Pressure-Induced Bandgap Engineering and Photoresponse Enhancing of Wurtzite $CuInS_2$ Nanocrystals

Meiyan Ye,[a] Yan Li,[a]* Ruilian Tang,[b,c]* Siyu Liu,[a] Shuailing Ma,[d] Haozhe Liu,[c] Qiang Tao,[a] Bin Yang,[c] Xin Wang,[a] Huijuan Yue,[e] and Pinwen Zhu[a]*

[a]State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun, 130012, China.

[b]School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, 130022, China.

[c]Center for High Pressure Science and Technology Advanced Research, Changchun, 130012, China.

[d]Deutsches Elektronen-Synchrotron DESY, Hamburg, 22607, Germany.

[e]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, China.

***Corresponding author:**

liyan2012@jlu.edu.cn, tangruilian626@cust.edu.cn, and zhupw@jlu.edu.cn

By using the Scherrer formula, $S = K\lambda(\beta\cos\theta)^{-1}$, where λ is the wavelength of the X-ray (1.5406(4) Å), K is a constant (0.9), θ is the Bragg angle of the diffraction peak, and β is the full width at half-maximum of the diffraction. The mean sizes of the as-prepared sample were estimated to be 21 nm for (100) peak and 20 nm for (110) peak, respectively.

The XPS results (Figure S2) show that the Cu $2p_{3/2}$ peak at 932.0 eV and Cu $2p_{1/2}$ peak at 952.0 eV can be assigned to the binding energy for Cu^+ in CIS, while the In $3d_{5/2}$ peak at 444.4 eV and In $3d_{3/2}$ peak at 452.0 eV are representative of In^{3+} in CIS. Two additional peaks at 161.4 eV and 162.5 eV match well with the S $2p$ binding energy for lattice S^{2-}.[1] Further analysis shows that Cu, In, and S elements each account for 28.90%, 23.96%, and 47.14%, respectively. The EDX analysis yielding an average mole ratio Cu : In : S = 27.42% : 24.64% : 47.94% , as shown in Figure S3 and Table S1. This result is consistent with the elemental stoichiometry determined by XPS within experimental error. The slight excess of Cu can be considered resulting from Cu nucleating faster than In and S.[2]

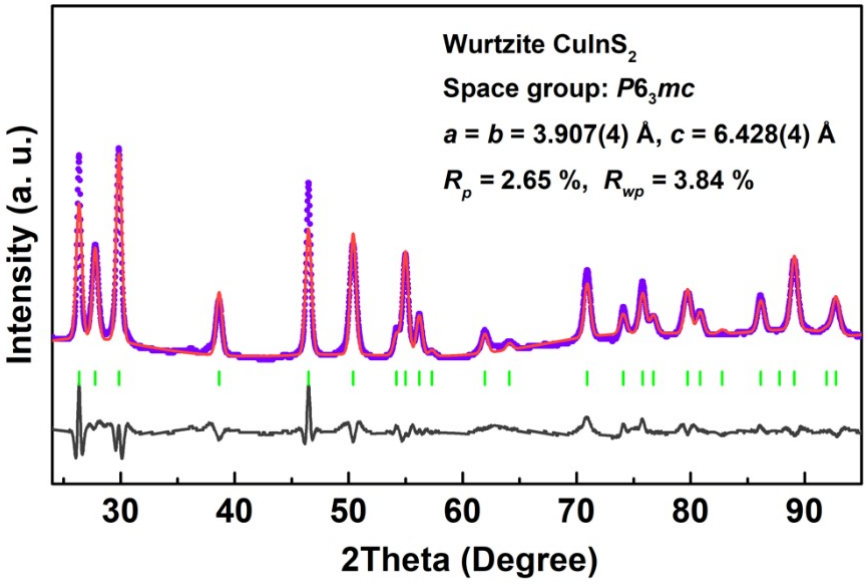

Figure S1. Rietveld refinement result of WZ-CIS nanocrystals at ambient condition. Purple circles: experimental data. Red line: calculated XRD profile. Black line: difference. Green bars: Bragg reflection positions.

