

Supplementary Information of Near-Ambient-Pressure A7 Phase by High-Pressure Quenching of Few-layered Violet Phosphorus and Black Phosphorus

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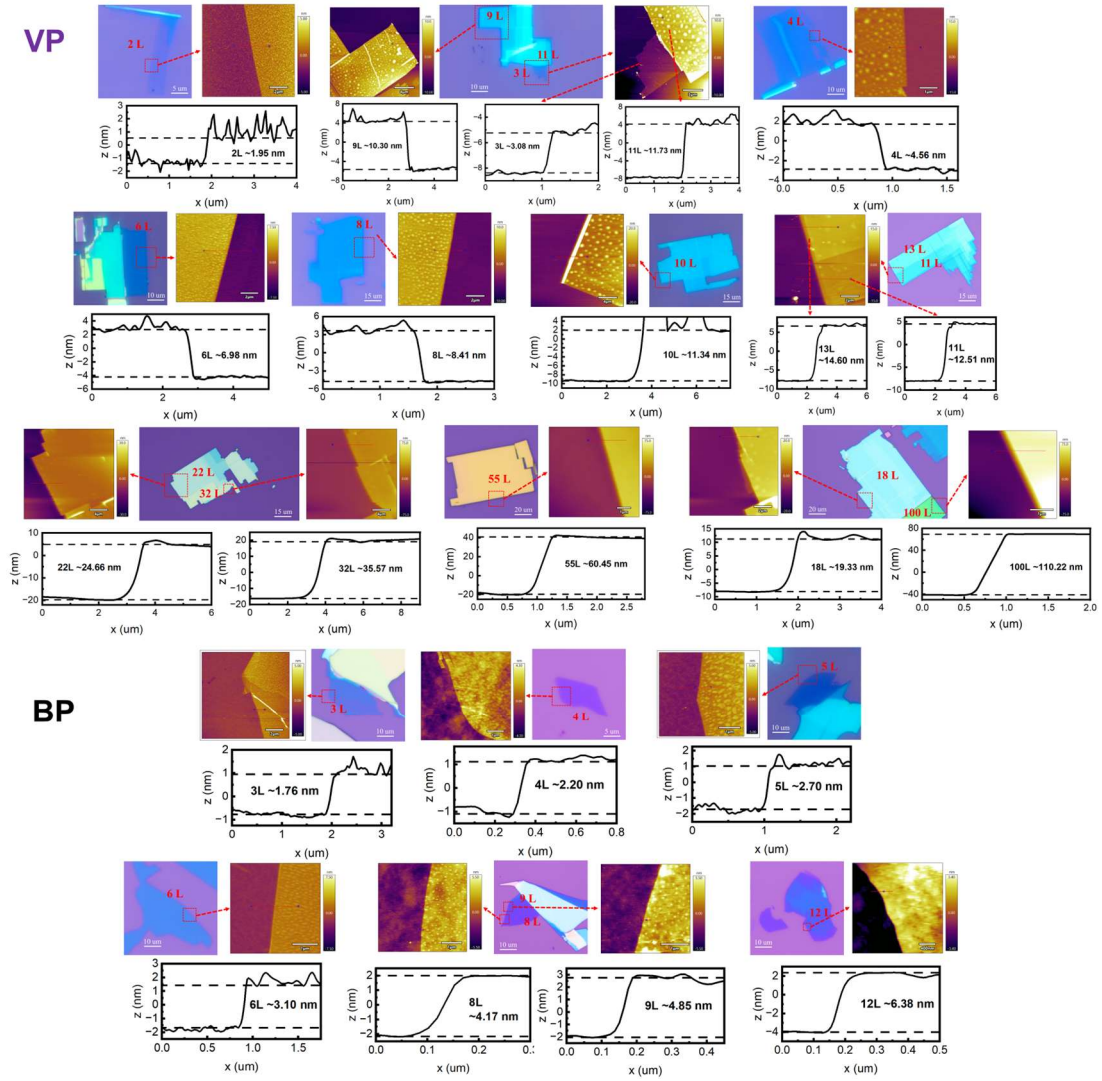


Figure S1. Optical images, AFM images on SiO₂/Si substrate and height profiles as indicated by the red lines of VP and BP samples.

