray image

(a)



(b)

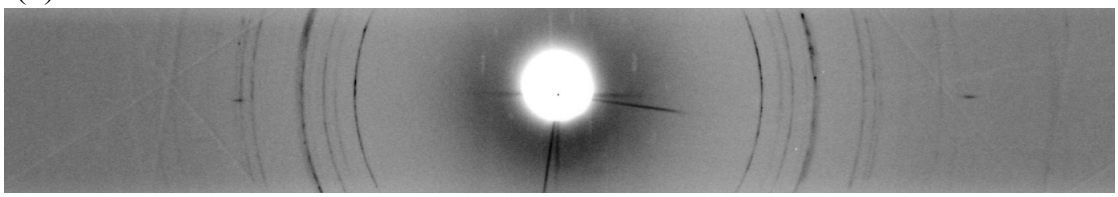


Figure S2. The 2D X-ray image of new high-pressure/high-temperature phase (HPHT2) obtained at (a) 17.5 GPa and 200°C, and (b) 10.1 GPa and 200°C.

3. Dihydrogen bonds formed by the H1n site in HPHT2 at 17.5 GPa and 200°C

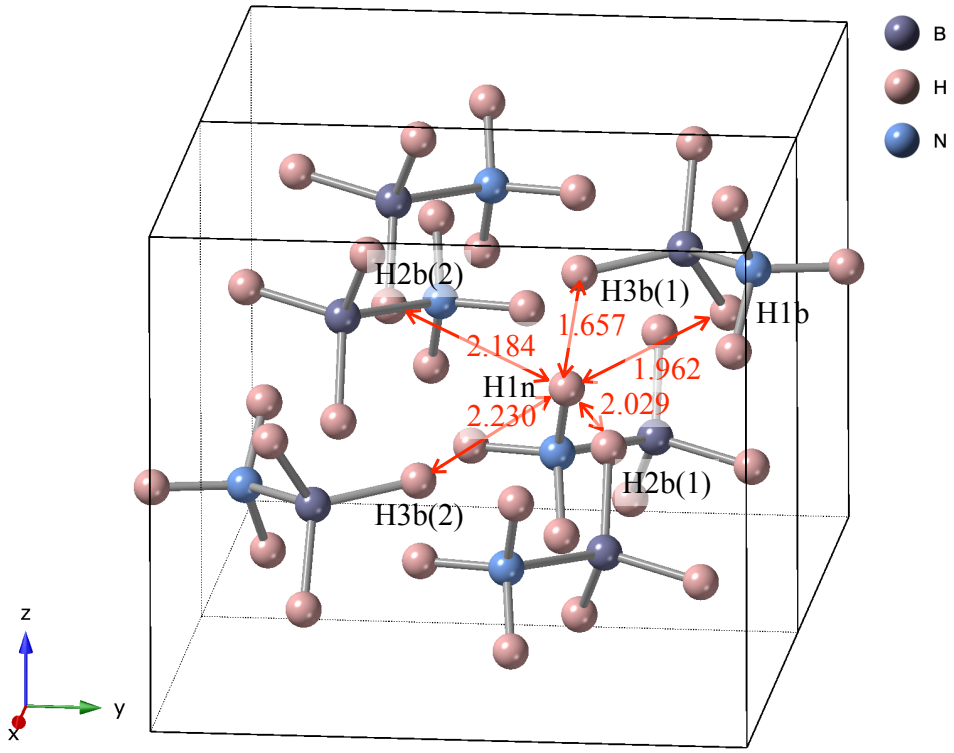


Figure S3. Illustration of the dihydrogen bonds that the H1n site forms with adjacent molecules in the crystal structure of HPHT2 at 17.5 GPa and 200°C. The purple, blue, and red balls represent boron, nitrogen, and hydrogen atoms, respectively. The numbers in red represent the H–H distance in Å.