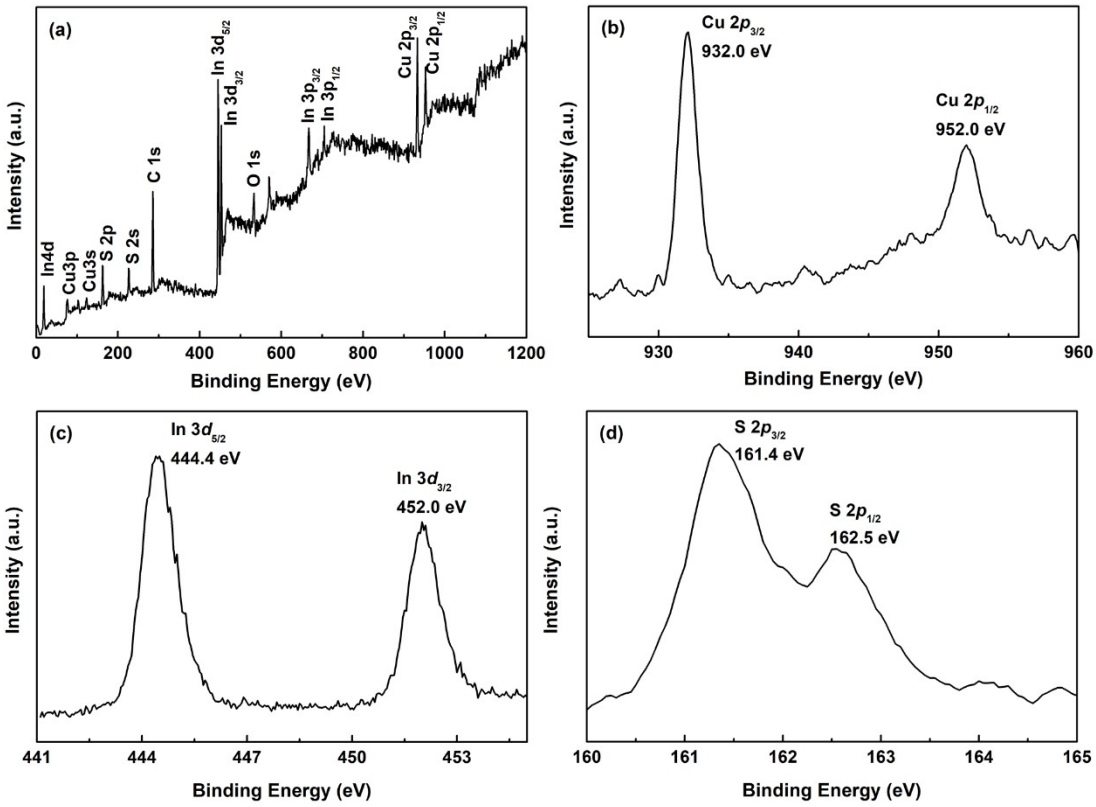

Figure S2. (a) XPS survey spectrum of WZ-CIS nanocrystals. Core level spectrum for (b) Cu 2*p,* (c) In 3*d*, and (d) S 2*p*.

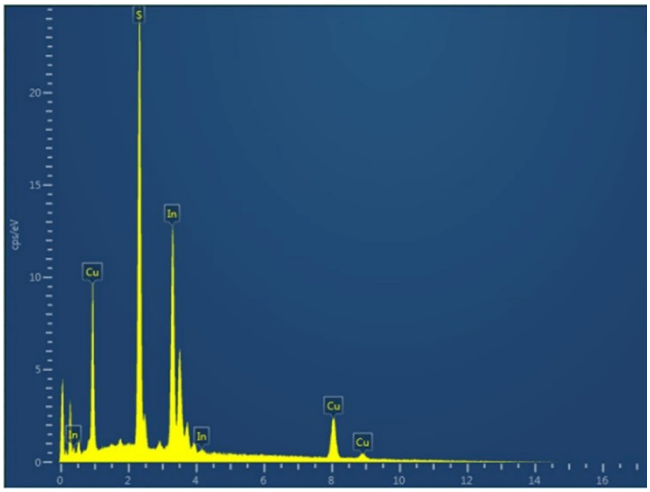

Figure S3. Representative EDX spectrum of the WZ-CIS nanocrystals.

