

Supplementary Information for

Enhanced piezoresponse in van der Waals 2D CuCrInP₂S₆ through nanoscale phase segregation

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1. $CuCrInP_2S_6$ composition determined by SEM-EDS

Table S1: A list of elemental atomic percentages of different CCIPS flakes obtained from SEM-EDS

Sample	Cu at%	Cr at%	In at%	P at%	S at%
1	4.71	5.24	13.34	19.92	56.79
2	4.11	5.78	13.44	19.67	57
3	3.62	4.63	13.70	19.94	58.11
4	4.92	4.51	13.11	19.84	57.62
5	4.28	4.53	13.60	20.03	57.56
6	3.94	4.68	14.02	20.28	57.08
7	3.38	4.96	13.97	20.32	57.37
8	3.94	4.92	13.57	19.91	57.67
9	3.54	4.48	13.89	20.18	57.91
10	3.31	5.59	14.82	20.22	56.06
11	3.18	5.25	14.66	20.40	56.52
12	3.06	4.96	14.63	19.94	57.42
Average	3.8325	4.96	13.89	20.05	57.30417
Standard Deviation	0.141	0.389	0.847	0.906	1.200

Table S1: EDS and elemental composition table and explanation. EDS determined stoichiometry of the compound used in this study is roughly $\sim Cu_{0.4}Cr_{0.5}In_1P_2S_6$ within the detection limit of SEM-EDS and considering any calculation errors. Composition is for estimation only; it may vary based on accuracy of measurement or on a different sample sourced from another similar bulk crystals.





Figure S1: **a-b**, large and small area SEM image of a random CCIPS flake, visualizing the domains and the domain boundaries with different greyscale contrast





Figure S2: **a**, Schematic showing SiN grid for TEM measurements. Samples were transferred after drop casting ethanol solvent containing dilute concentration of CCIPS flakes. **b**, A typical CCIPS sample on 30 nm thick SiN area where it is essentially suspended.





Figure S3: **a**, Large area AFM topography image of CCIPS sample shown in main text. **b-c**, Height profile along the purple and blue dotted lines in **a**, showing the variation in thickness of the sample. Thickness of the sample ranges from 30nm to 80nm.



a **Inphase**



c Inphase

b Quadrature



d Quadrature



Figure S4: a-b, Large Area and **c-d,** small area Inphase and Quadrature images of the same sample shown in main text. Minimum inphase and maximum quadrature was obtained for recording the maximum PFM amplitude. Inphase represents the component of the Piezo response signal that expands and contracts in unison or in phase with the applied electric field. Quadrature represents the component of the Piezo response signal that expands and contracts 90 degrees out of phase with the applied electric field.





Figure S5: **a**, Large area PFM image of the same CCIPS sample shown in main text and Fig S3a. **b**, Topography of bulk and multilayer CCIPS samples from main text. **c-d**, Small area topography and piezo response amplitude of the green box in **b**. Minimal effects of topographic cross-talk on piezoelectric signal of domain walls can be confirmed as very little correlation is observed between topography and piezo response is observed. Some of the domain boundaries are marked with white dotted line in **c** for visual aid and comparison.





Figure S6: AFM topography and PFM images of another bulk and multilayer sample.





Figure S7: Small area PFM amplitude, phase, inphase and quadrature of the sample shown in fig S6.





Figure S8: a, AFM topography of another ~80 nm thick sample. **b**, Corresponding PFM amplitude image showing the formation of domain patterns and boundaries. Piezo response has increased across the boundaries as witnessed in all samples. This also ensures repeatability.





Figure S9: a, Large scale PFM image from figure 2c in main text. **b**, Line Profile across the green dotted line in **a** showing the comparison of piezo amplitudes across domains and domain boundaries in comparison with substrate. As witnessed, there is negligible background noise or electrostatic contributions. **c**, Small area AFM topography of the sample shown in Fig 2e-f. **d**, Line profile across the dotted line in **c**, showing the domain patterns are obtained independent of topography.





Figure S10: PFM measurements using a stiffer cantilever: **a**, Topography and **b-c**, Corresponding PFM amplitude and phase images of a CCIPS flakes captured using a stiff cantilever (DDESP-FM-V2) with k=6 N/m. **d-e**, Line profile across the green dotted line in **b** and **c**, showing similar amplitude and phase variations across domain and domain variations.





Figure S11: **a-b**, AFM and corresponding PFM amplitude of a CCIPS flake showing the domain and boundaries. **c-d**, Small area PFM amplitude at +5V and -5V showing a closer look at few domain and domain boundary. **d-e**, Corresponding PFM images at +5V and -5V; application of a negative pulse predominantly flips the phase direction.



Piezoelectric Materials		d33 (pm/V)	Comments	Reference
	α-In ₂ Se ₃	0.34	Monolayer, PFM Measurements	1
Van der Waals Materials	3R-MoS ₂	0.27		
	3R-WS ₂	0.30	Bulk/Multilayer, DFT	2
	3R-MoSe ₂	0.45	Calculations	2
	3R-WSe ₂	0.35		
	MoSSe	5.248	Bilayer, DFT Calculations	. 3
	WSSe	5.319	Bilayer, DFT Calculations	-
	SnS ₂	5	Thin Layer, PFM Measurements	4
	CIPS	-5.12	Monolayer, PFM Measurements	5
	VSSe	4.92	Multilayer, First Principle	6
	g-C ₃ N ₄	1	Nanosheets, PFM Measurements	
	CCIPS	6.67	Multilayer and Bulk, PFM	This work
		measurements		
	Wurtzite GaN	2.8-3.7		7
	Wurtzite AlN	5.1		
III-V	InP	0.5	Bulk and/or Thin Films,	
Semiconductors	GaP	0.82	Experiential Deductions	8
	GaAs	1.54		
	InAs	0.72		
	ZrSeS	0.34		
Janus Materials	HfSeS	0.21		
	MoSO	-5.23		
	MoSeS	2.58	Bulk, DFT Calculations	9
	WSeO	-6.53		
	WSO	-2.86		
	WSeS	2.56		
	MoSTe	5.7	Multilayer, First Principle	

Table-S2: A summary of piezoelectric coefficients of common 2D piezoelectric. Note that most results are theoretical or compute calculations while some of them are experimental results.





