Hidden spontaneous polarisation in the chalcohalide photovoltaic absorber Sn$_2$SbS$_2$I$_3$†

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Perovskite-inspired materials aim to replicate the optoelectronic performance of lead-halide perovskites, while eliminating issues with stability and toxicity. Chalcohalides of group IV/V elements have attracted attention due to enhanced stability provided by stronger metal-chalcogen bonds, alongside compositional flexibility and $ns^2$ lone pair cations – a performance-defining feature of halide perovskites. Following the experimental report of solution-grown tin-antimony sulfioiodide (Sn$_2$SbS$_2$I$_3$) solar cells, with power conversion efficiencies above 4%, we assess the structural and electronic properties of this emerging photovoltaic material. We find that the reported centrosymmetric Cmcm crystal structure represents an average over multiple polar Cmc2$_1$ configurations. The instability is confirmed through a combination of lattice dynamics and molecular dynamics simulations. We predict a large spontaneous polarisation of 37 $\mu$C cm$^{-2}$ that could be active for electron–hole separation in operating solar cells. We further assess the radiative efficiency limit of this material, calculating $\eta_{\text{max}} > 30\%$ for film thicknesses $t > 0.5\, \mu$m.

The photovoltaic performance of lead-halide perovskites has spurred major research efforts toward the discovery of ‘perovskite-inspired materials’ (PIMs).1–3 Through the use of lead-free and stable alternative materials, PIMs aim to replicate the ability of halide perovskites to combine high optoelectronic performance with low-cost solution processing methods, while overcoming their infamous stability and toxicity drawbacks. The applications of PIMs are not solely limited to solar cell devices. In fact, these materials have seen successful implementation in a wide range of optoelectronic applications, such as light-emitting diodes, photocatalysts, radiation detectors, thin film transistors and memristors.1

A defining feature of halide perovskites is the combination of a lone-pair cation with a halide anion which can produce, inter alia, dispersive valence and conduction bands, defect tolerance, and strong dielectric screening.1,4 On the other hand, the soft metal-halide bonding contributes to the poor chemical and thermal stabilities of these materials.5 Chalcohalide PIMs offer a route around this issue, demonstrating remarkably higher air and water stability – due to the increased strength of metal-chalcogen bonding4,5 – while retaining the $ns^2$ cation–halide anion combination. These materials have already demonstrated promising efficiencies (> 4%).6–8 Alongside low-cost fabrication methods, representing a fertile area for stable, non-toxic high-performance solar cells.8 Further increases in power-conversion efficiencies (PCEs) will be required to achieve commercial viability.5

New concepts

Mixed-metal chalcohalides have emerged at the forefront of perovskite-inspired materials. A rigorous description of their atomistic properties and performance potential is lacking. In particular, Sn$_2$SbS$_2$I$_3$ contains two lone-pair cations which are known to drive unusual structure–property relations. Using a range of first-principles modelling techniques, we reveal a spontaneous symmetry breaking away from the known non-polar crystal structure. We link this local polarisation, which was previously hidden to macroscopic diffraction techniques, to the high optoelectronic efficiency potential and defect-tolerant properties of this system. The results shine a spotlight on the largely-unexplored class of A$_2$BCh$_2$X$_3$ mixed-metal chalcohalides. These are candidates for solution-processed ferroelectric and optoelectronic devices, with the substitutional flexibility for engineering band gaps, band energies, and lattice polarisation.

‡ Electronic supplementary information (ESI) available: Additional structural, dielectric, electronic and optical analysis. See DOI: 10.1039/d1mh00764e
research group in 1984. Later, Dolgikh prepared both Sn$_2$SbS$_2$I$_3$ and the isostructural, iso-electronic Pb$_2$SbS$_4$I$_4$ compound and investigated the optical dielectric response. Then in 1990, Starosta et al. prepared both antimony sulfioiodide compounds and used photoconductivity measurements to determine optical band gaps of 1.5 and 2.0 eV for the Sn and Pb-based materials, respectively. They also discussed the seemingly anomalous trend of increased band gap with chemical substitution of heavier elements.

