Thermodynamics, Electronic Structure, and Vibrational Properties of Sn \( n (S^{1– x} Se^x) \) m Solid Solutions for Energy Applications

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**ABSTRACT:** The tin sulphides and selenides have a range of applications spanning photovoltaics and thermoelectrics to photocatalysts and photodetectors. However, significant challenges remain to widespread use, including electrical and chemical incompatibilities between SnS and device contact materials and the environmental toxicity of selenium. Solid solutions of isostructural sulphide and selenide phases could provide scope for optimising physical properties against sustainability requirements, but this has not been comprehensively explored. This work presents a detailed modelling study of the $Pnma$ and rocksalt Sn$_x$(S$_{1-x}$Se$_x$)$_2$ and Sn$_x$(S$_{1-x}$Se$_x$)$_3$ solid solutions. All four show energetically favourable and homogenous mixing at all compositions, but rocksalt Sn$_x$(S$_{1-x}$Se$_x$) and Sn$_x$(S$_{1-x}$Se$_x$)$_2$ are predicted to be metastable and accessible only under certain synthesis conditions. Alloying leads to predictable variation of the bandgap, density of states and optical properties with composition, allowing Sn$_x$S$_{1-x}$ to be “tuned down” to the ideal Schockley-Queisser bandgap of 1.34 eV. The impact of forming the solid solutions on the lattice dynamics is also investigated, providing insight into the enhanced performance of Sn$_x$(S$_{1-x}$Se$_x$) solid solutions for thermoelectric applications. These results demonstrate that alloying affords facile and precise control over the electronic, optical and vibrational properties, allowing material performance for optoelectronic applications to be optimised alongside a variety of practical considerations.

**Introduction**

The current drive towards energy solutions to reduce our dependence on fossil fuels has prompted wide-ranging research to identify new, improved functional materials for cleaner energy generation and storage. Photovoltaics (PV) is an established technology for primary energy generation, but identifying cost-effective and environmentally benign materials for efficient light-to-electricity conversion remains an active research area.\(^1\) Thermoelectric materials are another highly promising development area,\(^2,3\) allowing waste heat to be recovered as electricity from e.g. industrial processes and combustion engines, and recent breakthroughs are steadily pushing towards higher-efficiency thermoelectric generators.\(^4\) Hydrogen has long been seen as a clean alternative fuel for combustion engines, and identifying efficient photocatalysts to generate H$_2$ by splitting water remains an important research goal.\(^5,6\)

The tin sulphides and selenides are unique in having broad applications across the energy materials domain. $Pnma$ SnS has a large optical-absorption coefficient and a bandgap well matched to the solar spectrum, and as such has been widely studied as a PV absorber.\(^6-8\) The structurally analogous $Pnma$ SnSe was recently shown to have a record-breaking thermoelectric figure of merit,\(^9\) with hole doping enabling efficient energy harvesting over a wide range of operating temperatures.\(^10\) SnS$_2$ and SnSe$_2$ have potential applications as photocatalysts for water splitting\(^11\) and as photodetectors,\(^12\) respectively, with the added advantage that the pseudo-2D layered structure can be formed into a variety of high surface-area nanomaterials.\(^13\) The tin selenides have also shown potential for PV applications\(^11,14-16\) and as components in lithium-ion batteries\(^11,16\) and supercapacitors.\(^17\)

These materials are not without their drawbacks, however. The environmental toxicity of selenium limits the widespread use of tin selenides, but while $Pnma$ SnS has been studied as an alternative thermoelectric,\(^18-20\) the greatly reduced performance indicates that complete substitution of selenium by sulphur cannot sustain the requisite material properties. Another major issue is that while SnS has been intensively researched as a cost-effective PV absorber, SnS-based devices have so far fallen short of the efficiencies obtained with alternative materials,\(^5,7,21\) which may be due to several factors including the propensity of SnS to form phase impurities, for example by excess oxidation of Sn during synthesis, a mismatch in energy levels (band offsets) between SnS and the contact materials in devices, and chemical incompatibility between SnS and the contact materials leading to the formation of impurities through detrimental reactions.\(^21,22\)

Due to the ability of Sn to adopt both Sn(II) and Sn(IV) oxidation states\(^23\) and the structural flexibility of the Sn lone pair, the tin sulphides and selenides form several isostructural stable and metastable phases. Five monosulphide/monoselenide phases have been identified or proposed, viz. orthorhombic $Pnma$ and $Cmcm$,\(^24-26\) and cubic rocksalt,\(^27\) zincblende\(^28\) and $P2_13$ (“π-cubic”),\(^29,30\) alongside the di- and sesqui-sulphide/selenide phases SnS$_3$/SnSe$_2$ and Sn$_2$S$_3$/Sn$_2$Se$_3$.\(^31-33\)
The starting point for our calculations is a set of optimised supercells built from the primitive cells of *Pnma* and rocksalt SnS, SnS$_2$ and Sn$_2$S$_3$ with the sulphur and tin atoms shown in yellow and blue, respectively. The images were prepared using VESTA.$^{35}$

![Image](image_url)

**Figure 1.** Structures of *Pnma* and rocksalt SnS, SnS$_2$ and Sn$_2$S$_3$ with the sulphur and tin atoms shown in yellow and blue, respectively. The images were prepared using VESTA.$^{35}$

<table>
<thead>
<tr>
<th>System</th>
<th>Supercell (# Atoms)</th>
<th># Structures (Unique)</th>
<th>k-Point Sampling</th>
<th>Phonon Supercell (# Atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pnma</em> Sn(S$_1$,Se$_x$)$_2$</td>
<td>2×1×2 (32)</td>
<td>65,536 (2,446)</td>
<td>4×4×4</td>
<td>2×1×2 (128)</td>
</tr>
<tr>
<td>Rocksalt Sn(S$_1$,Se$_x$)$_2$</td>
<td>2×4×2 (32)</td>
<td>65,536 (652)</td>
<td>4×2×4</td>
<td>2×1×2 (128)</td>
</tr>
<tr>
<td>Sn(S$_1$,Se$_x$)$_3$</td>
<td>2×2×2 (24)</td>
<td>65,536 (1,056)</td>
<td>4×4×2</td>
<td>2×2×2 (192)</td>
</tr>
<tr>
<td>Sn$_2$(S$_1$,Se$_x$)$_3$</td>
<td>1×1×1 (20)</td>
<td>4,096 (1,072)</td>
<td>4×8×3</td>
<td>2×2×2 (160)</td>
</tr>
</tbody>
</table>

