

**A Study of an Amorphous to Amorphous Phase Transition in Red Phosphorus: The importance of using synchrotron x-ray diffraction and Raman spectroscopic results to constrain computationally derived amorphous structures**

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“Conclusive” evidence for the existence of pressure induced polyamorphic transitions only exists for two systems: liquid phosphorus and supercooled water. As part of a search for additional occurrences we discovered a third polyamorphic transition in amorphous red phosphorus (aRP). A high-pressure aRP phase was quenched at ambient conditions and is found to be denser than the original phase where intermediate-range order (IRO) exists. Inverse Monte-Carlo (IMC) analysis constrained by x-ray diffraction data (obtained from a unique ultra wide aperture diamond anvil cell) and Raman data shows that the transition begins with P<sub>9</sub> cages scattered throughout a 3-coordinate covalently bonded random phosphorus atom. At a specific pressure the periodic coherence of P<sub>9</sub> cage volume or perhaps the interstitial void space, weakens while the network structure uniformly collapses with hydrostatic compression. The high-pressure aRP phase exhibits a significantly less intense first strong diffraction peak (FSDP) thus indicating less IRO. Fragments of the original ambient pressure 3-coordinate structural framework exhibit similarities to Hittorf’s phosphorus, albeit with no long-range atomic order. Details concerning data collection, normalization, and analysis using IMC simulations will be presented together with results from computed changes in average atomic structural parameters (bond lengths, bond angles, distribution of coordination numbers) across the pressure-induced transition.

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