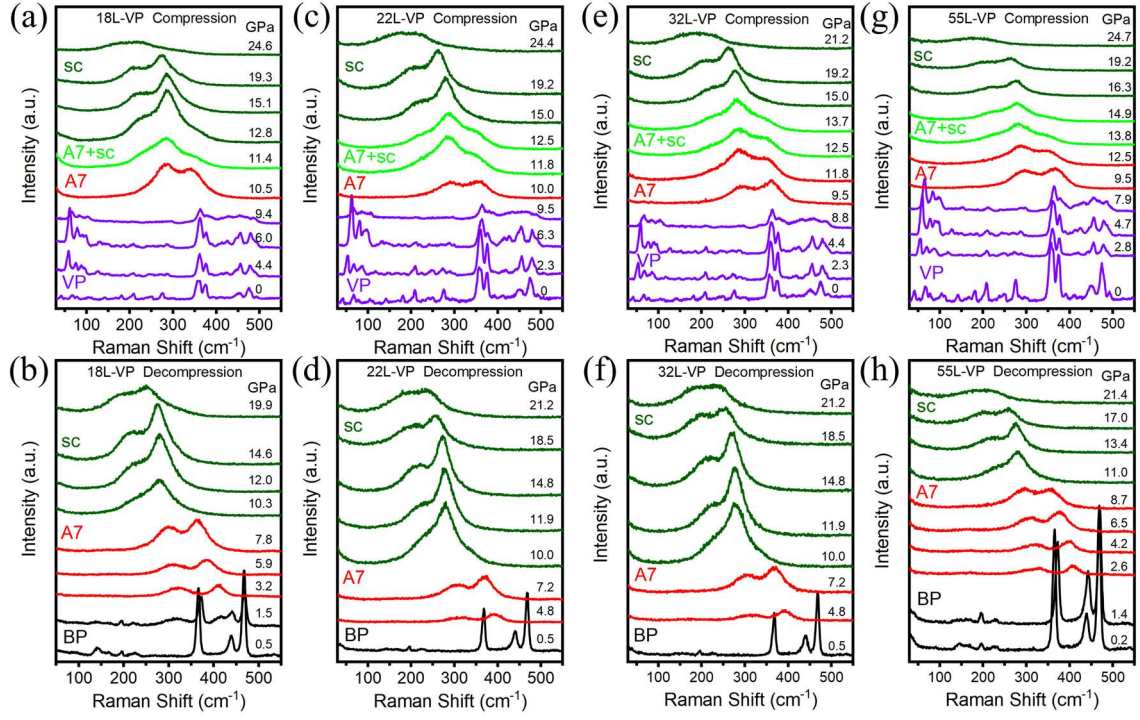


Figure S2. Pressure evolution of Raman spectra during (a, c, e, g) compression and (b, d, f, h) decompression: (a, b) 18L, (c, d) 22L, (e, f) 32L and (g, h) 55L VP, where different colored lines denote different phases.

