Supplementary Information

for

High-refractive index and mechanically cleavable non-van der Waals $InGaS_3$

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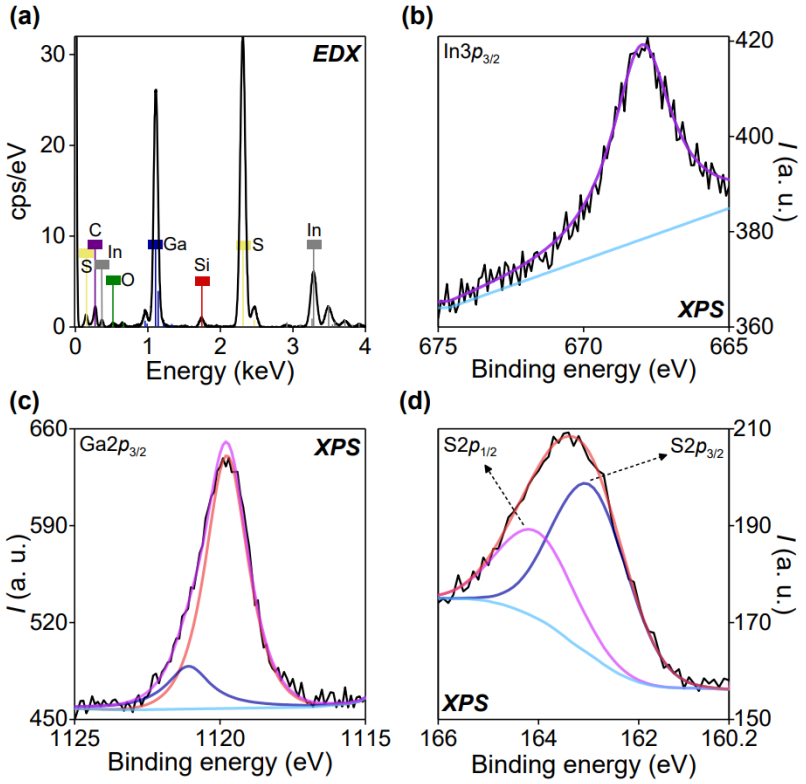
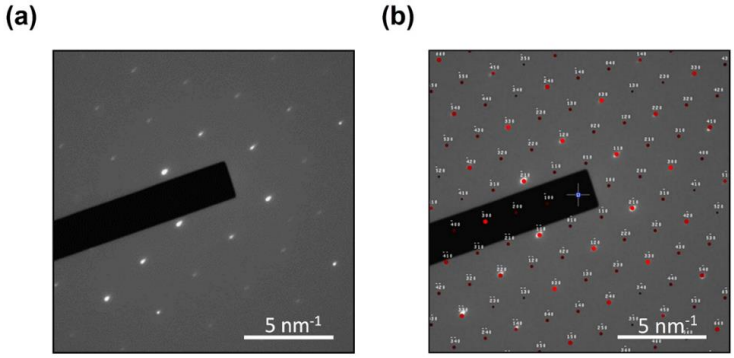
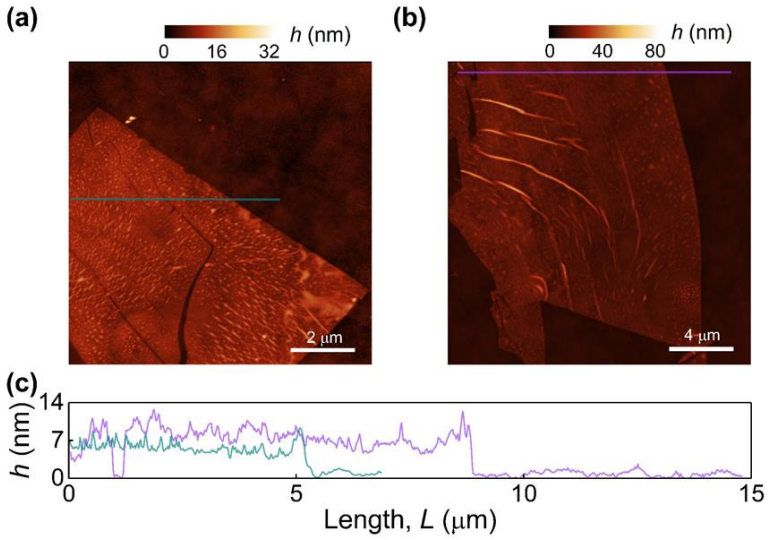