Table S1. Composition of the WZ-CIS nanocrystals calculated by EDX spectra.

	Cu%	In%	S%
1	25.91	25.49	48.60
2	27.45	24.35	48.20
3	27.79	24.76	47.45
4	28.54	23.95	47.51
Average	27.42	24.64	47.94

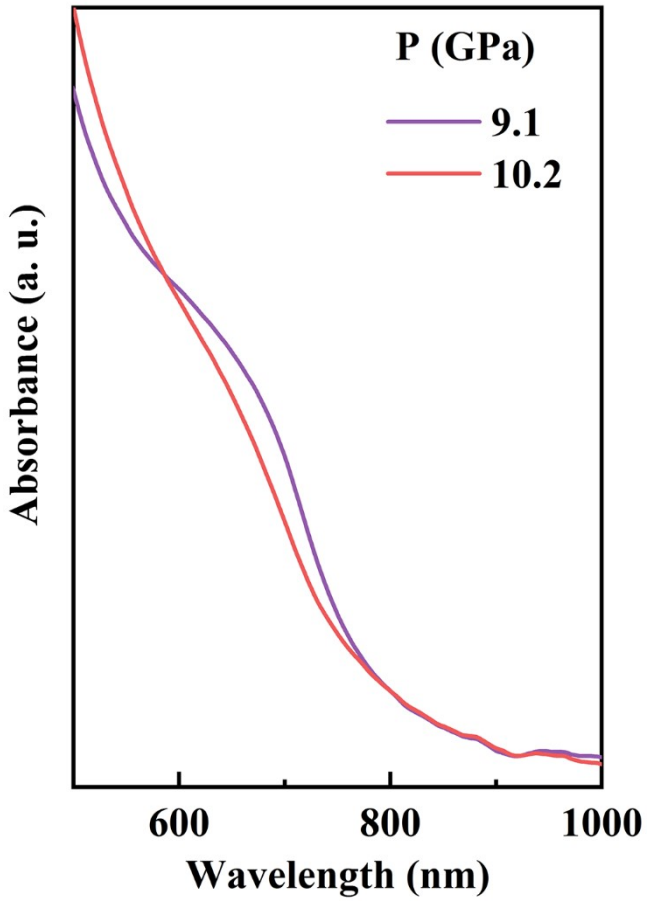

Figure S4. Absorption spectra of CIS at 9.1 and 10.2 GPa.