Table 1. Summary of the solid solutions studied in this work with the supercell sizes, number of configurations, k-point sampling and phonon supercells used for finite-displacement lattice-dynamics calculations. $^a$The k-point sampling is specified as the number of subdivisions along each reciprocal lattice vector in a Monkhorst-Pack k-point grid.$^{36}$

The similar sulphide and selenide phase spaces and the similar covalent radii of S and Se (100 vs. 115 pm)$^{35,36}$ makes it a natural step to consider Sn$_x$(S$_1$.Se$_2$)$_n$ solid solutions as a route to fine-tuning the material properties and balancing performance against sustainability requirements. A small number of studies have explored this in the context of thermoelectric materials,$^{35-37}$ and have demonstrated that substituting a small amount of the Se in *Pnma* SnSe can enhance the performance compared to both the SnS and SnSe endpoints. However, there has been very little research into solid solutions of the other phases, nor more generally into using this strategy to adapt the material properties for other applications.

In this work, we expand our recent theoretical studies of the Sn$_x$S$_m$ system$^{23,38,39}$ and make use of high-throughput first-principles computational modelling and statistical thermodynamics to explore the stability and properties of *Pnma* and rocksalt Sn(S$_1$. Se$_x$)$_2$, Sn(S$_1$. Se$_x$)$_3$, and Sn$_2$(S$_1$. Se$_x$)$_3$ solid solutions. Our results show that forming the solid solutions is facile and enables the structural, electronic and vibrational properties of the four systems to be systematically tuned between the endpoints, providing a route to optimising the properties for energy applications. We also address the practical challenges associated with accurate, high-throughput calculations on large collections of structures, providing general direction for future studies on other solid solutions.

**Experimental section**

The starting point for our calculations is a set of optimised supercells built from the primitive cells of *Pnma* and rocksalt SnS, SnS$_2$ and Sn$_2$S$_3$ and the corresponding isostructural selenides. The structures of the sulphide endpoints$^{23,38}$ are shown in Figure 1.

Solid-solution models were built using the open-source Transformer library$^{40}$ by enumerating all the symmetry-invariant structures formed by successively substituting the halogen atoms in the parent supercells together with the associated degeneracies.

We found that taking supercells with 20-32 atoms yielded a manageable number of unique configurations for high-throughput density-functional theory (DFT) calculations (Table 1).

Each unique structure was fully volume relaxed. To speed up this process, structures with higher S and Se content were optimised starting from the lattice parameters of the respective sulphide and selenide endpoints. The total energies after optimisation were combined with the degeneracies to construct the thermodynamic partition functions and to obtain the free energies of mixing and statistical averages of material properties.

The DFT calculations were performed within the pseudopotential plane-wave DFT formalism implemented in the Vienna Ab initio Simulation Package (VASP) code.$^{31}$ Based on previous work on the tin sulphide system,$^{23}$ we used the PBEsol generalised-gradient approximation (GGA) exchange-correlation functional$^{42}$ with the DFT-D3 dispersion correction$^{43}$ (i.e. PBEsol-D3). The basis set was defined with a 600 eV kinetic-energy cutoff, and the k-point sampling listed in Table 1 was used to integrate the electronic Brillouin zone. The core electrons were treated with projector augmented-wave (PAW) pseudopotentials including the Sn 5s, 5p and 4d, S 3s and 3p and Se 4s and 4p electrons in the valence shell.$^{44,45}$

Tolerances of 10$^{-8}$ eV and 10$^{-2}$ eV Å$^{-1}$ were applied to the total energy and forces during wavefunction minimisation and geometry optimisation, respectively. The precision of the charge-density grids was set automatically to avoid aliasing errors, the PAW projection was performed in reciprocal space, and non-spherical contributions to the gradient corrections inside the PAW spheres were accounted for.

As detailed in the Results and discussion, after benchmarking the accuracy and efficiency of several techniques for modelling the electronic structure we opted to use the SCAN meta-GGA functional$^{46}$ for calculations on the full set of structures in the four solid-solution models, and to assess the accuracy of a subset using “single-shot” (non-self-consistent)$^{47}$ hybrid calculations with the HSE 06 functional.$^{48}$ For both, the plane-wave cutoff was reduced to 400 eV, which we found sped up the calculations without significant
loss of accuracy. The origin of the k-point meshes was shifted to \( k = (0, 0, 0) \) (Γ) to include a larger number of irreducible k-points in the Brillouin-zone sampling, and the integration was performed using the Blöchl-corrected tetrahedron method. Optical properties were evaluated from frequency-dependent dielectric functions obtained within the independent-particle approximation, with equal numbers of occupied and virtual states being included in the calculations to converge the sum over empty states.

Lattice-dynamics calculations were performed using the Phonopy package\(^{31,52}\) with VASP as the force calculator. The supercell expansions used to evaluate the force-constant matrices with the Parlinski-Li-Kawazoe method\(^{53}\) are listed in Table 1. For the single-point force calculations, the k-point sampling was reduced according to the chosen supercell expansions and the same tolerance of 10^-6 eV on the total energy used for the other calculations was applied during the wavefunction optimisation. Phonon calculations on the sulphide endpoints for comparison were taken from our previous work, and analogous calculations were performed on the selenide endpoints. Phonon DoS curves were computed by interpolating the phonon frequencies onto uniform Γ-centred q-point meshes with between 24x24x24 and 48x48x48 subdivisions and applying a Gaussian broadening with \( \sigma = 0.15 \) THz (approx. 5 cm^(-1)). As discussed below, it was not feasible to perform lattice-dynamics calculations on all the structures, so selected compositions were sampled using a structural-fingerprinting technique to assess structural similarity and thereby identify structurally diverse chalcogen arrangements.

Results and discussion

Mixing energies. To assess the thermodynamic stability of the solid solutions, we calculated for each system the Gibbs free energy of mixing \( G_{mix}(x_{Se}, T) \) as a function of Se fraction \( x_{Se} \) and temperature \( T \).

