

High Pressure Chemistry of Phosphorus and Hydrogen

M. Ceppatelli^{1,2*}, D. Scelta^{1,2}, M. Serrano-Ruiz¹, K. F. Dziubek^{1,2}, G. Garbarino⁴, R. Bini^{1,2,3}, M. Peruzzini¹

¹ICCOM-CNR, Institute of Chemistry of OrganoMetallic Compounds, National Research Council of Italy, Via Madonna del Piano 10, I-50019 Sesto Fiorentino (FI), Italy

²LENS European Laboratory for Non-Linear Spectroscopy, Via N. Carrara 1, I-50019 Sesto Fiorentino (FI), Italy

³Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino (FI), Italy

⁴ESRF European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble (France)

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*e-mail: matteo.ceppatelli@iccom.cnr.it and ceppa@lens.unifi.it

The crystalline A17 layered structure of Phosphorus, commonly indicated as Black Phosphorus, was first high pressure synthesized by Bridgman back in 1914 [1] and is currently attracting a growing attention from the community of chemists, physicists and materials scientist due to the appealing properties of its monolayer counterpart named Phosphorene [2]. Recently, high pressure studies have reported the observation of a pseudo simple cubic structure (p-sc) in the phase diagram of Phosphorus up to 30 GPa. This observation significantly raises the pressure limit for the layered structures of P and opens new perspectives for their stabilization and functionalization, possibly leading to the recovery of new materials at ambient conditions [3-4].

On the other side, the experimental report of superconductivity in compressed PH₃ [5], with still no structural characterization and ascribed to the formation of different chemical species at high pressure in analogy to H₂S, has been so far stimulating experimental and theoretical efforts to investigate the stability of different systems containing Phosphorus and Hydrogen at high pressure which can be responsible for such behavior [6,7].

In this study we investigated the chemical reactivity of black Phosphorus and molecular Hydrogen under high pressure and high temperature conditions, which were generated using a membrane Diamond Anvil Cell (DAC) in combination with laser heating. The sample was probed by means of synchrotron X-ray diffraction at ESRF-ID27 and by FTIR and Raman spectroscopy at LENS. A detailed Raman analysis of the sample with micron sized spatial resolution was performed in different spectral regions.

The visual inspection of the sample after laser heating below the melting line and within the phase boundary of the A17 structure, clearly showed the consumption of Phosphorus. Correspondingly, the analysis of the experimental XRD and spectroscopic data indicated the formation of different reaction products containing P-H bonds, particularly PH₃ and H-functionalized Phosphorus fragments.

A further increase in pressure after laser heating was responsible for the crystallization of a solid product identified as a van der Waals compound made of PH₃ and H₂, whose crystal structure was accurately determined from single crystal data. The identification of this

compound, representing so far a missing piece, consistently fills a gap in the periodic table for Phosphorus, in agreement with analogous compounds reported in literature formed by the hydrides of Carbon (CH₄), Sulphur (H₂S), Selenium (H₂Se) and Iodine (HI) in the presence of H₂ [8-11]. Furthermore, the observation of this compound provides new experimental evidence for the formation of unexpected chemical species originating from the high pressure chemistry of Phosphorus and Hydrogen, possibly shedding new light on the high pressure superconductivity of Phosphorus hydrides.

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