In a major breakthrough, Sn$_2$SbS$_2$I$_3$ was recently reported to exhibit a photovoltaic efficiency exceeding 4% in the first experimental device fabrication. Nie et al. used a low-cost single-step deposition method and reported good stability under conditions of high temperature, humidity and illumination. The achievement of a power conversion efficiency exceeding that first reported for methylammonium lead-iodide (MAPI) is promising. While Sn$_2$SbS$_2$I$_3$ has been known for several decades, it is now at the forefront of potential defect-tolerant PIMs for optoelectronic applications. In this work, we characterise the physical properties of Sn$_2$SbS$_2$I$_3$ using *ab initio* methods in order to understand the atomistic origins of impressive PV performance, and to assess the efficiency potential going forward.

**Computational methods**

We employ a combination of methods to probe the static and dynamic crystal structure of Sn$_2$SbS$_2$I$_3$, in addition to its electronic and optical properties. All base calculations were performed using Density Functional Theory (DFT) within periodic boundary conditions through the Vienna *Ab Initio* Simulation Package (VASP). After testing several DFT exchange-correlation functionals (Section S2.2, ESI†), the optB86b-vdW functional was chosen for geometry optimisation, yielding the closest agreement with experiment for the $c/a$ lattice parameter ratio. The ability of this dispersion-corrected functional to incorporate van der Waals interactions in solids has been well demonstrated, yielding accurate predictions of lattice parameters in lone-pair materials. To calculate relative formation energies and the ferroelectric-switching barrier with accuracy beyond DFT, the Random Phase Approximation (RPA) to the correlation energy was employed, using electronic wavefunctions calculated with the HSE06 screened hybrid DFT functional. The HSE06 functional, with full inclusion of spin–orbit coupling effects, was also used for calculations of optical and electronic behaviour – having been demonstrated to yield accurate predictions of band gaps in semiconductor materials. Comprehensive details of the computational implementation are provided in Section S1 of the ESI, † and all calculation data and analyses are provided in an online repository at doi.org/10.5281/zenodo.4683140.

**Structural analysis**

Geometry optimisations were performed for Sn$_2$SbS$_2$I$_3$ in both Cmcm and Cmc2$_1$ space groups, using the entries on the Materials Project repository as the starting points. The relaxed crystal structures and unit cell dimensions are provided in Fig. 1 and Table 1, respectively.

The Cmcm structure comprises infinite chains of (Sn$_2$S$_2$I$_2$)$_n$ along the a direction, tightly-packed along the b direction to form layers in the ab plane, with antimony and iodine atoms located between layers, yielding the overall (Sn$_2$SbS$_2$I$_3$)$_n$ stoichiometry. The (Sn$_2$S$_2$I$_2$)$_n$ chains are formed from face-sharing SnS$_4$I$_3$ pyramids, comprising a parallelepiped base of S$_2$I$_2$ and an apical sulfur atom. In fact, this (Sn$_2$S$_2$I$_2$)$_n$ structural motif matches the 1D chain structures of the AChX (A = Bi, Sb; Ch = S, Se; X = Br, I) $\text{ns}^2$-cation chalcocohalide family. Moving to the Cmc2$_1$ crystal structure, the coordination environments of Sb and (to a lesser extent) Sn shift to produce connected chains of the formula unit (Sn$_2$SbS$_2$I$_3$)$_n$ along the a direction, as the Sb atoms attach to the (Sn$_2$S$_2$I$_2$)$_n$ layers. The a and b cell lengths are similar for both polymorphs, with the greatest difference occurring along the c direction.

Much of the structural behaviour in this system is governed by the lone-pair activities of Sb and Sn cations. While the antimony cations are found to exhibit significant localisation of the ns$^2$ electrons, only minimal distortion from spherical symmetry is witnessed for the Sn(II) lone-pair, due to a preferential alignment and thus enhanced interaction with anion p states (Section S3, ESI†). In both polymorphs, the Sb lone-pair is directed toward halide-bordered voids; either along the interchain gap (b direction) for Cmcm symmetry or toward the...
lower-symmetry the primary driving factors behind the formation of the distorted, crystal structure for Sn$_2$SbS$_2$I$_3$.