For a given composition, the Gibbs energy \( G(x_{Se}, T) \) is calculated from the thermodynamic partition function \( Z(x_{Se}, T) \):

\[
Z(x_{Se}, T) = \sum_{n=1}^{N} g_n \exp(-E_n/k_B T)
\]

where the sum runs over \( N \) symmetry-in-equivalent structures with total energy \( E_n \) and degeneracy \( g_n \) and \( k_B \) is Boltzmann’s constant. Since the structures are fully volume relaxed (i.e. \( p = 0 \)), the enthalpy \( U + pV \) is equal to the internal energy \( U \) and \( G(x_{Se}, T) \) can be calculated via the bridge relation:

\[
G(x_{Se}, T) = -k_B T \ln Z(x_{Se}, T)
\]

Further details can be found in Ref. 54. We note that the effect of finite pressure could be accounted for by adding a correction \( pV_n \) to each \( E_n \), and that the total energies do not include vibrational contributions to the free energy\(^{23}\) as to do so would be infeasible for the ~5,000 configurations in this study.

\( G_{mix}(x_{Se}, T) \) is then calculated by comparing the free energy of the mixed phase to the phase-separated endpoints according to:

\[
G_{mix}(x_{Se}, T) = G(x_{Se}, T) - [(1 - x_{Se}) G(x_{Se} = 0) + x_{Se} G(x_{Se} = 1)]
\]

where \( G(x_{Se} = 0) \) and \( G(x_{Se} = 1) \) are the Gibbs energies of the sulphide and selenide endmembers, respectively, which, since \( g_n \) is unity, are simply equal to the calculated DFT total energies \( E_n \).

Figure 2 shows the calculated mixing energies for each of the four systems as a function of composition and formation temperature. We predict favourable mixing at all compositions, with \( G_{mix} \) for the 50/50 mixtures ranging from -1.63 kJ mol\(^{-1}\) atom\(^{-1}\) for rocksalt \( \text{Sn}(\text{S}_{x}\text{Se}_{1-x}) \) to -2.24 kJ mol\(^{-1}\) atom\(^{-1}\) for \( \text{Sn}(\text{S}_{x}\text{Se}_{1-x}) \) at a formation temperature of 900 K. Comparing the enthalpy and entropy terms (see Figure S1.1) shows a mixing enthalpy \( H_{mix} \) of -0.49-0.70 kJ mol\(^{-1}\) atom\(^{-1}\), which we ascribe to the strain induced by the small size difference between S and Se, and a larger \( T S_{mix} \) term of 2.18-2.93 kJ mol\(^{-1}\) atom\(^{-1}\) from configurational entropy.

A recent study employed an alternative first-principles cluster expansion technique to examine the stability of \( \text{Pnma} \) \( \text{Sn}(\text{S}_{x}\text{Se}_{1-x}) \) solid solutions.\(^{57}\) This study reported formation energies ranging from 0.24-0.48 kJ mol\(^{-1}\) atom\(^{-1}\) for structures with the 50/50 composition, and predicted homogenous mixing with calculated mixing energies of -0.96, -1.93 and -2.89 kJ mol\(^{-1}\) atom\(^{-1}\) at 300, 450 and 600 K. Our calculations reproduce the mixing enthalpy of 0.48-0.59 kJ mol\(^{-1}\) atom\(^{-1}\) between 300-1100 K and mixing energies between -0.25 and -0.99 kJ mol\(^{-1}\) atom\(^{-1}\) from 300-600 K, which we consider sufficiently similar given the differences in methodology and computational setup.

To check the convergence of our results with respect to the supercell size, we performed additional calculations on the \( \text{Pnma} \) \( \text{Sn}(\text{S}_{x}\text{Se}_{1-x}) \) and \( \text{Sn}(\text{S}_{x}\text{Se}_{1-x}) \) solid solutions using smaller 1x1x2 and 2x2x1 expansions with 12 and 16 atoms, respectively. We obtained differences of up to 0.04 and 0.26 kJ mol\(^{-1}\) atom\(^{-1}\) in the values of \( H_{mix} \) and \( G_{mix} \) calculated 900 K, which suggests that our results are reasonably well converged with respect to the cell size.

In our recent computational study of the energetic and dynamical stability of the tin sulphides,\(^{23}\) we established that \( \text{Pnma} \) \( \text{SnS} \) was energetically more stable than the rocksalt phase, and that the sesquisulphide \( \text{SnS}_3 \) was slightly above the energetic convex hull but ultimately stabilised with respect to decomposition by its larger vibrational entropy. The calculated energies of rocksalt \( \text{SnS} \) and \( \text{SnSe} \) place them 10.45 and 2.6 kJ mol\(^{-1}\) per \( \text{Sn} \) formula unit (F. U.), respectively, above the corresponding \( \text{Pnma} \) phases on the convex hull (see Figure S1.2). The difference falls almost linearly with increasing Se content, indicating that the rocksalt structure becomes more energetically accessible towards the selenide endmember but remains metastable with respect to the competing \( \text{Pnma} \) phase.

\( \text{SnS}_3 \) is predicted based on lattice energy to be unstable to decomposition into \( \text{SnS}_2 \) and \( \text{Pnma} \) \( \text{SnS} \), but only by 0.03 kJ mol\(^{-1}\) per F. U., which is in the range of differences in vibrational zero point energy.\(^{23}\) On the other hand, the hypothetical selenide \( \text{SnSe}_3 \) is somewhat less stable, with disproportion into \( \text{SnSe} \) and \( \text{SnSe}_2 \) favoured by a much larger 2.4 kJ mol\(^{-1}\) per F. U. (Figure S1.2). Disproportion of the mixed composition \( \text{Sn}_x(\text{Se}_{3-x}) \) into \( \text{SnSe}_2 \) and \( \text{SnSe}_3 \) is favoured by 0.9 kJ mol\(^{-1}\) at 300 K, and higher temperatures further destabilise the mixed phase, with the energy difference rising to ~1.8 kJ mol\(^{-1}\) at 900 K. This suggests that it may be possible to prepare \( \text{Sn}_x(\text{Se}_{3-x}) \) solid solutions with small Se content, whereas higher Se content would lead to phase separation. We note that an alternative structure has been proposed for \( \text{SnSe} \) which was found to be 1.7 meV per atom (0.8 kJ mol\(^{-1}\) per F. U.) lower in energy than the \( \text{SnS}_2 \) structure examined here,\(^{33}\) although based on the present results this would still be unstable to phase separation.
Figure 2. Per-atom mixing free energies $G_{\text{mix}}$ as a function of Se fraction $x_{\text{Se}}$ for \textit{Pnma} (a) and rocksalt (b) Sn($S_{1-x}Se_x$), Sn($S_{1-x}Se_x$)$_2$ (c) and Sn$_2(S_{1-x}Se_x)$$_3$ (d) solid solutions. The line colours denote formation temperatures from 300 K (blue) to 1100 K (orange).

