High-refractive index and mechanically cleavable non-van der Waals InGaS₃

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The growing family of two-dimensional crystals has been recognized as a promising platform for investigation of rich low-dimension physics and production of a variety of devices. Of particular interest are recently reported atomic sheets of non-van der Waals materials, which reshape our understanding of chemical bonds and enable heterostructures with novel functionality. Here, we study the structural and optical properties of ultrathin non-van der Waals InGaS₃ sheets produced by standard mechanical cleavage. Our ab initio calculations reveal weak out-of-plane covalent bonds, responsible for the layered structure of the material. The energy required for isolation of a single layer is as low as ~50 meVÅ⁻², which is comparable with the conventional van der Waals material's monolayer isolation energies of 20–60 meVÅ⁻². A comprehensive study of the structural, vibrational, and optical properties of the material reveals its wide bandgap (2.73 eV), high refractive index (>2.5) and negligible losses in the visible and infrared spectral ranges. These properties make it a perfect candidate for visible-range all-dielectric nanophotonics.

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Further details on data collection, across microscopy (see Supplementary Figure 2 for diffraction pattern material was alternatively verified through transmission electron microscopy (see Supplementary Figure 2 for diffraction pattern across $a^*b^*$-plane. $c$ Same as (b), but across $c^*b^*$-plane. $d$ Schematic illustration of layer separation achieved by cutting off the weak non-van der Waals bonds. UC, 1 L stand for unit cell and cleaved monolayer, respectively. $e$ Typical exfoliation energies of conventional van der Waals (black pentagons) and non-van der Waals (red pentagons) materials evaluated via first principles calculations. Green hexagon presents our estimation of the exfoliation energy along the proposed minimal energy atomic plane.

The hexagonal InGaS$_3$ contains various structural bonds, whose strengths were estimated by first-principles calculations based on the density functional theory (DFT). To obtain isolation energy of individual atomic sheets, we estimated the difference between the ground-state energy of the relaxed structure and all of its unrelaxed substructures. Afterwards, we looked for the planes with the minimal binding energies to determine potentially breakable, or, in our case, cleavable directions. Excluding the relaxation energy of substructures, we found the exfoliation energy $E_{exf} = 53$ meVÅ$^{-2}$ for the plane shown in Fig. 1d. Notably, the exfoliation energy decreased when we added more atomic layers into our model. In the case of five layers, we obtained $E_{exf} = 47$ meVÅ$^{-2}$. After accounting for the further relaxation of the isolated layers$^{23}$, we obtained an even smaller value of $E_{exf} = 21$ meVÅ$^{-2}$. It is important to note, that some alternative and DFT accuracy approaches, such as MLIP provide computationally faster studies of mechanical properties of materials under the external deformations including exfoliation effects$^{24,25}$. Figure 1e compares our results with the evaluated exfoliation energies of conventional van der Waals (and non-van der Waals) materials. Notably, the energies of conventional van der Waals materials cover the range of 20 to 60 meVÅ$^{-2}$, whereas non-van der Waals materials fall into a broader range from 25 to 180 meVÅ$^{-2}$. Among non-van der Waals materials, InGaS$_3$ has a relatively low exfoliation energy, which is even lower than that of some van der Waals materials, such as PdS$_2$ and PdSe$_2$.

Slightly elevated temperature treatment within the standard exfoliation procedure (see Methods)$^7$ allows for the cleavage of InGaS$_3$ crystals into individual nanosheets with atomically smooth surfaces (see Fig. 2a). However, ultrathin flakes are often highly inhomogeneous or cracked (see Supplementary Figure 3 for the atomic-force micrographs of inhomogeneous atomic sheets). This can be attributed to the lack of strength of some in-plane bonds within the material, leading to their random breakage during exfoliation. Figure 2b–d show AFM scans of pristine atomic sheets with nearly atomically flat surfaces (root-mean-square roughness of 0.3 nm). Thicknesses of these sheets correspond to one (1 L), two (2 L), three (3 L), four (4 L) and five (5 L) monolayers.

