White Phosphorus: The Equation of State and Pressure-Induced Transitions

Joseph M. Zaug[a], Simon M. Clark[b], Martin Kunz[b], Raymond Jeanloz[c],
[a]*Lawrence Livermore National Laboratory*. [b]*Lawrence Berkeley National Laboratory*. [c]*University of California at Berkeley*. E-mail: zaug1@llnl.gov

We conducted angle dispersive x-ray powder diffraction measurements of hydrostatically compressed white phosphorous, P_4, to determine the equation of state and pressure dependant thermal expansion coefficients. We discovered a pressure-induced change in the powder pattern at ambient temperature. In addition, we have preliminary data that partially details the melting curve of P_4. Our condensed fluid state diffraction results will be used to deduce radial structure factor information. Our measurements were conducted on the new California high-pressure science observatory BL12.2.2 (http://xraysweb.lbl.gov/bl1222/HOME.htm) located at the Advanced Light Source at Lawrence Berkeley National Laboratory. An externally heated and membrane driven diamond anvil cell was employed to confine samples at controlled pressures and temperatures.

Ambient condition white phosphorus exists as a bcc crystalline solid with a I-43m space group. Upon increasing pressure, P_4 transforms at approximately 2.5 GPa to the orthorhombic black allotrope with a Cmca space group. The exact allotropic transition pressure depends most likely on the magnitude of shear forces present within the sample. For example, temperature annealing seems to extend the pressure stability of the bcc phase to nearly 6 GPa. When heated to modest temperatures, P_4 transforms, upon increased pressure, to what we describe as an amorphous black phase.

Keywords: phosphorus, equations of state, phase transitions