Finally, it is also worth noting that the mixing energy from alloying could potentially be used to stabilise a bulk phase and minimise or prevent unfavourable reactions with contact materials, such as have been identified as a major contributing factor in the poor performance of SnS PV devices.\textsuperscript{21}

\textit{Structural properties.} The thermodynamic average $\langle X(x_{\text{Se}}) \rangle$ of a general physical property $X$ at a given composition can be formed by weighting the properties of each structure in the solid-solution model by the occurrence probabilities $P_n$ obtained from the partition function as:

$$P_n = \frac{1}{Z} g_n \exp(-E_n/k_BT)$$

The averaged volume for a specific composition, for example, can be calculated according to:

$$\bar{V} = \sum_{n=1}^{N} P_n V_n$$

Our calculations predict that the volume expansion of all four solid solutions is close to linear with Se content (Figure 3). The relative expansion between the sulphide and selenide endpoints mirrors the chalcogen content, falling in the order of Sn($S_{1-x}Se_x$)$_2$ > Sn$_2(S_{1-x}Se_x)$$_3$ > Sn($S_{1-x}Se_x$)$_3$ > \textit{Pnma} Sn($S_{1-x}Se_x$) ≈ rocksalt Sn($S_{1-x}Se_x$).
To quantify the trend, we fitted the $\tilde{V}(x_{\text{Se}})$ data to the model function:

$$\tilde{V}(x_{\text{Se}}) = (1 - x_{\text{Se}})V(x_{\text{Se}} = 0) + x_{\text{Se}}V(x_{\text{Se}} = 1) - bx_{\text{Se}}(1 - x_{\text{Se}})$$

where $V(x_{\text{Se}} = 0)$ and $V(x_{\text{Se}} = 1)$ are the volume per formula unit of the sulphide and selenide endpoints, respectively, and $b$ is a “bowing parameter” that captures the deviation from linearity. The fitted $b$ values are small, ranging from 0.49% of the cell volume of the SnS$_2$ endpoint to 1.12% of the volume of $Pnma$ SnS (see Table S2.1). Comparing the results for the $Pnma$ Sn(S$_1$,Se$_3$) and Sn(S$_1$,Se$_2$)$_2$ alloys against those obtained using the smaller supercell expansions (see previous section) showed a difference in the averaged volume of $<0.2$ Å$^3$ per formula unit, indicating the structural properties to be well converged with respect to supercell size.

A comparison of the averaged lattice parameters (see Tables S2.2-S2.5) indicates that all four solid solutions maintain the parent lattice structure and suggests homogenous mixing. This was confirmed by calculating averaged pair-distribution functions (PDFs; $g_{AB}(r)$) as a function of composition for each of the four phases. $g_{AB}(r)$ expresses the probability of finding an atom of species B between $r$ and $r + \Delta r$ from a reference atom of species A relative to the number density $\rho_A = N_A/V$:

$$g_{AB}(r) = \frac{1}{4\pi\Delta r\rho_B} \frac{1}{N_B} \sum_{i=1}^{N_B} \sum_{j=1}^{N_B} \frac{\delta(r - r_{ij})}{r_{ij}}$$

$g_{AB}(r)$ shows peaks at preferred interatomic distances and can be evaluated for pairs of a given atom type (i.e., A = B), for pairs of two different atoms (A $\neq$ B), or across all atomic pairs in the structure.

The all-atom and Sn-S/Sn-Se partial PDFs for five compositions in the Sn$_2$(S$_{1-x}$Se$_x$)$_2$ solid solution are shown in Figure 4. $g(r)$ shows a series of sharp peaks at the various interatomic distances in the Sn$_2$(S$_{1-x}$Se$_x$)$_2$ structure, and the features corresponding to the tin-chalcogen distances can be assigned with reference to $g_{\text{Sn-S}}(r)$ and $g_{\text{Sn-Se}}(r)$. At intermediate compositions, the peaks split into two components that can be assigned to shorter Sn-S and longer Sn-Se distances, indicating that chalcogen substitution leads to small local variations in the Sn coordination environment. Despite this, there is a smooth progression between the PDFs of the sulphide and selenide endpoints, further supporting a homogenous distribution of the chalcogen ions over lattice sites. Simulated PDFs of the $Pnma$ and rocksalt Sn(S$_{1-x}$Se$_x$) and Sn(S$_1$,Se$_2$)$_2$ compositions show similar phenomena (see Figs. S2.1-S2.3).

The ability to fine-tune the cell volume and lattice parameters by varying the composition is noteworthy because it could be used to optimise the lattice match to other materials in a device structure. One example where this would be of value is in the recently reported use of SnS$_2$ in place of CdS as a buffer layer in Cu(In$_{1-x}$Ga$_x$)$_2$Se$_2$ (CIGS) and Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ (CZTS) solar cells. The homogenous distribution of the chalcogen ions is also noteworthy as the microscopic interfaces introduced by preferential clustering could negatively affect the electronic/thermal transport and/or act as recombination centres for electrons and holes. Furthermore, the ability to accommodate the lattice strain induced by cation substitution suggests that these materials may be relatively defect tolerant, with further implications for doping e.g. to improve electrical properties for thermoelectric applications.

**Electronic structure and optical properties.** Several of the endpoints in the tin sulphide and selenide families have optoelectronic properties that make them well suited to important technological applications. The monosulphide and selenide SnS/SnSe have both been extensively studied as PV absorbers, while SnS$_2$ has been highlighted as a potential photocatalyst for water splitting$^{11}$ and SnSe$_2$ has been used in high-performance photodetectors.$^{12}$ The electronic structure of SnSe also plays a key role in its application as a high-performance thermoelectric.$^{9,10}$ However, to see a small number of experimental studies on tin sulphide/selenide thermoelectric materials,$^{35-37}$ relatively little attention has been given to the possibility of tuning the electrical properties by alloying. It is therefore of interest to investigate how forming solid solutions affects the electronic structure and optical responses of these systems.
High-throughput modelling studies must necessarily balance the accuracy of calculated properties against the computational cost of obtaining them. Modelling the electronic structure and related properties presents a particular challenge, as lower-level quantum-mechanical methods such as semi-local DFT invariably underestimate the size of the electronic bandgap with a consequent effect on the dielectric function and derived properties such as the optical absorption coefficient. The PBEsol functional used for geometry optimisation was found to underestimate the bandgaps of the end-point structures by ~0.5-1 eV with respect to experimental measurements. More seriously, whereas more accurate electronic-structure methods showed SnS2 to be narrow-gap semiconductor, PBEsol predicted a qualitatively incorrect near-metallic electronic structure. As discussed in detail in Section 3 of the Supporting Information, we compared the predicted bandgaps obtained with a range of electronic-structure methods against available experimental measurements and found that the SCAN meta-GGA functional struck a good balance between accuracy and cost, allowing us to evaluate the bandgap, density of states and optical properties of the ~5,000 structures in our model with reasonable accuracy.