Figure S12: **a**, Small area KPFM image of another bulk sample showing the formation of domains and change in work functions along the domain boundaries. **b**, Cross section line profile of surface potential along the blue dotted line in **a**.





Figure S13: Further examples of SHG mapping taken across different positions in different samples. All SHG images shows variation in intensity along the domain boundaries and domains.



Note-1: DFT Simulations

Ab initio calculations were performed using the Projector-Augmented Wave (PAW) method within the density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP).^{10,11} To capture the exchange-correlational effect, Perdew-Burke-Ernzerhof (PBE) within the Generalized gradient approach (GGA) was used for all the electronic structure and surface calculations. Grimme's DFT-D3 method¹² with Becke-Johnson damping function was implemented on the top of PBE to take into consideration van der Waals correction term. ¹³ Pseudopotentials Cu(3d¹⁰4s¹) Cr(3p⁶3d⁵4s¹) In(5s²5p¹) S(3s²3p⁴) and P(3s²3p³) recommended within the PAW method were employed for all the calculations.

The plane-wave cut-off energy was set to 520 eV. Ionic relaxation was performed using the conjugate gradient algorithm.¹⁴ The atomic positions were optimized until residual forces on each atom were less than 0.001 eVÅ-1, while the tolerance value for energy optimization was kept as 10-6 eV. A Γ -centered k-point mesh with density of $2\pi \times 0.01$ Å⁻¹ was selected to sample the Brillouin-zone (BZ) using the tetrahedron method with Blöchl corrections.¹⁵

CCIPS structure was simulated in the P_C phase within an enlarged $2 \times 2 \times 1$ supercell. To investigate the minimum energy migration pathway and sizes of *Cu* hopping barriers, we computed in and out-of-plane hopping barriers using the transition state nudge elastic band (NEB)¹⁶ calculations within the framework of DFT in conjunction with the climbing image NEB (CI-NEB),¹⁷ in which the highest activation energy image is driven up to the saddle point. The five transition images considered along the migration pathway in each of the three cases were optimized until the forces were less than 0.01 eVÅ⁻¹. Activation energy barrier (*E_A*) was calculated considering initial and final state of one of the *Cu* atoms in a plane and five transition states were accounted for the *Cu* atom to complete the site exchange. Formation enthalpy of the domain and boundary region with varying Cu vacancies (0%, 5%, 12%, 25%, 40%, Cu content and Cr content kept constant at 50% as indicated by EDX analysis) was calculated from using elemental ground state DFT energies and the total ground state energy of the CCIPS structure within a 8 × 1 × 1 supercell and is used to determine the stability of the domain and boundary region with varying Cu vacancies for optimized CCIPS structure was performed using Bader code¹⁸ from the Henkelman's Group.





Figure S14: Formation energy of CCIPS as a function of different Cu composition. Both domain and domain boundary have negative formation energy allowing them to co-exist at the same time with thermodynamic stability.





Figure S15: a, XPS spectra in the region of Cu 2p, Cr 2p, In 3d, P 2p and S 2p. XPS further proves the presence of all elements in the 2D CCIPS crystal. In addition, the oxidation states can be derived with good match with literature. **b**, XPS spectrum of carbon peak for reference. All XPS were corrected to the BE of C at 284.8 eV.







Note -2

XPS measurements were carried out to calculate the possible oxidation state of the elements to gain an insight on the charge neutrality of CCIPS. Measurements were carried out on exfoliated flakes of bulk and multilayer CCIPS with similar thickness on which PFM measurements were done. All BEs were corrected for surface charging by correcting the C1s line centroid (main peak, adventitious carbon or C–C, C–H) to a BE of 284.8 eV. It might be worthy to note, that there is



uncertainty on this is at least 0.2 eV because there is increasing evidence that the adventitious carbon signal is not constant on all surfaces.¹⁹ The photoelectron energy levels of *Cu*, *Cr*, *In*, *P* and *S* in shown in Fig S15. Cu:2P_{3/2} and Cu:2P_{1/2} peaks are centered at 932 ev and 952 ev, with no sub peaks or satellite peaks present, indicating the *Cu* cation is mostly of +1 valence.²⁰⁻²² Spectra for other elements are also typical and in accordance with previous reports. *Cr* 2p_{3/2} and *Cr* 2p_{1/2} peaks on the energy scale indicated a mix of multiple oxidation states while +3 remains the majority. For this particular element, the five multiplet splitting peaks are fitted to the envelope with half-widths of ~0.9 eV.^{19,22} Metallic nature of In can be supplemented by In 3d_{5/2} and 3d_{3/2} orbitals, with binding energies at 445.57ev and 453.5eV suggesting In^{3+} ions.²³ Both phosphate and Sulphur manifest 2p_{3/2} and 2p_{1/2} orbitals as expected, indicating +4 and -2 oxidation state respectively.²⁴⁻²⁷ However, Sulphur oxidation can also change in different octahedral to accommodate for *Cu* hopping.^{27,28}

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