High-Coordinate Transition Metal Phosphides via High-Pressure Synthesis

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Abstract ()

Similar to oxides and nitrides, the transition metal–phosphorus system offers a wide variety of functional materials. For instance, Ni–P–based compounds have been extensively studied as electrocatalysts for the hydrogen evolution reaction [1]. Meanwhile, the Mo–P system hosts various binary phosphides with distinct chemical compositions, several of which exhibit superconductivity [2]. To overcome the experimental challenges associated with phosphorus, ultrahigh-pressure synthesis is highly advantageous, as it allows the reaction of highly volatile phosphorus within a closed system. This approach is exceptionally effective for synthesizing high-crystallinity phosphides, while also enabling the development of novel ultrahigh-pressure phases that are inaccessible under ambient pressure.

In this study, we explored new high-coordinate phases within binary systems of phosphorus and early transition metals (e.g., Nb, Mo, Ta, and W), with a particular focus on TMP_2 (*TM*: transition metal) at pressures up to approximately 50 GPa. A recent room-temperature compression experiment on MoP_2 demonstrated that the ambient-pressure phase remains stable up to 55 GPa, although an anomalous change in the axial ratio was observed at around 36 GPa [3]. In contrast, theoretical calculations predicted the emergence of a novel, highly coordinated phase under high-pressure conditions. This discrepancy suggests that additional thermodynamic factors, such as temperature, may be crucial for overcoming kinetic barriers to synthesize the new high-pressure phase. Consequently, we investigated the high-pressure phase relations across a wide pressure and temperature regime using a laser-heated diamond anvil cell.

The starting materials were synthesized via a solid-state reaction of stoichiometric mixtures of the constituent metal and phosphorus. The mixed powder was pelletized, sealed in an evacuated silica glass tube, and subsequently heated in a furnace at 600–800 °C for several tens of hours. The phase purity of the synthesized products was verified using powder X-ray diffraction (XRD) measurements. For the high-pressure experiments, the starting sample was pelletized again and loaded into the sample chamber, sandwiched between alkali halide layers (e.g., NaCl or KCl) that served as both a pressure-transmitting medium and thermal insulator. After compression to the target pressure at room temperature, the sample was heated using an infrared laser for a few minutes. The laser-heated sample was characterized via high-pressure in-situ optical microscopy, Raman scattering spectroscopy, and synchrotron powder XRD measurements.

Raman scattering measurements during room-temperature compression revealed that MoP_2 remains stable up to approximately 40 GPa, consistent with a recent study reporting its stability up to around 60 GPa. In contrast, laser heating at approximately 40 GPa led to the disappearance of the starting phase, yielding numerous new diffraction peaks that could not be indexed to any known phases. The intensity of these novel peaks increased when the starting composition was shifted toward the metal-rich side. By screening reproducible peaks from multiple experiments, the new phase was successfully indexed to a tetragonal symmetry. A similar tetragonal profile was obtained for the W–P system at comparable pressures. The lattice parameters of the tetragonal phases in both the Mo–P and W–P systems were highly similar, consistent with the comparable atomic sizes of Mo and W. Upon decompression from 40 GPa, the diffraction peaks gradually broadened, accompanied by an anomalous compression behavior; however, the high-pressure phase was successfully recovered to ambient pressure. The lattice parameters and axial ratios of this tetragonal phase strongly resemble those predicted by theoretical calculations. On the day of the presentation, the crystal chemistry of the novel early transition metal phosphides synthesized under high pressure will be discussed.

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