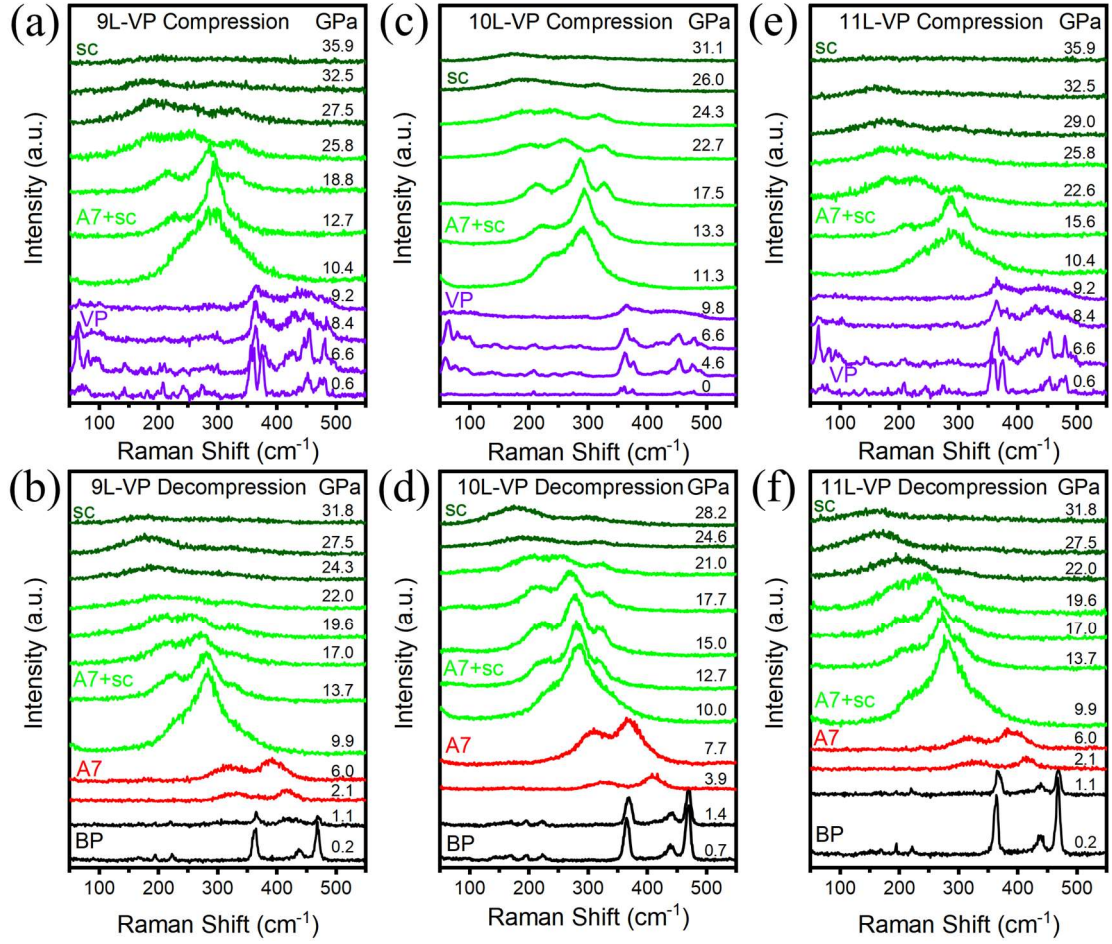


Figure S3. Pressure evolution of Raman spectra during (a, c, e) compression and (b, d, f) decompression: (a, b) 9L, (c, d) 10L and (e, f) 11L VP, where different colored lines denote different phases.