Figure 2f shows Raman spectra of the hexagonal InGaS$_3$ nanosheets taken at room and liquid nitrogen temperatures. Obtained spectral profiles have a complex form due to the overlapping bands, although peaks are slightly sharper at lower temperatures. The profiles display depths at wavenumber ranges of 180–200 cm$^{-1}$ and 270–290 cm$^{-1}$, which is in good agreement with our lattice dynamics calculations (see vertical bars on the inset of Fig. 2f). Those predict an absence of vibrational modes within these wavenumber ranges (see Methods for calculation details). For hexagonal InGaS$_3$ in the P6$_3$ space group, we found 90 normal vibrational modes in the centre of the first Brillouin zone. Those can be represented by the expression $\Gamma_v = 15A + 15B + 15E_1 + 15E_2$. Here, $A + E_1$ are acoustical translational modes, $B$ are...
We investigated the anisotropic dielectric tensor (Fig. 3a) of hexagonal InGaS$_3$ through imaging spectroscopic ellipsometry in the tiny region of interest of 10 $\mu$m$^2$ within the area of exfoliated sheets. The ability to focus on the homogeneous high-quality region is a key benefit of our imaging technology\cite{26}. Furthermore, we simultaneously recorded and analysed optical response from four InGaS$_3$ sheets to ensure a great precision and reproducibility of our results (see Methods and Supplementary Information for details). The dielectric function of hexagonal InGaS$_3$, similarly to transition metal dichalcogenides, is best represented by the Tauc-Lorentz oscillators\cite{27,28} and the Cauchy model\cite{29} across the crystallographic $ab$-plane and $c$-axis, respectively. Despite this, owing to the high thickness of monolayers and the non-van der Waals interaction in InGaS$_3$, the measured birefringence is relatively weak with $\Delta n \sim 0.1$ (the inset in Fig. 3a), contrasting the huge anisotropy of $\Delta n \sim 1.5$ in transition metal dichalcogenides with natural van der Waals bonds\cite{30}. To explain this relatively weak anisotropy, we have performed additional DFT calculations (see Fig. 3b). The comparison of plots in Fig. 3a, b reveals a good agreement between experimental and theoretical results. Furthermore, our evaluations independently confirm the crystal structure of InGaS$_3$ (see inset of Fig. 1a) since the dielectric response is a fingerprint of the material’s electronic bandstructure (see Supplementary Information for details). We also evaluated optical constants for the orthorhombic phase of InGaS$_3$ predicted theoretically in recent work\cite{20}. The obtained constants, presented in Supplementary Figure 7, clearly disagree with our experimental results, which indirectly indicates the hexagonal crystal structure of our sample.

Additionally, a good agreement between experimental and theoretical optical responses (see Fig. 3) implicitly shows a small influence of spin-orbit coupling (SOC) in contrast to transition metal dichalcogenides,\cite{34} where SOC leads to noticeable mismatch between DFT and experimental results. Hence, our technique, which combines a spectroscopic ellipsometry with density functional calculations unambiguously confirms the hexagonal structure of InGaS$_3$ in addition to the X-ray analysis and can be
potentially used for the identification of crystal structures of other materials.

Apart from optical constants, we also evaluated the electronic bandstructure of hexagonal InGaS₃ (Fig. 3c) and individual orbital-resolved density of electronic states (see Supplementary Figure 6) using the Heyd-Scuseria-Ernzerhof hybrid functional (see Methods). For the latter, the main contributions to the bottom of conduction bands come from s-states of Gallium, Indium, and p-states of Sulphur atoms. From Fig. 3c, we conclude that InGaS₃ is an indirect bandgap semiconductor with $E_g = 3.0 \text{ eV}$, which is close to bandgap ($E_g = 2.73 \text{ eV}$) obtained experimentally from ellipsometry analysis. Moreover, we observed an excitonic peak at $E_{\text{exc}} = 2.67 \text{ eV}$ (464 nm) in optical response of the material, which is shown in Fig. 3a.