Experiment 3.85 4.25 13.99 16.38 973.9

Table 1 Calculated lattice parameters of the conventional orthorhombic unit cell for both polymorphs of Sn$_2$SbS$_2$I$_3$, using the optB86b-vdW DFT functional. Experimental values taken from low-temperature ($T = 173$ K) X-ray diffraction measurements.$^{10}$

| Polymorph | $c/a$  | $a/\text{Å}$  | $b/\text{Å}$  | $c/\text{Å}$  | Vol./Å$^3$ |
|-----------|--------|--------------|--------------|--------------|------------|
| Cmcm      | 3.75   | 4.27         | 14.02        | 16.00        | 957.9      |
| Cmc2$_1$  | 3.85   | 4.29         | 13.41        | 15.51        | 1013.8     |
| Experiment| 3.85   | 4.25         | 13.99        | 16.38        | 973.9      |

interchain gap (c direction) for Cmc2$_1$ – with more pronounced localisation visible in the Cmc2$_1$ case (Figs. S6–S8, ESI†). Indeed, this dynamic stereoechemical activity of the Sb lone-pair is one of the primary driving factors behind the formation of the distorted, lower-symmetry Cmc2$_1$ polymorph – through a second-order Jahn–Teller instability, often observed in lone-pair chalcogenides.$^{22,33–35}$

While all experimental works have reported the Cmcm crystal structure for Sn$_2$SbS$_2$I$_3$, Ibanez et al.$^{10}$ noted that assignment of Sb to an 8f Wyckoff position (i.e. the Sb Wyckoff site in Cmc2$_1$ symmetry) with 50% occupancy, as opposed to the 4c site for Cmcm, gave a significant reduction in $R$-factor – a measure of agreement between the structure model and diffraction data$^{38}$ – from 0.105 to 0.066. Moreover, both Olivier-Fourcade et al.$^9$ and Ibanez et al.$^{10}$ observed large Debye–Waller (B) displacement factors for the Sb and Sn sites in Sn$_2$SbS$_2$I$_3$ (i.e. the site positions which differ most between Cmc2$_1$ and Cmc2$_1$ structures), even at temperatures as low as $T = 173$ K, alongside large anisotropy in the atomic displacement ellipsoids. Further structural and lone-pair analysis, with direct comparison to experiment (Fig. S4, ESI†), is provided in Sections S2 and S3 (ESI†).

Thermodynamic & dynamic stability

To ensure a high level of accuracy in the calculated phase stabilities, the Random Phase Approximation (RPA) to the correlation energy was employed. This beyond-DFT method has been demonstrated to yield predictions in excellent agreement with experimental results for the relative formation energies of structural polymorphs.$^{1,18,19}$ With this method, the lower-symmetry Cmc2$_1$ phase was predicted to be the thermodynamically-favoured polymorph, with a formation energy 35.8 meV per atom below Cmcm.

Further evidence of Cmcm instability was obtained by computing the phonon dispersions of both Sn$_2$SbS$_2$I$_3$ polymorphs – shown in Fig. 2. Imaginary harmonic modes in the phonon dispersion (i.e. those with negative frequencies; $\omega < 0$) indicate the presence of atomic displacements which lower the system energy. Two strong imaginary modes are witnessed in the Cmcm dispersion, demonstrating dynamic structural instability for this polymorph. Using the ISODISTORT$^{30,41}$ package to visualise the imaginary-mode phonon eigenvectors, we confirm that these energy-lowering distortions correspond to different, equivalent Cmcm $\rightarrow$ Cmc2$_1$ structural transitions (Fig. S5, ESI†).

In contrast, no imaginary modes are observed for the Cmc2$_1$ polymorph. Thus we find the Cmc2$_1$ polymorph to exhibit both thermodynamic and dynamic stability, with converse behaviour for the Cmcm phase. We propose that experimental reports of centrosymmetric Cmcm Sn$_2$SbS$_2$I$_3$ are the result of macroscopic averaging over locally non-centrosymmetric Cmc2$_1$ configurations. Similar to other ns$^2$ cation materials,$^{22,29,33}$ this polar phase behaviour is driven by a second-order (pseudo) Jahn–Teller instability, in which the off-centring of the Sb(III) ions leads to enhanced bonding interactions between the sp-hybridised Sb ns$^2$ lone pair and the anion $p$ states (yielding a small degree of Sb $p$ character at 5 eV below the valence band maximum (VBM); Fig. 5a).