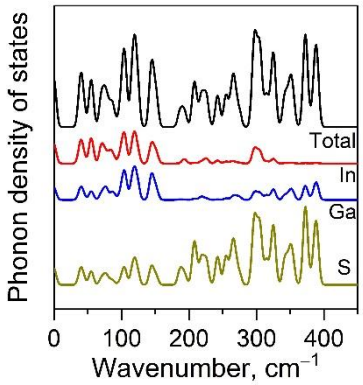
Supplementary Figure 1: EDX and XPS patterns of $InGaS_3$ exfoliated sheets on Si/SiO_2 substrate. a EDX pattern. Element ratio 22 (± 2.6) : 20.7 (± 1.8) : 57.3 (± 1.5) for In:Ga:S. **b-d** Core level XPS spectra corresponding to In (b), Ga (c) and S (d) atoms. Black lines represent raw spectra and coloured ones correspond to deconvoluted peaks on top of smooth background (light blue lines). Element ratio 18:24:58 for In:Ga:S.



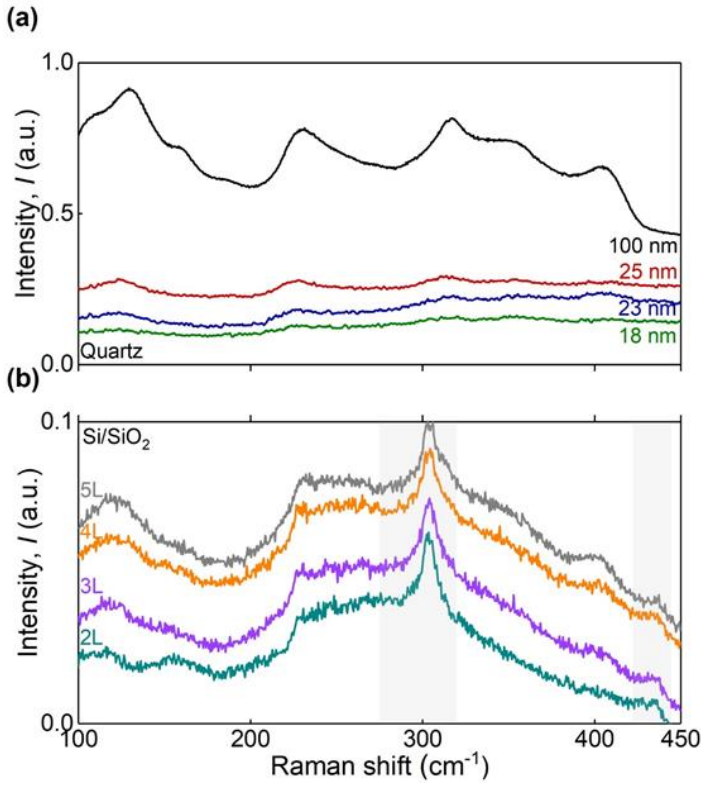
Supplementary Figure 2: TEM patterns $InGaS_3$ exfoliated sheets on standard grids: **a** experimental diffraction pattern across a^*b^* plane. **b** Simulated Miller index pattern on top of the experimental micrograph presented in (a).



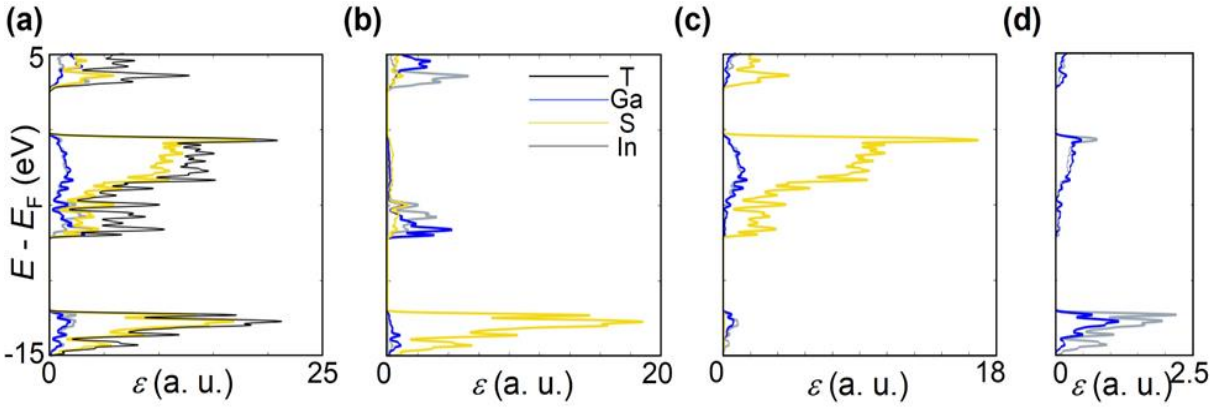
Supplementary Figure 3: AFM images of inhomogeneous atomic sheets of $InGaS_3$. a and **b** topography micrographs of typical ultrathin sheets. **c** Height histogram taken along green (a) and purple (b) lines presented in (a) and (b).