Its excitonic binding energy is $E_b = E_g - E_{\text{exc}} = 60 \text{ meV}$. Interestingly, these values ($E_g = 2.73 \text{ eV}$ and $E_b = 60 \text{ meV}$) are in line with bandgaps and excitonic binding energies of traditional semiconductors but contrast with transition metal dichalcogenides, such as MoS₂ (Fig. 3d). We believe it results from two main reasons: (i) the unit cell along the crystallographic c-axis of InGaS₃ is about 3 times larger than for MoS₂; (ii) InGaS₃ refractive index is about 2 times smaller compared to MoS₂. Hence, we estimate that InGaS₃ should have much weaker quantum confinement making it closer to 3D rather than 2D materials. Therefore, InGaS₃ does not exhibit extraordinary excitonic effects and birefringence as MoS₂. This indicates that the exciton in InGaS₃ has the same physical origin as in traditional semiconductors, and thus, can be described by the Wannier-Mott model.

Finally, we would like to highlight the strong dielectric response of InGaS₃ (Fig. 4a). Its refractive index is comparable to indices of classical high-index materials, such as silicon (Si) and titanium oxide (TiO₂) as well as emerging high-index materials, such as Gallium Phosphide (GaP) and tin(IV) Sulphide (SnS₂), as shown in Fig. 4a. More importantly, InGaS₃ has zero optical losses up to 2.57 eV (485 nm), as can be seen in Fig. 4b. This value lies between optical bandgaps of SnS₂ ($E_g = 2.18 \text{ eV}$) and TiO₂ ($E_g = 3.35 \text{ eV}$). Hence, InGaS₃ covers an important gap in visible spectral range for high-refractive index materials (see inset in Fig. 4b). As a result, we conclude that InGaS₃ outperforms other transparent materials in the visible range, we have studied planar waveguides on a quartz substrate. Setting the operating free space wavelength to 500 nm, we find (Fig. 4c) that InGaS₃ allows for a much stronger field confinement than TiO₂ ($\lambda/5.6$) and with the much thinner core layer (32 nm vs 57 nm). These results are surprising in light of a relatively small refractive index difference of about 18% between InGaS₃ and TiO₂ at 500 nm. Although InGaS₃ and TiO₂ waveguides are both very small, mode length evaluated here governs the Purcell enhancement of spontaneous emission. As a result, single-photon sources and nanoLEDs coupled to InGaS₃ waveguides would have higher internal quantum efficiency and their radiation would be better collected by the waveguide.

**DISCUSSION**

To sum up, we have demonstrated that hexagonal InGaS₃ can be cleaved down to thicknesses of individual monolayers even though it is not composed of atomic layers connected by van der Waals bonds within its unit cell. It is made possible due to a specific arrangement of atoms across the crystallographic c-axis, where the exfoliation energy diminishes to 53 meVÅ⁻² for a
selected atomic plane. This exfoliation energy value is comparable to conventional van der Waals materials. Furthermore, the hexagonal InGaS₃ is well suited for next-generation nanophotonics, Mie-tronics³⁹ and expands high-refractive index palette¹⁰. In particular, it meets two major requirements of Mie-tronics: high-refractive index (n > 2.5) and broadband transparency (k ≈ 0 above 465 nm). Although, its refractive index is only about ~18 % higher than of traditional TiO₂⁴¹, we show that InGaS₃ planar waveguides have by 55 % stronger field confinement achieved at 40 % lower thickness than TiO₂ waveguides. Hence, we expect that all-dielectric nanostructures, such as waveguides⁴², Mie-resonance nanoparticles⁴₃, and subwavelength metasurfaces⁴⁴ based on InGaS₃ would benefit greatly from its higher refractive index. Additionally, it exhibits an out-of-plane optical anisotropy (Δn ~ 0.1), in contrast to conventional high-refractive index materials, which may greatly extend its scope of applications. Therefore, InGaS₃ possesses a unique combination of optical properties, such as high-refractive index, zero optical losses and out-of-plane anisotropy also offering convenient thickness control due to its structural properties.