Figure 5 shows the thermodynamically averaged bandgaps of the four systems as a function of composition, with tabulated values in Tables S3.9-S3.12. The bandgaps fall roughly in the order of Sn(S1−xSex)2 > Pnma Sn(S1−xSex) > rocksalt Sn(S1−xSex) > Sn2(S1−xSex)3. Strikingly, for the Sn(S1−xSex)2 solid solution (Figure 5c), the composition dependence is close to linear and suggests that the gap can be tuned through ~0.9 eV by varying the ratio of S and Se. The calculated SCAN bandgaps of the SnS2 and SnSe2 endpoints are both underestimated at 1.6 and 0.7 eV, respectively, compared to the experimental values of 2.28 and 0.9 eV, suggesting that a wider range of ~1.38 eV would be achievable in practice. For a single-junction solar cell, the Shockley-Queisser limit points to a bandgap of 1.34 eV for the theoretical maximum conversion efficiency of 33.7 %. Presuming a simple linear variation in the gap with composition, and taking the experimental gaps as the endpoints, our calculations suggest this could be achieved by a solid solution with (2.28−1.34)/(2.28−0.9) ≈ 70 % Se content, i.e. Sn(S0.3Sn0.7)2. Taking into account the slight curvature of the graph in Figure 5c, our results predict a lower Se content of about 60 % would be optimum, i.e. Sn(S1−ySey)2. The possibility of “tuning down” SnS2 for PV applications as an alternative to Pnma SnS is an interesting one, as the dichalcogenide system has several practical advantages: the 2D van der Waal’s structure should allow for better control over the crystal growth and alignment, and the Sn(IV) oxidation state would avoid the need to carefully control the chalcogen chemical potential during synthesis to prevent the introduction of phase impurities by “over oxidation” of the metal. We also note that the calculated mixing energies predict that the ~1:2 SnS2/SnSe2 solid solution should be readily formed (c.f. Figure 2).

The calculations predict a much smaller variation in the bandgap of the monochalcogenide Sn(S1−xSex)2 solid solutions (Figure 5a/5b). The SCAN calculations give a range of ~0.2 eV between the bandgaps of the Pnma SnS and SnSe endpoints of 0.85 and 0.66 eV respectively (Figure 5a), compared to the experimental values of 1.06 and 0.95 eV. As for Sn(S1−ySey)2 the dependence is approximately linear with a comparably narrow spread, and the linear trend is consistent with experimental measurements on SnS endpoint solid solutions. The bandgap of Pnma SnS is below the Shockley-Queisser limit for optimum efficiency, and both the present calculations and experimental measurements on the endpoints suggest that alloying with SnSe will not improve upon this. On the other hand, the smaller bandgap could lead to improved electrical properties for thermoelectric applications, which is supported by experi-
imments demonstrating larger carrier concentrations and higher mobilities towards the SnSe endpoint, leading to improved electrical conductivity and better thermoelectric performance.35,36

The rocksalt Sn(S\(_{1-x}\)Se\(_x\)) solid solutions show markedly different behaviour (Figure 5b). The SnS and SnSe endpoints are predicted to have very similar bandgaps, and the calculations suggest a small reduction of \(\sim 0.1\) eV for compositions close to Sn(S\(_{1-x}\)Se\(_x\)) midpoint, this behaviour together with the narrow spread, suggests the rocksalt solid solutions would be tolerant to local variations in composition, although given its predicted metastability the presence of Pnma impurities is likely to be a much larger issue.

Whereas the experimental bandgaps of Pnma SnS and SnS\(_2\) are very similar at 1.06 and 1.10 eV,22 the predicted bandgap of the SnS\(_2\)SnSe endpoint is considerably smaller than that of Pnma SnSe, suggesting a higher degree of compositional tunability in this system (Figure 5d). The SCAN calculations predict SnS\(_2\) to be a narrow-gap semiconductor with a 0.63 eV bandgap, while SnS\(_2\)SnSe is predicted to be a near-metallic system with a gap of 0.19 eV, suggesting highly tunable high electrical conductivity that, in conjunction with the “pseudo 1D” structure (see Figure 1), would in principle make Sn\(_2\)S\(_{1-x}\)Se\(_x\) solid solutions attractive for electronics applications. However, as noted above, stabilising this solid solution may be challenging, and for this reason we do not envisage these materials finding widespread applications.

To estimate the error on the SCAN bandgaps, the gaps of a subset of the structures were evaluated with more accurate “single-shot” (non-self-consistent) HSE 06 calculations using the SCAN wavefunctions (see Section 3 of the Supporting Information). Calculations on the endpoint structures indicated that these non-self-consistent hybrid calculations typically yield bandgaps within a few percent of the self-consistent results at an order of magnitude lower computational cost, and compare favourably to available experimental measurements. The SCAN calculations underestimate the bandgaps of the Pnma Sn\(_{1-x}\)Se\(_x\) (Table S3.13), Sn\(_{1-x}\)Se\(_x\)Pnma and Sn\(_{1-x}\)Se\(_x\)Sn\(_{1-x}\)SnSe\(_x\) structures give bandgaps around 1.4 and 1.2 eV respectively (see Table S3.15), in support of the 70 % Se content predicted to give a target bandgap close to 1.34 eV, and the 0.93/0.37 eV HSE 06 gaps of SnS\(_2\) and SnSe\(_2\) support the qualitative conclusion above regarding the potential for tuning the electrical conductivity.

We also computed averaged bandgaps for the Pnma Sn\(_{1-x}\)Se\(_x\) and Sn\(_{1-x}\)Se\(_x\)Sn\(_{1-x}\)SnSe\(_x\) solid solutions using smaller supercell expansions as outlined above. For the monoclinic solid solution, we observed a large deviation of around 100 meV for all compositions, which suggests this property is more sensitive to the chosen supercell expansion than the structural properties. However, the deviation also occurs for both endpoints, suggesting that the error is constant across the set of structure and the relative changes in bandgaps are reasonably well converged. The two expansions tested for the dichalcogenide solid solution show smaller absolute differences of up to 46 meV. Crucially, for both systems the trends shown in Figure 5 are reproduced with both the supercell expansions tested, and so we would not expect our conclusions on the compositional tunability to be affected by our choice of cell size.