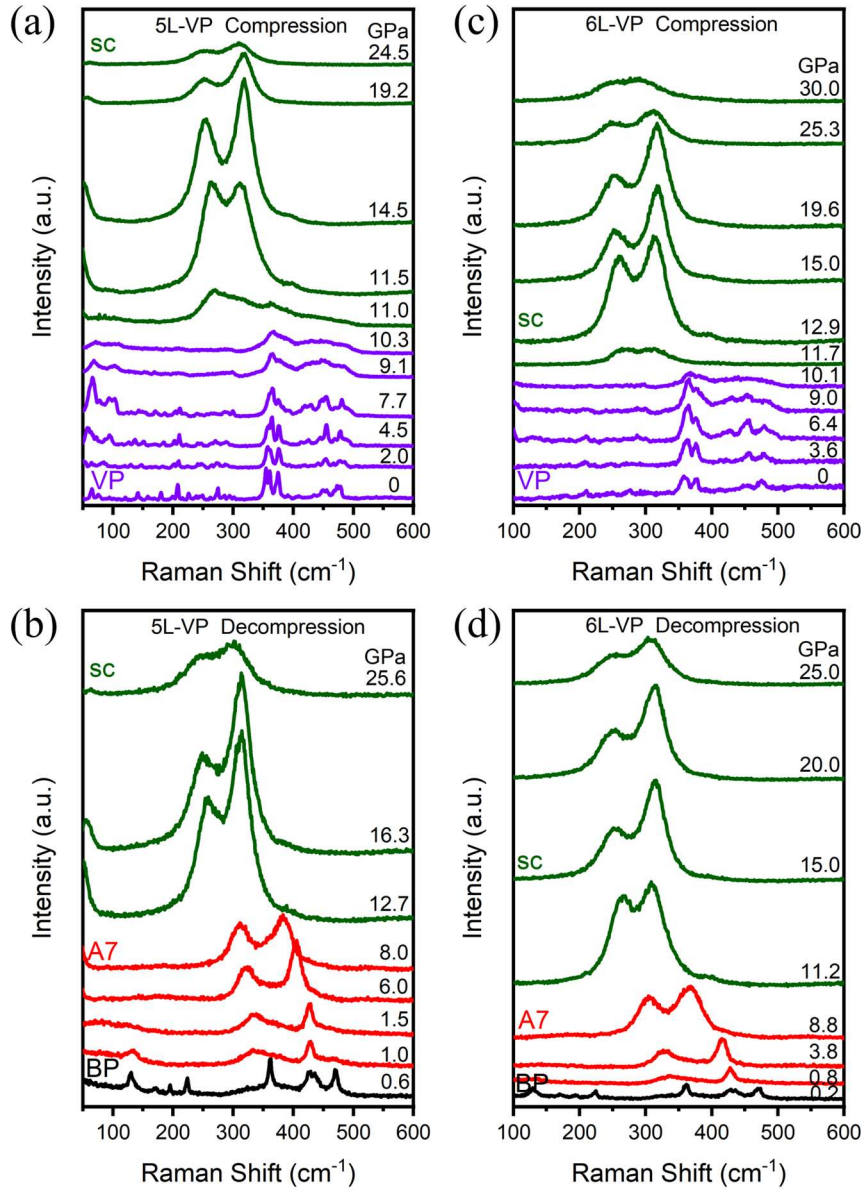


Figure S4. Pressure evolution of Raman spectra during (a, c) compression and (b, d) decompression: (a, b) 5L and (c, d) 6L VP, where different colored lines denote different phases.