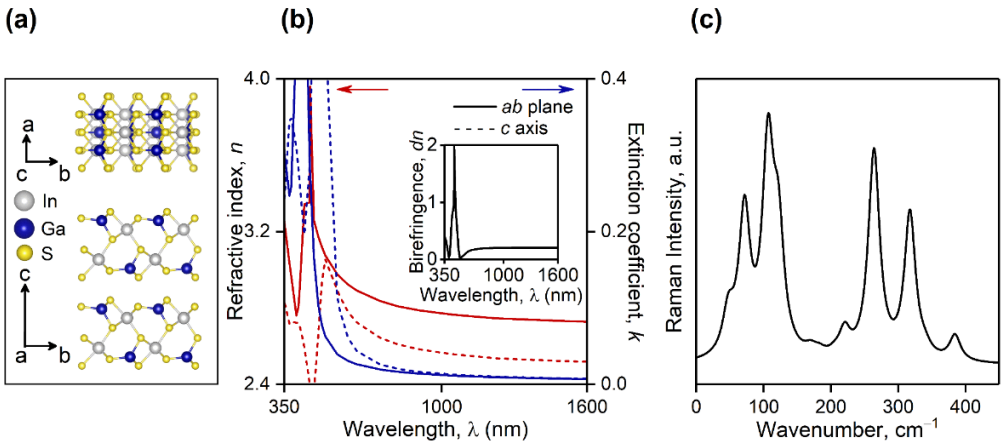
Supplementary Figure 4: Partial phonon density of states of hexagonal phase of $InGaS_3$. Black line represents the total phonon density of states, the coloured ones correspond to the contribution from each of the elements: In (red), Ga (blue), yellow (S).



Supplementary Figure 5: Raman spectra of thin $InGaS_3$ sheets placed on various substrates. a Quartz, and **b** Si/SiO_2 substrates. Grey shaded regions correspond to Si modes. Measurements performed at 532 nm.



Supplementary Figure 6: eDOS obtained *via* HSE. a Total spectrum: partial eDOS calculated by orbitals. **b** *s*-orbital. **c** *p*-orbital. **d** *d*-orbital. E_F is shifted to zero for clarity throughout the figure. Grey lines correspond to the contribution of *In*, blue – *Ga*, yellow – *S* atoms, and black ones, to the total eDoS throughout the figure



Supplementary Figure 7: Orthorhombic phase of $InGaS_3$ obtained through first-principle calculations. a Space group: $Pmn2_1$, lattice constants: a = 6.21 Å and b = 3.78 Å. **b** Refractive index and extinction coefficient for *ab*-plane (straight line) and *c*-axis (dashed line) with non-zero absorption in the entire considered range obtained by HSE. The inset shows material's birefringence. **c** Evaluated Raman spectrum for the orthorhombic $InGaS_3$.

Formula	$InGaS_3$
Formula weight (g/mol)	280.72
Diffractometer	Bruker D8 Quest
X-ray source	Micro-focus Mo Kα tube
Data collection method	ω scans
Temperature (K)	100
Crystal system	Hexagonal
Space group	$P6_5$
a (Å)	6.6309(3)
b (Å)	6.6309(3)
c (Å)	17.9293(9)
α (°)	90
β (°)	90

γ (°)	120
V (Å^3)	682.71(7)
Z	6
Color, habit	Yellow, block
Crystal dimensions (mm)	0.020 × 0.033 × 0.035
Density D_{calc} (g·cm^{-3})	4.097
μ (mm^{-1})	12.151
Unique reflections (R_{int})	1194 (0.0472)
Observed reflections [I > 2σ(I)]	1165
Parameters	47
R_1[I > 2σ(I)], ωR_2	0.0249, 0.0587
Goodness of fit on F^2	1.151
Absorption correction	multi-scan
T_{min}, T_{max}	0.6522, 0.7473
ρ_{min}, ρ_{max} (eÅ^{-3})	-0.713, 1.638

Supplementary Table 1: Summary of data collection and structure refinement details for hexagonal phase of $InGaS_3$.