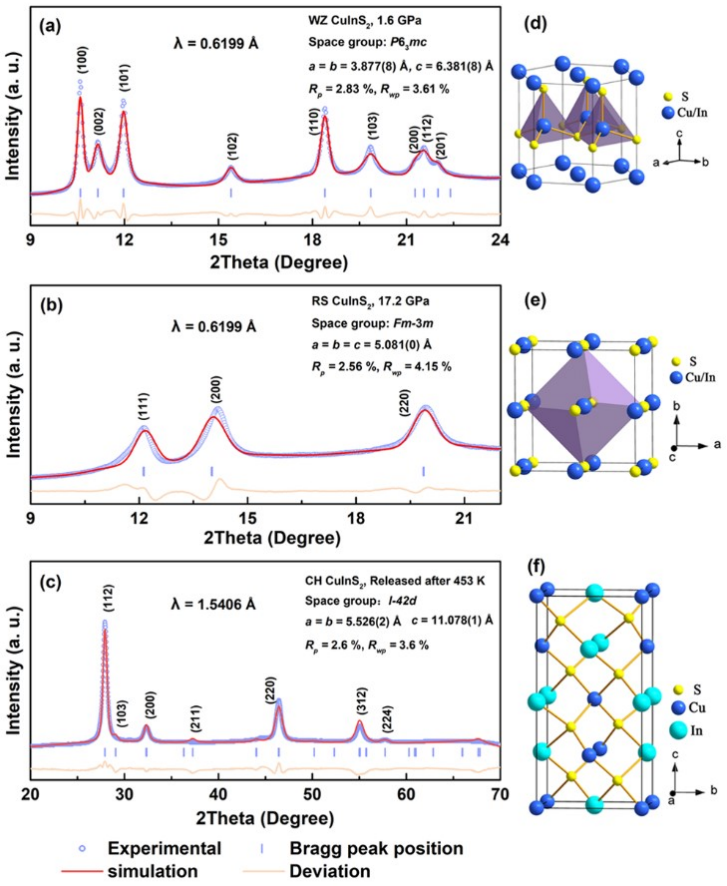

Figure S5. (a)-(c) Rietveld refinements of the XRD patterns at the indicated condition.

(d)-(f) The corresponding crystal structures of different phases of CIS.

Table S2. Crystal data and atomic coordinates of CIS in the WZ (hexagonal $P6_3mc$), RS (cubic Fm-3m), and CH (tetragonal I4-2d) phase.

Phase	P (GPa)	Cell parameters (Å)	Atom	Wyckoff	*x y z*
Hexagonal $P6_3mc$	1.6	a = 3.877(8) c = 6.381(8)	Cu/In S	2b 2b	(1/3, 2/3, 0.392) (1/3, 2/3, 0.004)
Cubic Fm-3m	17.2	a = 5.081(0)	Cu/In S	4a 4b	(0, 0, 0) (1/2, 1/2, 1/2)
Tetragonal I4-2d	Released	a = 5.526(2) c = 11.078(1)	Cu In S	4a 4b 8d	(0, 0, 0) (0, 0, 1/2) (0.214, 1/4, 1/8)

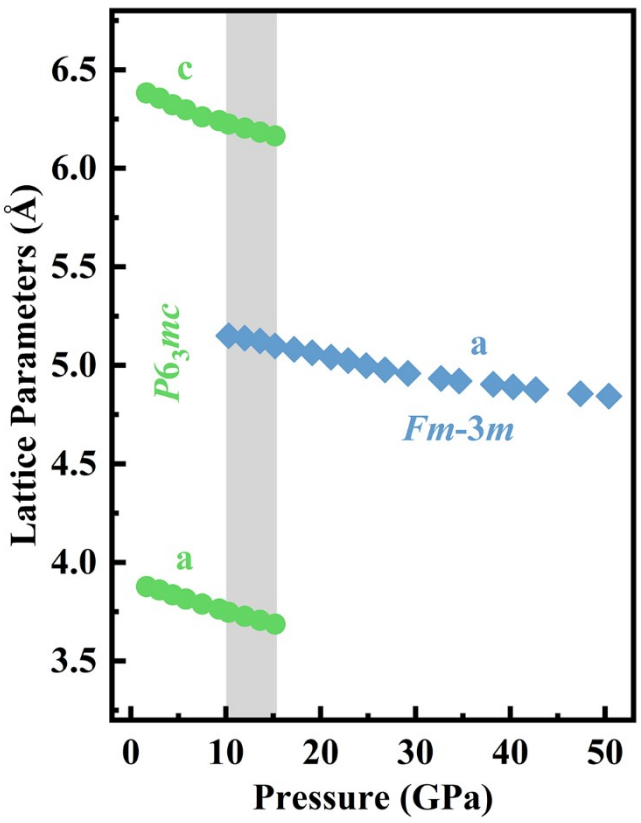

Figure S6. Pressure evolution of the lattice parameters.

References

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2 M. E. Norako, M. A. Franzman, R. L. Brutchey, *Chem. Mater.*, 2009, **21**, 4299-4304.