METHODS
Sample preparation
Bulk InGaS₃ crystals were purchased from 2D Semiconductors (Scottsdale, USA) and exfoliated on top of required substrates: Si/SiO₂ and quartz. Prior to exfoliation, the corresponding substrates were subsequently cleaned in acetone, isopropanol alcohol, and deionized water. Then, those were subjected to oxygen plasma (O₂) to remove the ambient adsorbates. Following the plasma cleaning, substrates were put on a hot plate at the temperatures of 120–140 °C for 2 min. After the heating, the scotch-tape from Nitto Denko Corporation (Osaka, Japan) with loaded crystal InGaS₃ was brought in contact with substrates. Afterwards, the tape was removed completing the exfoliation procedure.

X-ray crystallography
X-ray diffraction analysis of InGaS₃ single crystals was performed on a Bruker D8 QUEST diffractometer with Photon III CMOS detector using Mo Kα radiation (λ = 0.71073 Å) focused by multilayer Montel mirror. The full dataset was collected at the temperature of 100 K within ω-scans indexed with cell-now. It was integrated through SAINT from the SHELXTL PLUS package⁴⁵. Absorption correction was completed by a multiscan approach implemented from SADABS⁴⁶. The crystal structure was solved by direct methods and refined anisotropically with full-matrix F² least-squares technique using SHELXTL PLUS package. The structure was refined in a chiral P6₃ space group with the resulting Flack parameter of 0.06 (2) being close to zero⁴⁷. The second virtual inversion twin-component was added to refinement by TWIN/BASF instruction to account for the absolute structural parameter. This led to a slight reduction of R-value from 2.50 to 2.49%.

Density functional theory
Calculations of electronic bandstructure and optical constants were performed using the Vienna ab-initio simulation package VASP⁴⁸,⁴⁹ within generalized gradient approximation (GGA)⁵⁰. The Heyd-Scuseria-Ernzerhof (HSE) hybrid functional⁵¹ in combination with Perdew-Burke-Ernzerhof (PBE)⁵² potentials was applied for accurate description of the electronic bandstructure. Electron-ion interactions were described by projector-augmented wave (PAW) method⁵²,⁵³. The cutoff energy for the plane-wave basis was set to 400 eV. The first Brillouin zone of the supercells was sampled with a 6 × 6 × 3 Monkhorst-Pack mesh⁵⁴ of k-points for bulk supercell and 6 × 6 × 1 for monolayer case. The maximal force convergence tolerance settings for geometry optimization were set to 0.01 eV Å⁻¹.

Lattice dynamics calculations
First-principle lattice dynamics calculations were carried out with the CASTEP code package⁵⁵. The crystal structure was fully optimized using LD approximation with CA-PZ exchange-correlation functional based on Ceperley and Alder numerical representation⁵⁶ parameterized by Perdew and Zunger⁵⁷. Maximal force and stress tensor convergence tolerance settings for geometry optimization were set to 0.01 eV Å⁻¹ and 0.02 GPa, respectively. 5S₂, 5P₃, 3D₁₀, 4S₂, 4P₁, and 3S₂, 3P₂ orbitals were considered occupied with valence electrons for Indium, Gallium and Sulphur, respectively. Plane-wave cutoff energy was set to 880 eV for 4 × 4 × 2 sampling of the first Brillouin zone by the Monkhorst-Pack method.

Atomic Force Microscopy
The thickness and surface morphology of InGaS₃ sheets were accurately characterized by an atomic force microscope (NT-MDT Ntegra II) operated in a HybriD mode at ambient conditions. AFM images were acquired using silicon tips from TipsNano (GOLDEN, NSG 10) with spring constant of 11.8 N/m, head curvature radius <10 nm, and resonant frequency of 240 kHz. The measurements were...
were performed at a scan rate of 0.3 Hz and 512-pixel resolution. The obtained datasets were analysed by the Gwyddion software.