Parameter	Distance, Å
Ga1 – S1	2.2494(14)
Ga1 – S3	2.2533(16)
Ga1 – S2	2.2890(16)
Ga1 – S2 ^{i}	2.323(2)
S1 – In1	2.4323(19)

S1 – In1^{ii}	2.745(2)
S2 – In1^{iii}	2.4883(18)
S3 – In1^{iv}	2.4549(17)
S3 – In1^{v}	2.6703(19)

Supplementary Table 2: Selected interatomic distances of hexagonal phase of $InGaS_3$. Symmetry codes: (*i*) x-y, x, z-1/6; (*ii*) x-y+1, x, z-1/6; (*iii*) x, y-1, z; (*iv*) x-1, y-1, z; (*v*) y-1, -x+y, z+1/6.

№	*A* (T.O.)	*A* (L.O.)	*B*	E_1 (T.O.)	E_2
1	383.5	391.1	388.4	389.9	387.8
2	371.0	375.9	372.0	373.3	372.2
3	341.5	351.3	342.9	353.6	349.3
4	314.2	323.0	324.8	322.8	325.6
5	304.1	305.1	314.5	304.3	305.5
6	297.3	297.3	295.3	298.4	296.7
7	255.0	270.2	274.9	264.1	268.2
8	192.7	226.0	255.0	225.1	242.5
9	186.5	186.6	209.7	207.1	218.7
10	151.5	151.7	151.2	145.4	144.0
11	105.7	106.5	122.6	118.5	123.8
12	88.5	89.5	115.8	105.7	118.6
13	45.2	45.2	98.7	78.8	103.3
14	39.6	39.6	83.6	55.5	71.2
15			56.8		41.5

Supplementary Table 3: Calculated wavenumbers of vibrational modes of hexagonal phase of $InGaS_3$. Units are in cm^{-1}.

Crystallographic Information File (CIF) of hexagonal phase of $InGaS_3$ crystal structure used in first-principle calculations

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#------------------------------------------------------------------------
# InGaS3 crystal
#------------------------------------------------------------------------
_cell_length_a                         6.6152940
_cell_length_b                         6.6152940
_cell_length_c                         17.753407
_cell_angle_alpha              90.000000
_cell_angle_beta               90.000000
_cell_angle_gamma                      120.00000
_cell_volume                           672.838179
_space_group_name_H-M_alt                    'P 1'
_space_group_IT_number     1
loop_
_space_group_symop_operation_xyz
  'x, y, z'
loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_U_iso_or_equiv
  _atom_site_type_symbol
  In1     1.0   0.668420   0.992314   0.154321   Uiso  ? In
  In2     1.0   0.007686   0.676106   0.820987   Uiso  ? In
  In3     1.0   0.323894   0.331580   0.487654   Uiso  ? In
  In4     1.0   0.331580   0.007686   0.654321   Uiso  ? In
  In5     1.0   0.992314   0.323894   0.320987   Uiso  ? In
  In6     1.0   0.676106   0.668420   0.987654   Uiso  ? In
  Ga1     1.0   0.319414   0.326485   0.126589   Uiso  ? Ga
  Ga2     1.0   0.673515   0.992929   0.793255   Uiso  ? Ga
  Ga3     1.0   0.007071   0.680586   0.459922   Uiso  ? Ga
  Ga4     1.0   0.680586   0.673515   0.626589   Uiso  ? Ga
  Ga5     1.0   0.326485   0.007071   0.293255   Uiso  ? Ga
  Ga6     1.0   0.992929   0.319414   0.959922   Uiso  ? Ga
  S1      1.0   0.689371   0.628974   0.138550   Uiso  ? S
  S2      1.0   0.371026   0.060397   0.805217   Uiso  ? S
  S3      1.0   0.939603   0.310629   0.471883   Uiso  ? S
  S4      1.0   0.310629   0.371026   0.638550   Uiso  ? S
  S5      1.0   0.628974   0.939603   0.305217   Uiso  ? S
  S6      1.0   0.060397   0.689371   0.971883   Uiso  ? S
  S7      1.0   0.277257   0.976053   0.163639   Uiso  ? S
  S8      1.0   0.023947   0.301204   0.830306   Uiso  ? S
  S9      1.0   0.698796   0.722743   0.496973   Uiso  ? S
  S10     1.0   0.722743   0.023947   0.663639   Uiso  ? S
  S11     1.0   0.976053   0.698796   0.330306   Uiso  ? S
  S12     1.0   0.301204   0.277257   0.996973   Uiso  ? S
  S13     1.0   0.029602   0.380062   0.170811   Uiso  ? S
  S14     1.0   0.619938   0.649540   0.837478   Uiso  ? S
  S15     1.0   0.350460   0.970398   0.504145   Uiso  ? S
  S16     1.0   0.970398   0.619938   0.670811   Uiso  ? S
  S17     1.0   0.380062   0.350460   0.337478   Uiso  ? S
  S18     1.0   0.649540   0.029602   0.004145   Uiso  ? S
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