Spontaneous lattice polarisation

In the Cmc2$_1$ ground-state structure, the lack of inversion symmetry results in a spontaneous lattice polarisation $\Delta P = 37.0 \mu\text{C cm}^{-2}$ (calculated within the Berry phase formalism of the Modern Theory of Polarisation).$^{42}$ The strong polarity places Sn$_2$SbS$_2$I$_3$ next to the likes of ferroelectric oxide perovskites such as BaTiO$_3$ ($\approx 27 \mu\text{C cm}^{-2}$)$^{43}$ and KNbO$_3$ ($\approx 30 \mu\text{C cm}^{-2}$), well above that of MAPbI$_3$ (‘MAPI’) (4.4 $\mu\text{C cm}^{-2}$)$^{44}$ and the archetypal ‘photoferroic’ SbSI (11 $\mu\text{C cm}^{-2}$).$^{29,45}$ The mirror (m) and $c$-glide planes of the Cmc2$_1$ space group result in zero polarisation in

![Fig. 2](image-url)

Fig. 2 Simulated harmonic phonon dispersions of Sn$_2$SbS$_2$I$_3$ in the Cmcm (a) and Cmc2$_1$ (b) crystal structures, alongside vertical plots of the atom-projected phonon density of states. Generated using ThermoPlotter.$^{27}$ Brillouin zone path shown in Section S10a (ESI†).
I, CmcS, metal halides. 1,32,46 Significant covalency is indicated by the small Born effective charges (Table 2) due to structural instability. 47,49 Comparison to their formal oxidation states

To calculate the barrier to polarisation switching, the Nudged Elastic Band (NEB) method was employed to map out the potential energy surface (PES) along the minimum-energy path between Cmc21 configurations (Fig. 3).

We find that the Cmcm phase corresponds to the transition state between Cmc21 configurations, with no local stability around this saddle point on the PES. Consequently, the energetic barrier to ferroelectric switching corresponds to the relative energy of the Cmcm and Cmc21 polymorphs: \( \Delta E = 35.8 \text{ meV per atom} \). This value gives rise to a moderate coercive field – calculated as 750 kV cm\(^{-1}\) for a single-crystal ferroelectric domain, using Landau theory (eqn (S1), ESI†). While the actual value will likely be at least an order of magnitude below this, due to a number of effects including domain formation, it places this material in a range intermediate between the weakly-polar lead-halide perovskites52 and the stronger oxide perovskites, as might be expected for a lone-pair chalcogenide material.

To demonstrate the stability of lattice polarisation at finite temperatures, we performed Molecular Dynamics (MD) simulations for Sn2SbS2I3 within an NVT ensemble at temperatures of 300 K and 500 K (Section S8, ESI†). Upon distortion from Cmcn to Cmc21, the two nearest-neighbour S atoms for Sb become inequivalent, forming short (in the polarisation direction) and long Sb–S bonds (Fig. 4) for a single-crystal ferroelectric phase. The Sb–S bond lengths become equivalent and the probability densities (at which point the transition state between Cmc21 configurations (Fig. 3). The resulting mixed ionic-covalent bonding gives rise to strong lattice polarisation, with large, anisotropic Born effective charges (Table 2) and dielectric tensor \( (e_{\alpha\beta\gamma} = [51.3, 18.2, 22.4]) \). 1,32,47,48

![Fig. S25, ESI†](https://example.com/figs25.png), allowing the polarisation dynamics to be visualised through the Sb–S bond lengths. As shown in Fig. 4, no appreciable switching of the Sb–S bonds (corresponding to polarisation switching) is observed for the room-temperature MD runs, within the simulation timescale. On the other hand, transient hopping of Sb atoms occurs during the \( T = 500 \text{ K} \) runs, as the material approaches a phase transition to higher-symmetry Cmcm at which point the Sb–S bonds become equivalent and the probability densities merge; Fig. S25, ESI†, indicating a significant decrease in both the strength and stability of lattice polarisation at elevated temperatures. These results confirm the persistence of polar...
distortions at room temperature and dynamic fluctuations at 500 K. We cannot comment on the size of the polar domains that would be formed, however.