![Figure 6. Electronic density of states (DoS) of the valence and conduction bands of Sn(S\(_{1-x}\)Se\(_x\)) solid solutions with Se fractions x_{Se} = 0 (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The DoS curves are drawn as stacked area plots showing the projections onto Sn (blue), S (red) and Se (orange) atomic states. The energies are referenced to the average Sn 1s core-level eigenvalues and the zero is set to the valence-band maximum of the SnS\(_2\) endpoint (x_{Se} = 0; subplot a).](image)
These analyses show that forming solid solutions provides a means to tune both the band-edge positions and the bandgap. It has previously been shown that poor band alignment to the contact materials in SnS-based PV devices is a likely contributor to the low efficiency realised experimentally,\(^{21,66}\) and indeed forming a solid solution to improve the energy level alignment between SnS and the Zn(Si,Ge) buffer layer led to a significant improvement in efficiency.\(^{6}\) The present results demonstrate that alloying could be used to adjust the band offsets at interfaces for better device performance,\(^{65}\) perhaps balancing this against conversion efficiency if required, or to optimise the electronic structure for photocatalytic reactions.\(^3\)

For thermoelectric applications, the changes in the density of states at the band edges also suggests that alloying could be used to promote so-called “band convergence”, where increasing the density of states at the band edges allows the Seebeck coefficient to be increased without degrading the electrical conductivity. This is a proven mechanism for stabilising the performance of thermoelectric devices over a wider range of operating temperatures.\(^{3,66}\) This is in addition to the potential enhancements in carrier concentrations and mobilities and electrical conductivity that can result from lowering the bandgap, albeit often at the expense of a reduced Seebeck coefficient, as well as the potential for higher defect tolerance in the mixed phases.

The electronic structure defines the energy-dependent complex dielectric function \(\varepsilon(E) = \varepsilon_{\text{re}}(E) + i\varepsilon_{\text{im}}(E)\), which in turn determines optical properties including the wavelength-dependent absorption coefficient \(\alpha(\lambda)\), a key parameter for PV and photocatalysis applications. Using the SCAN electronic-structure calculations on the four solid solutions, we modelled the composition dependence of the dielectric functions,\(^{50}\) allowing us to predict the variation in the wavelength-dependent refractive index \(n(\lambda)\), the extinction coefficient \(k(\lambda)\) and the absorption coefficient \(\alpha(\lambda)\) (Fig. 7, Figs. S15-S18).

The optical properties of all four solid solutions are predicted to vary smoothly with composition, which again suggests that alloying should enable controlled tuning between the sulphide and selendide endpoints. There is a consistent red shift in the absorption profile with increasing Se content, as expected given the typical bandgap reductions in Figure 5, together with an enhancement of \(\alpha(\lambda)\) at infrared and high-energy UV wavelengths and a decrease in the visible and mid-to-near UV. It should be noted that underestimation of the bandgap with SCAN would lead to a red-shifted absorption profile, and thus it is likely that the enhanced infrared absorption would translate to enhanced visible absorption in practice. On the other hand, the independent-particle approximation used to simulate the dielectric function tends to overestimate transition energies and blue shift the simulated absorption profile,\(^{67}\) so there may be a partial cancellation of errors.

As for the bandgaps, we recalculated the DoS and optical properties of a subset of the structures in each solid solution using non-self-consistent HSE 06 (see Figs. S19-S38). Comparing the SCAN and HSE 06 DoS curves shows a rigid shift of the band edges and some scaling of the energies of deeper valence and conduction states with relatively small changes to feature intensity. The shifts of the band edges produce a uniform shift and reduction in intensity of the low-energy dielectric functions, confirming both that the absorption intensity shifts towards shorter visible wavelengths with more accurate electronic-structure techniques and that the qualitative changes in band positions and optical properties with composition are reasonably well reproduced by the SCAN calculations.
Perhaps the most important result in Figure 7 is that the \textit{Pnma} Sn(Si$_x$Se$_{1-x}$) and Sn(Si$_{0.5}$Se$_{0.5}$)$_2$ solid solutions are predicted to have a comparable $\alpha$, which suggests that the exemplary optical-absorption properties of SnS should be similar in Sn(Si$_x$Se$_{1-x}$)$_2$, allowing it to be applied in a thin-film configuration. Indeed, experiments have highlighted the strong optical absorption of very thin SnSe flakes for photodetection.\cite{12} For the more established SnS, the calculations suggest that alloying with SnSe would enhance the absorption in the longer-wavelength part of the visible spectrum, although this would be counteracted by a reduction in the absorption at shorter wavelengths, suggesting little overall benefit for PV applications.

\textbf{Lattice dynamics.} Designing an optimised thermoelectric material entails balancing the electrical conductivity $\sigma$ and Seebeck coefficient $S$ against a low lattice and electronic thermal conductivity $\kappa_{\text{latt}} \div \kappa_{\text{el}}$, which is usually expressed by the dimensionless figure of merit $ZT$:\cite{3}

$$ZT = \frac{S^2\sigma}{\kappa_{\text{latt}} + \kappa_{\text{el}}} T$$

$\kappa_{\text{el}}$ is typically negligible in semiconducting systems, so a major focus of thermoelectric research has been maintaining $\kappa_{\text{latt}}$ while exploiting phonon anharmonicity,\cite{68,74} together with their favourable electrical properties.\cite{66} However, while a $ZT > 2$ can be achieved with nanostructured PbTe,\cite{71} the environmental toxicity of Pb and the rarity of Te are both major barriers to widespread application.