Imaging spectroscopic ellipsometry

To analyze anisotropic optical response of InGaS$_2$p, we used commercial imaging spectroscopic ellipsometer Accurion nanofilm-m$_{ep4}$ in the nulling mode. Ellipsometry spectra were recorded for four sheets with various thicknesses ($h \approx 3.6$ nm, 68.5 nm, 103.0 nm, and 277.4 nm) in the spectral range from ultraviolet (360 nm) to near infrared (1700 nm). For ellipsometry analysis, we followed the algorithm described in Supplementary Note 2 of our recent work.²⁶

Eigenvmode simulations

To study planar photonic waveguides with anisotropic InGaS$_2$ and isotropic TiO$_2$ cores, we employed a finite element method solver implemented in COMSOL Multiphysics software. The mode length was evaluated as:

$$l_{mode} = \int_{-\infty}^{\infty} \frac{W_{em}}{\max(W_{em})} \, dy$$

where

$$W_{em} = \frac{1}{16\pi} \frac{\partial (|\omega|)}{\partial \omega} \left( |E|^2 + |H|^2 \right)$$

is the electromagnetic energy density in dispersive non-magnetic media.

DATA AVAILABILITY

The data that support the plots and other findings of this study are available from the corresponding authors upon reasonable request. The X-ray crystallographic coordinates for the structure reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 2145523. It can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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REFERENCES

1. Friisenda, R., Niu Y, Gant P, Muñoz M, Castellan-Castellanos A. Naturally occurring van der Waals materials. npj 2D Materials and Applications, 4, (2020).
2. Velický, M. et al. Exfoliation of natural van der Waals heterostructures to a single unit cell thickness. Nat. Commun. 8, 14410 (2017).
3. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. Nature 499, 419–425 (2013).
4. 2D Materials and Van der Waals Heterostructures. MDPI Books. https://doi.org/10.3390/books978-3-09328-769-7.
5. Bonaccorso, F. et al. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. Science 347, 1246501 (2015).
6. Ferrari, A. C. et al. Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. Nanoscale 7, 4598–4810 (2015).
7. Novoselov, K. S., Mishchenko, A., Carvalho, A. & Castro Neto, A. H. 2D materials and van der Waals heterostructures. Science 353, aaa9439 (2016).
8. Mounet, N. et al. Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds. Nat. Nanotechnol. 13, 246–252 (2018).
9. Choudhary, K., Kalish, I., Beams, R. & TavaZZ, F. High-throughput Identification and Characterization of Two-dimensional Materials using Density functional theory. Sci. Rep. 7, 5179 (2017).
10. Björkman, T., Gulans, A., Krasheninnikov, A. V. & Nieminen, R. M. van der Waals bonding in layered compounds from advanced density-functional first-principles calculations. Phys. Rev. Lett. 108, 235502 (2012).
11. Serles, P. et al. Friction of magnetene, a non–van der Waals 2D material. Sci. Adv. 7, eabc2041 (2021).
12. Jin, C. & Kous, L. Two-dimensional non-van der Waals magnetic layers: functional materials for potential device applications. J. Phys. D. Appl Phys. 54, 413001 (2021).
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AUTHOR CONTRIBUTIONS
D.A.G. and V.S.V. suggested and directed the project with help from A.V.A., A.N.T. fabricated the samples, G.A.E., A.S.S., N.V.D., D.I.Y., A.V.S., D.M.T., S.M.N., R.I.R., A.M.M. and D.A.G. performed the measurements and analysed the data, A.N.T., E.V.S., A.S.O., Z.I.P., D.G.K. and A.A.V. provided theoretical support. A.N.T., G.A.E., A.A.V., A.V.A., D.A.G., and V.S.V. contributed to the interpretation of experimental results. A.N.T. wrote the original draft with the help from G.A.E. D.A.G., A.A.V., A.V.A., and V.S.V. reviewed and edited the paper. All authors contributed to the discussions and commented on the paper.

COMPETING INTERESTS
The authors declare no competing interests.

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