4. Optical micrograph of HPHT3 at almost ambient condition

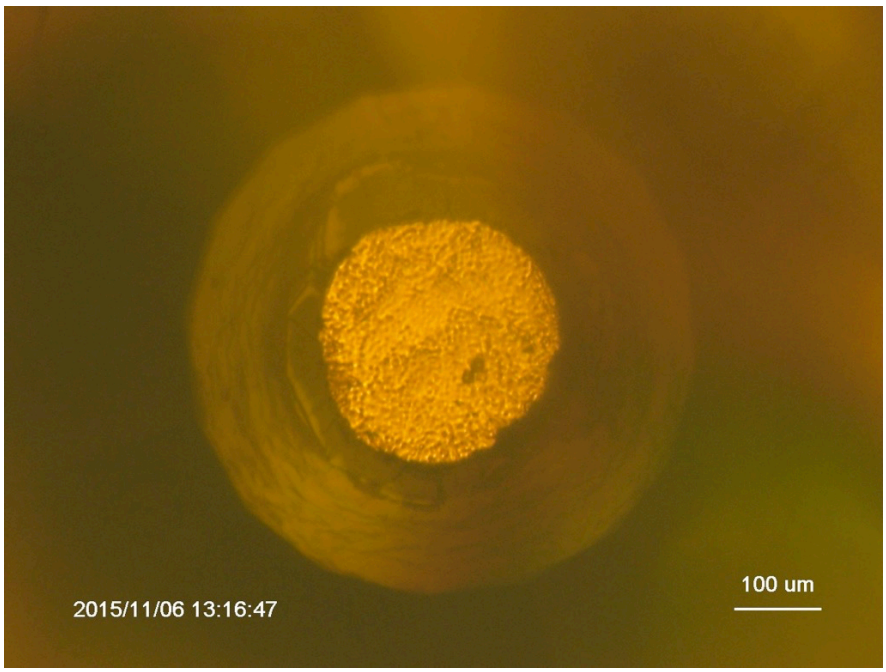


Figure S4. Optical micrograph of HPHT3 quenched to room temperature and decompressed to ~0.2 GPa. HPHT3 was formed from HPHT2 in decompression from 14.7 to 9.7 GPa at 200°C–251°C. Two 15-μm-diameter spheres visible in the sample are ruby balls.

5. Crystal structure of the second HP phase (HP2)

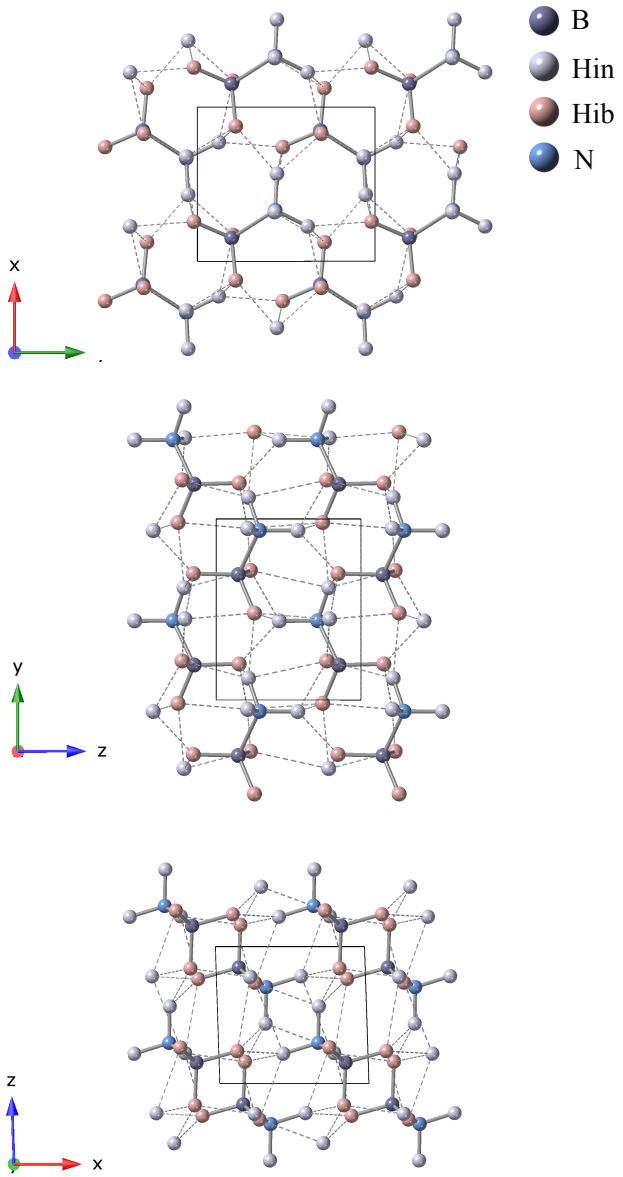


Figure S5. The crystal structure of HP2 viewed in *ab*-, *bc*-, and *ca*-planes. The purple, blue, gray, and red balls represent boron, nitrogen, nitrogen-bonded hydrogen, and boron-bonded hydrogen atoms, respectively. The dashed lines represent the dihydrogen bonds.