For a commercially-viable thermoelectric device, materials with a $ZT$ score above 2 are considered to be the benchmark. The lead chalcogenides, in particular PbTe, have been widely researched due to their intrinsically low lattice thermal conductivity,\cite{73} arising from strong phonon anharmonicity and very low lattice thermal conductivity.\cite{69,70} Although the headline efficiency was only observed over a narrow temperature range, it was subsequently found that doping allows good thermoelectric performance to be achieved over a wide range of operating temperatures by optimising the electronic structure.\cite{70}

Alloying is a natural approach to optimising thermoelectric performance, since the larger variations in atomic mass and chemical bond strength generally promote stronger phonon scattering and reduce the lattice thermal conductivity.\cite{72} There are various reports of the thermoelectric properties of Sn(Si$_x$Se$_{1-x}$) solid solutions in the literature, with $ZT$ scores ranging from 0.64 to 1.67 in Ag-doped samples.\cite{35,37} In particular, several studies have shown that solid solutions with 80% Se improve the thermoelectric efficiency relative to either of the endpoints by reducing the thermal conductivity and increasing the electrical conductivity at the expense of a slight reduction in the Seebeck coefficient.\cite{35,36} More recent studies of Ag-doped Sn(Si$_x$Se$_{1-x}$) solid solutions achieved a $ZT$ of 1.67 at 823 K with 85% Se, and attributed the high thermoelectric performance to the formation of nanoscale phonon-scattering point defects.\cite{37}

As with accurate electronic-structure calculations, including lattice dynamics in high-throughput modelling studies is a technical challenge. To obtain an accurate set of force constants for evaluating the phonon frequencies using a finite-displacement approach requires up to 6N accurate force calculations, depending on crystal symmetry, on supercell expansions containing ~100-200 atoms. Taking the system sizes and phonon supercells listed in Table 1, this “worst-case scenario” ranges from 192 calculations on 128-atom cells to 144 calculations on 192-atom cells, which is not practical for our full set of ~5,000 structures.

To obtain instead a qualitative idea of how the phonon spectrum changes with composition, we adopted the “structural fingerprint” method proposed by Valle and Organov as a measure of structural similarity.\cite{75,76} This method uses a set of fingerprinting functions $F_{AB}(r)$ to characterise a structure in terms of its spectrum of interatomic distances, which is straightforwardly related to the pair-distribution function:

$$F_{AB}(r) = g_{AB}(r) - 1$$

A unique fingerprint for a given structure is obtained by concatenating the $F_{AB}(r)$ for all unique pairs of atoms $(A, B)$, computed out to a radius $r_{\text{max}}$ that captures all pair distances within a single crystallographic unit cell. The similarity between two structures can then be assessed by calculating the (vector) distance between their respective fingerprints, calculated for a common set of atomic pairs and $r_{\text{max}}$, for example using the cosine formula:

$$d_{ij} = 1 - \frac{F_i F_j}{|F_i||F_j|}$$

By computing the cosine distances of structures in the set to $\bar{F}$, we can then identify “most average” and “least average” structures, the phonon spectra of which can be used to obtain an approximate measure of the average and spread.

We performed this analysis for the 50/50 compositions of each of the four solid solutions, using a histogram bin width and Gaussian broadening of 0.05 and 0.02 Å, respectively, as suggested in Ref. \textsuperscript{75}. For all four systems, we found that the majority of the structures fell close to the centre of mass (see Figs. S4.1/S4.2). In the \textit{Pnma} and rocksalt Sn(Si$_x$Se$_{1-x}$) and Sn(Si$_{0.5}$Se$_{0.5}$)$_2$ solid solutions, the distances range from 0 to approx. 0.3, with > 90% of the structures within a range of 0.1. The $\text{Sn}_2(\text{Si}_{0.5},\text{Se}_{0.5})$ solid solution is an exception, with structures spread over a wider range of distances from the centre of mass and outliers at further extremes. This increased structural diversity is likely due to its more complex crystal structure and the presence of different chalcogen sites (c.f. Figure 1), as well as possibly to the relatively small number of atoms in the single cell used to build the solid-solution model.

Figure 8 compares the simulated phonon spectra of \textit{Pnma} SnS, SnSe and representative average structures selected from the Sn(S$_{0.5}$Se$_{0.5}$)$_2$ mixed phase. The phonon DoS of both endpoints consist of high- and low-frequency peaks corresponding predominantly to modes involving motion of the Sn and chalcogen atoms, respectively. The phonon modes in SnS span a larger range of frequencies than in the selenide, as expected given the larger difference in atomic mass and stronger chemical bonding.\cite{77}
In semiconductors, the dominant contributors to finite phonon lifetimes are three-phonon scattering events, either collisions (two phonons in, one out) or decay (one in, two out). The lifetimes are inversely related to the phonon linewidths $\Gamma_\lambda$, which can be approximated as:

$$\Gamma_\lambda(\omega_\lambda) = \frac{18\pi}{h^2} P_{-\lambda} N_2(\mathbf{q}_\lambda, \omega_\lambda)$$

Here, the quantity $P_{-\lambda}$ is the averaged three-phonon interaction strength and captures the physical coupling between interacting modes, and $N_2(\mathbf{q}_\lambda, \omega_\lambda)$ is a two-phonon density of states that gives the number of allowed energy- and momentum-conserving scattering events for a mode with wavevector $\mathbf{q}_\lambda$ and frequency $\omega_\lambda$.

Spreading the DoS over a larger range of frequencies, as in the 50/50 solid solution, should increase the number of energy-conserving three-phonon interactions without a large effect on the coupling strength, thereby resulting in an overall decrease of the thermal conductivity compared to either of the endpoints. The high-temperature (825 K) thermal conductivity of SnS and SnSe have been measured at ~0.5 and 0.2-0.3 W m$^{-1}$ K$^{-1}$, respectively. Measurements on Sn(S$_{1-x}$Se$_x$) solid solutions broadly show a reduction in thermal conductivity with increasing Se content up to $x_{Se} = 0.8$, with measured thermal conductivities ranging from 0.1-0.6 W m$^{-1}$ K$^{-1}$ depending on sample preparation and doping. Nonetheless, none of these three studies provide measurements for pure SnSe synthesised under the same conditions, and the wide variability in the experimental results makes it difficult to ascertain whether or not the alloys can show lower thermal conductivities than the selenide endpoint. Nonetheless, the softening of the phonon spectra with composition suggested by our analyses is consistent with a reduction in the lattice thermal conductivity, tentatively supporting the experimental observations that alloying optimises both the thermal transport and electrical properties for thermoelectric performance.

A similar analysis of the rocksalt Sn(S$_{1-x}$Se$_x$), Sn(S$_{1-x}$Se$_x$)$_2$, and Sn(S$_{1-x}$Se$_x$)$_3$ solid solutions (see Figures S4.4-S4.9) suggest similar trends, i.e. a systematic change in the phonon DoS between the sulphide and selenide endpoints with composition, albeit with notable deviations from linearity. We would therefore expect alloying to similarly allow for manipulation of the thermal conductivity of the other sulphide/selenide phases.