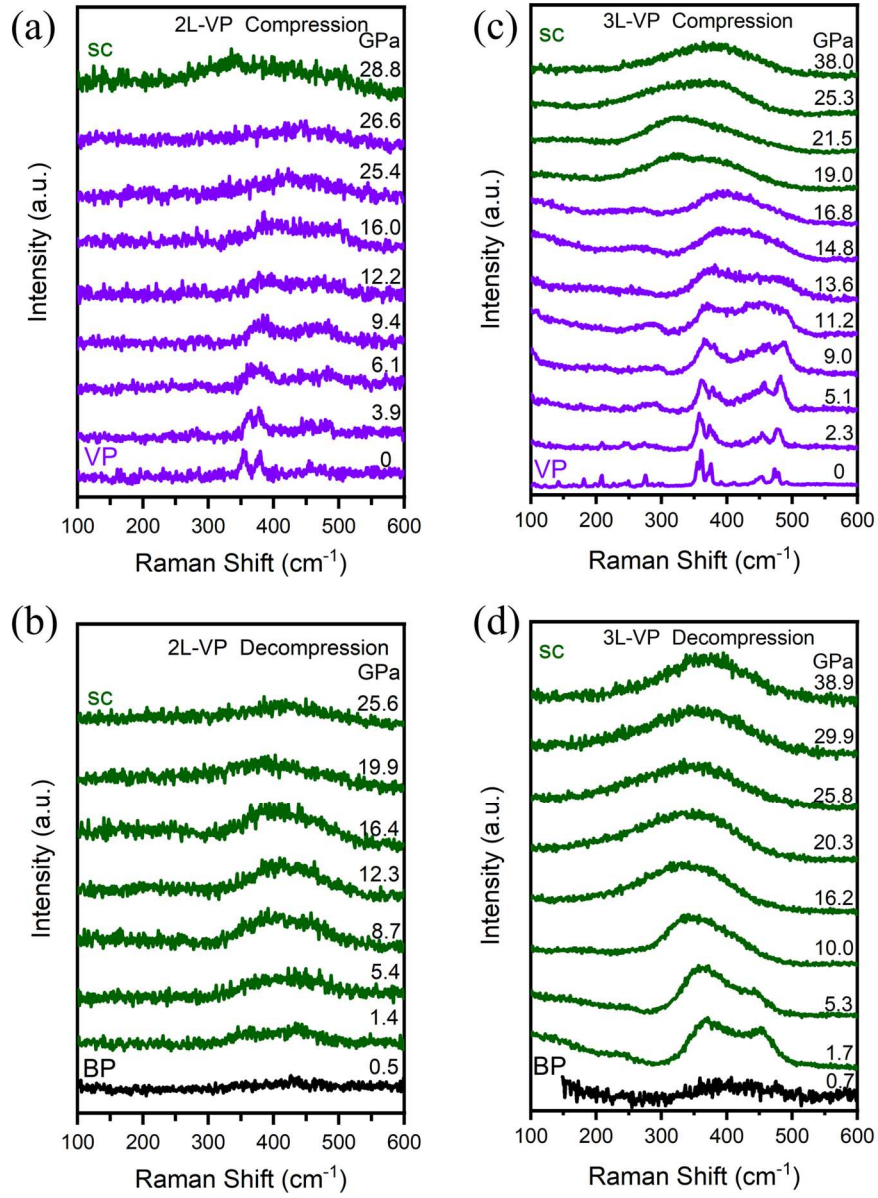


Figure S5. Pressure evolution of Raman spectra during (a, c) compression and (b, d) decompression: (a, b) 2L and (c, d) 3L VP, where different colored lines denote different phases.