The presence of this previously-hidden polar distortion in Sn₂SbS₂I₃ poses several exciting prospects. In terms of PV applications, spontaneous polarisation can produce open-circuit voltages above the electronic band gap, via the Bulk Photovoltaic Effect, potentially allowing efficiencies above the standard limit for a single-junction solar cell.⁵³-⁵⁶ Moreover, the combination of ferroelectric behaviour and spin–orbit coupling could permit switchable spin texture for ‘ferroelectric Rashba semiconductor’ applications,⁵⁷ while the effect on longitudinal optical (LO) phonons could favour polaron formation.⁵⁸

**Electronic structure**

The electronic band structure of Cmc₂₁ Sn₂SbS₂I₃ is shown in Fig. 4. The band gap is direct, occurring at the Y high-symmetry k-point – which corresponds to maximum antiphase interactions along the conventional a crystal direction (i.e. along the (Sn₂SbS₂I₃)ₙ chains in Fig. 1). The fundamental energy gap is calculated as $E_g = 1.08 \, \text{eV}$, placing it in the ideal range for a photovoltaic absorber material, with a ‘detailed-balance’ efficiency limit of 32.5%.⁶²

As illustrated by the orbital-projected density of states and band-edge charge densities in Fig. 5a and Fig. S13, S14 (ESI†), the conduction band minimum (CBM) arises from Sb p–I p interactions, while the VBM is comprised of antibonding interactions between the Sn 5s³ lone pair and both anion p states (Fig. 6). Notably, this electronic structure allows the explanation of the reported ‘anomalous’ trend in band gap energies within the (Sn₂SbS₂I₃)ₙ chains (Fig. 1). The fundamental energy gap is calculated as $E_g = 1.08 \, \text{eV}$, placing it in the ideal range for a photovoltaic absorber material, with a ‘detailed-balance’ efficiency limit of 32.5%.⁶²

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The optical absorption spectrum, shown in Fig. 4, exhibits a weak onset at the fundamental electronic band gap $E_g = 1.08 \, \text{eV}$. There are two primary origins of this behaviour. Firstly, we find a low electronic degeneracy at the band extrema (Fig. 5a and Fig. S16, S17, ESI†), itself a consequence of the low crystal symmetry, which rapidly increases with many more interband transitions available at $E \geq 1.4 \, \text{eV}$. Another contributing factor is a weak transition dipole moment between the VBM and CBM electronic states (Fig. S15–S17, ESI†) – a consequence of both symmetry restriction and low spatial overlap. In the centrosymmetric Cmc₂₁ structure, the even (gerade) parity of both the VBM and CBM wavefunctions about the crystal inversion centre results in a formally symmetry-forbidden transition at the direct gap (as the electric dipole operator is of odd parity, thus yielding an overall zero optical transition matrix element; Section S6, ESI†). For the Cmc₂₁ ground-state polymorph, this symmetry selection rule is broken by the shift in Sb positions (removing the inversion symmetry) as well as spin–orbit splitting, however these effects represent a relatively minor perturbation to the electronic structure ($\Delta E_{g,\text{Cmc}_{21} vs. \text{Cmc}_{21}} = 0.03 \, \text{eV}$; Fig. S11, ESI†). Consequently, while the direct VBM → CBM transition is no longer formally forbidden in the Cmc₂₁ structure, the optical transition matrix element remains weak due to symmetry restraints, compounded by a spatial separation of the VBM and CBM states (Fig. S14, ESI†). The combination of a rapidly increasing joint density of states...
By introducing electronic states within the bandgap, defects can facilitate carrier trapping and annihilation, thus reducing the open-circuit voltage \( (V_{oc}) \) and photovoltaic efficiency. A primary driving factor behind the surge in research interest for ns\(^3\)-cation PIMs is their potential to exhibit defect tolerance – facilitating high efficiencies despite low-cost solution synthesis.\(^{4,69}\) Sn\(_2\)SbS\(_2\)I\(_3\) exhibits several material properties which are known to contribute to defect tolerance. Firstly, we find the cation s\(^2\) and anion p orbitals interact to produce a valence band maximum of anti-bonding character. This bonding behaviour is illustrated by the Crystal Orbital Hamiltonian Population\(^{70,71}\) analysis shown in Fig. 6, which decomposes the electronic density of states into regions of bonding and anti-bonding orbital interactions. The cation ns\(^3\)-anion p anti-bonding interaction produces a high energy VBM, with an ionisation potential of 5.06 eV (Fig. S9, ESI\(^\dagger\)) – less than that of MAPI (5.70 eV),\(^{72}\) SbSI (5.37 eV),\(^{30}\) and Sb\(_3\)S\(_5\) (5.13 eV),\(^{35}\) and slightly larger than that of FaSnI\(_3\) (4.88 eV)\(^{73}\) – favouring the formation of shallow acceptor defects which are innocuous to PV performance. The substantial mixed iono-covalent character and lattice polarisability in Sn\(_2\)SbS\(_2\)I\(_3\), discussed previously, results in a strong dielectric screening \( (\varepsilon_{x,y,z} = [51.3, 18.2, 22.4]) \) that will limit the electrostatic interactions between defects and charge carriers, thus reducing the probability of carrier capture and trap-mediated recombination.\(^{1,32}\)