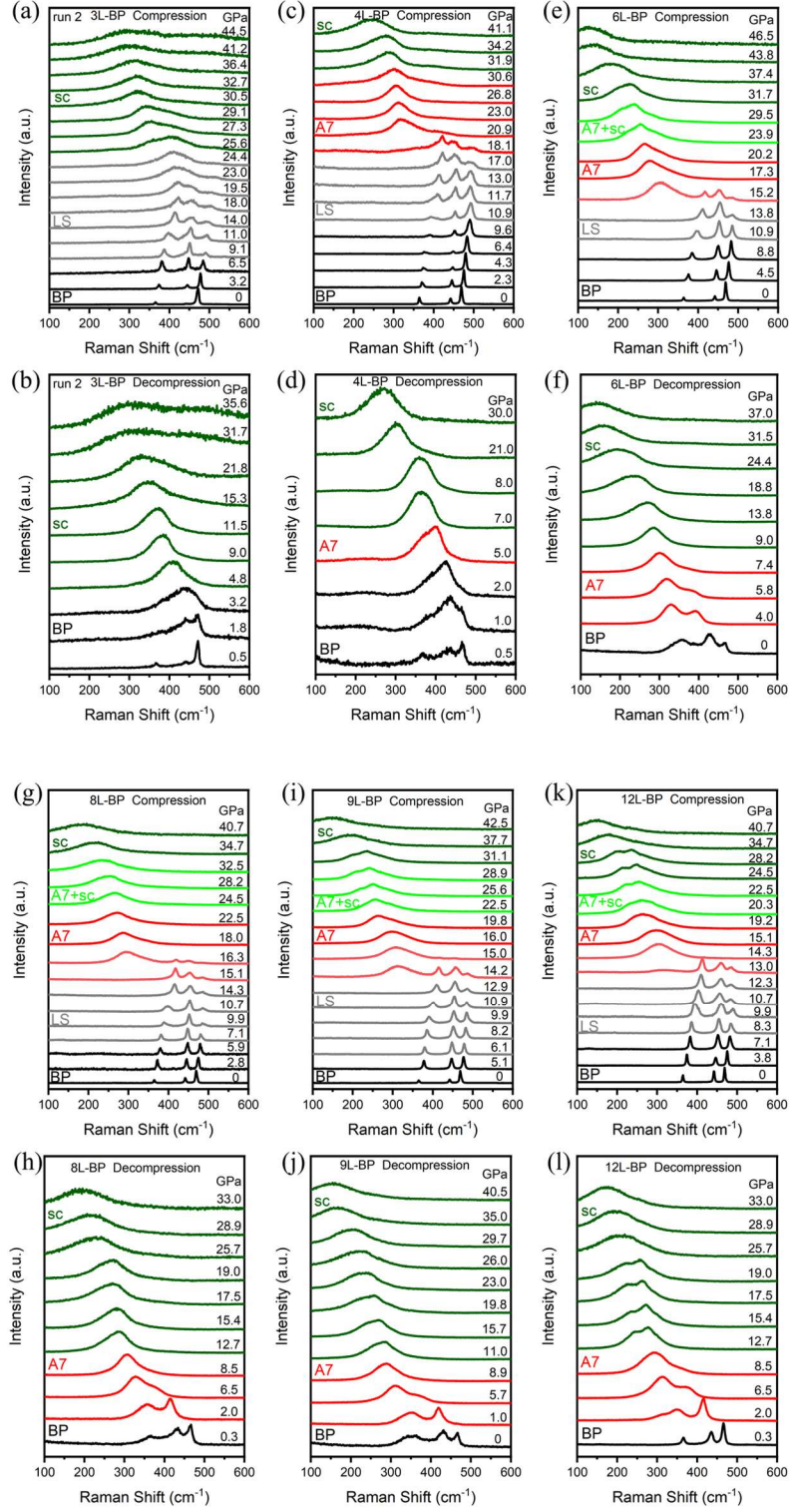


Figure S6. Pressure evolution of Raman spectra during (a, c, e, g, i, k) compression and (b, d, f, h, j, l) decompression: (a, b) 3L (run 2), (c, d) 4L, (e, f) 6L, (g, h) 8L, (i, j) 9L and (k, l) 12L BP, where different colored lines denote different phases.

Discussion on the Small Surface Energy Difference between VP-Derived BP and A7 Phases

Due to the approximately 50° angular difference between the planes of the A7 and BP phases during the high-pressure phase transition, the BP structure formed from the VP-derived A7 phase (~85° inclination angle) thus naturally retains some degree of inclination (the inset of Figure S7). This structural feature likewise leads to dangling bonds on surface atoms, thereby increasing the surface energy. Consequently, the difference in surface energy between the BP and A7 phases derived from VP is smaller than that between the A7 and sc phases. In the following discussion, evidence from Raman spectroscopy will be presented to confirm the inclined nature of the VP-derived BP phase.

The intensity of a Raman signal I is proportional to $\sum_j |\hat{e}_i \cdot R_j \cdot \hat{e}_s|^2$, where \hat{e}_i and \hat{e}_s are the polarizations of the incident and scattered light, respectively, and R is the Raman tensor for a given mode. When the normal direction of sample plane is tilted at an angle φ related to the incident light, the Raman tensor R is rewritten as $\tilde{R} = r^T R r$, where

$$r = \begin{pmatrix} \cos\varphi & 0 & \sin\varphi \\ 0 & 1 & 0 \\ -\sin\varphi & 0 & \cos\varphi \end{pmatrix}.$$

As shown in **Figure 2, S2-S4 and S7**, there are some Raman peaks around ~200 cm⁻¹ beside of the three characteristic peaks (A_g^1 , B_{2g} and A_g^2) of VP-derived BP phase. The peak at ~190 cm⁻¹ is identified as B_{1g} mode and peak at ~230 cm⁻¹ is identified as B_{3g}^2 mode¹. They are forbidden under backscattering in $\varphi=0$ (where the incident light

is $\begin{pmatrix} \alpha \\ 0 \\ \beta \end{pmatrix}$ and scattered light is $\begin{pmatrix} \alpha' \\ 0 \\ \beta' \end{pmatrix}$) due to their Raman tensor: $R(B_{1g}) = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$, $R(B_{3g}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}$. Thus, the existence of these peaks indicates the

existence of the inclination angle of VP-derived BP phase. In addition, there is no signs of these Raman modes near 200 cm⁻¹ in the BP phase in BP samples after decompression as shown in **Figure 3 and S6**.

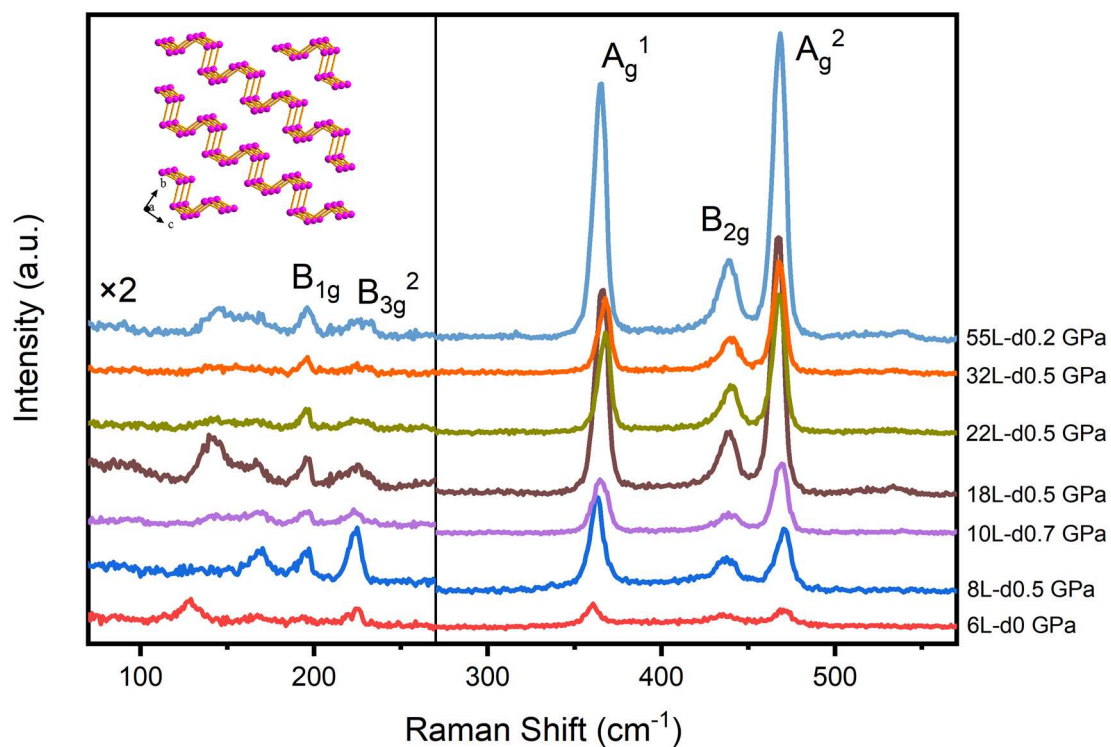


Figure S7. Raman spectra of the BP phase formed from VP after decompression, with an inset schematically illustrating this VP-derived BP structure. The intensity in the range of 80-280 cm^{-1} is scaled by a factor of 2.

References

1. Ribeiro, H. B.; Pimenta, M. A.; de Matos, C. J. S., Raman spectroscopy in black phosphorus. *Journal of Raman Spectroscopy* **2018**, 49 (1), 76-90.