One-dimensional atomic chain structures, exhibited by this (Fig. 1) and related materials such as Sb\(_2\)Se\(_3\),\(^{35}\) BiO\(_2\),\(^{12}\) and SbSI\(^{29,30}\) can yield benign grain boundaries, greatly reducing charge-carrier recombination in polycrystalline absorber materials.\(^{32,74}\) The small electronic band gap \( (E_g \sim 1.1 \text{ eV}) \), wide conduction and valence bands, and relatively small electron effective mass \( (m_e = 0.29) \) also favour defect-tolerant behaviour in this material.\(^1\) Indeed, the presence of moderate defect tolerance is partially suggested by the impressive PV efficiency \( (\eta > 4\%) \) and photoluminescence lifetimes \( (> 7 \text{ ns}) \) obtained by Nie \textit{et al.}\(^4\) in the first experimental device fabrication for this material.

In conclusion, we present a theoretical characterisation of the Sn\(_2\)SbS\(_2\)I\(_3\) photovoltaic absorber. While experimental investigations have reported a non-polar, centrosymmetric \( Cmcm \) crystal structure, we propose that this in fact represents a macroscopic average over multiple \( Cmcm \) configurations. Crucially, this leads to the prediction of ferroelectricity, with promising implications for high-efficiency photovoltaic operation and other technological applications.

Through \textit{ab initio} calculation of the electronic and optical properties, we identify an ideal electronic band gap for a photovoltaic absorber \( (E_g = 1.08 \text{ eV}) \), with power-conversion efficiencies \( \eta_{\text{max}} > 30\% \) at the radiative limit. These features, alongside several properties related to ‘defect tolerance’, present a promising outlook for the potential application of both this material and other unexplored members of the A\(_2\)BCh\(_2\)X\(_3\) class. Considering only isoelectronic, earth-abundant and non-toxic substituents, there are in fact 36 possible elemental combinations for the quaternary group IV/V chalcogenide family \( (A = \text{Sn, Ge}; \ B = \text{Sb, Bi}; \ Ch = \text{O, S, Se}; \ X = \text{I, Br, Cl}) \) which may be synthesisable – the majority of which have not yet been

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**Potential for defect tolerance**

One of the primary origins of non-radiative electron–hole recombination is defects in the bulk crystal and at interfaces.
investigated. Thus the performance potential in this system opens a zoo of compositional permutations for solution-processed ferroelectric and optoelectronic devices.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

† The substitution of Sn with Pb, Sb with Bi and S with Se has been demonstrated for Sn$_2$SbS$_2$I$_3$.‡

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