As noted above, the lattice dynamics also contribute to the thermodynamic free energy. Within the harmonic approximation employed here, the Helmholtz free energy $A(x_{Se}, T)$ for a given composition, including lattice dynamics contributions, can be written:

$$A(x_{Se}, T) = U_{latt}(x_{Se}, T) + U_{vib}(x_{Se}, T) - T [S_{config}(x_{Se}, T) + S_{vib}(x_{Se}, T)]$$

where $U_{latt}$ is the lattice energy, $S_{config}$ is the configurational entropy, and $U_{vib}$ and $S_{vib}$ are the contributions to the internal energy and entropy due to the occupation of phonon modes. Evaluating $U_{vib}$ and $S_{vib}$ quantitatively would require a statistical average over the full set of structures, which is not feasible. However, we can compare the vibrational free energies calculated for the endpoints and our selected $x_{Se} = 0.5$ structures to obtain an approximate magnitude of the contribution to the mixing energies. Across the four systems examined in this work, we calculate contributions to $G_{mix}(x_{Se}, T)$ ranging from ~0.75 to ~0.03 kJ mol$^{-1}$ atom$^{-1}$ at 900 K which, with reference to Fig. 2, is quite significant. For all bar one of the $x_{Se} = 0.5$ structures examined, the vibrational contribution decreases $G_{mix}$, suggesting that differences in lattice dynamics

Comparing the endpoints to the mixed phase suggests that the DoS varies somewhat systematically with composition, although a comparison of the spectrum to a linear combination of the endpoints shows some degree of deviation (Figure S4.3). Taking the difference between the spectrum of the “most” and “least” average structures as a measure of the anticipated spread in the phonon frequencies shows that, for this compound, the variation is likely to be relatively small, which in turn suggests that, as for the bandgap, predictable tuning of the lattice dynamics through the composition should be possible.

Although direct calculation of the lattice thermal conductivity is not feasible given the computational cost of doing so, the change in the DoS with composition does provide a qualitative basis to explore the likely effect of alloying on heat transport in the solid solutions. The macroscopic thermal conductivity can be written as a sum of contributions from individual phonon modes $\lambda$ according to:\n
$$\kappa_{latt} = \frac{1}{NV_0} \sum_{\lambda} C_{\lambda} v_{\lambda} \otimes v_{\lambda}^* \tau_{\lambda}$$

where $C_{\lambda}$ are the model heat capacities, $v_{\lambda}$ are the mode group velocities, $\tau_{\lambda}$ are the phonon lifetimes, $V_0$ is the unit-cell volume and $N$ is the number of phonon wavevectors included in the summation. We note that the product of $v_{\lambda}$ and $\tau_{\lambda}$ gives the phonon mean-free path (MFP), which appears in a widely-used alternative expression.

Figure 8. Phonon density of states (DoS, $g(\nu)$) curves for Prima Sn(S$_{1-x}$Se$_x$) solid solutions with Se fractions $x_{Se} = 0$ (a), 0.5 (b), and 1 (c). The curves are drawn as stacked area plots showing the projections of phonon modes onto Sn (blue), S (red) and Se (orange) atoms. For the $x_{Se} = 0.5$ composition in (b), the main curve shows the phonon spectrum of the “most average” structure, and the dashed black lines show ± the difference to the spectrum of the “least average” structure to give an indication of the expected spread (see text).

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would further stabilize the mixed phases. However, since our fingerprinting technique is designed to select configurations with structural - and not necessarily energetic - diversity, we would need to perform a full set of phonon calculations to confirm this.

Finally, we note that the relatively common use of alloying to optimise thermoelectric performance indicates that the exploration of methods for analysing more quantitatively the effect of alloying on the lattice dynamics is an important future development area. A potentially promising direction here would be to use the energetics calculations on the mixed phases to parameterise an empirical force field to perform these calculations, which could then allow for a fully thermodynamically-averaged phonon spectra and/or lattice thermal conductivities to be modelled with moderate computational cost, although this is beyond the scope of the present work.

Conclusions

In summary, we have carried out a detailed modelling study of four tin sulphide/selenide solid solutions, viz. Pnma and rocksalt Sn(S₁ₓSe₁₋ₓ), Sn(S₁₋ₓSeₓ)₂ and Sn₂(S₁₋ₓSeₓ), with a view to using alloying to optimise the physical properties for energy applications.

The calculated phase diagrams indicate facile formation with mixing strongly favoured by configurational entropy. We predict Pnma Sn(S₁₋ₓSeₓ) and Sn(S₁₋ₓSeₓ)₂ solid solutions to be accessible across the full range of compositions through high-temperature syntheses, while rocksalt Sn(S₁₋ₓSeₓ) and Sn₂(S₁₋ₓSeₓ) solid solutions with high and low selenium content, respectively, may also be accessible under certain synthesis conditions. Structural analyses of the solid-solution models indicate a homogeneous distribution of the chalcogen atoms over lattice sites, resulting in a predictable variation of the volume and lattice parameters with composition that should help with lattice matching to reduce interfacial strain in device structures.

Our calculations predict a systematic composition dependence of the bandgap, band-edge positions and dielectric properties in the Pnma Sn(S₁₋ₓSeₓ) and Sn(S₁₋ₓSeₓ)₂ solid solutions, providing a means to fine-tune the optoelectronic properties for their proven photovoltaic and photocatalysis applications. We also predict that the Sn(S₁₋ₓSeₓ)₂ bandgap can be tuned down to the theoretical optimum for PV while maintaining a similar absorption coefficient to Pnma SnS. To the best of the authors’ knowledge, Sn(S₁₋ₓSeₓ)₂ solid solutions have not been widely investigated for photovoltaic applications, but the present work suggests they could be a superior alternative to SnS: the crystal growth direction could be better controlled, given the 2D structure, and the full oxidation of Sn would reduce the need to tightly control the chalcogen chemical potential during synthesis. After the years of optimisation that have been spent on achieving the ~5% photovoltaic efficiency of SnS, we believe this result merits further investigation. For the Pnma Sn(S₁₋ₓSeₓ) solid solution, on the other hand, increasing the Se content decreases the band gap from what is already below the optimum for photovoltaic performance while not significantly improving the optical absorption coefficient.

Our calculations also show that alloying can allow the band levels to be adjusted for a better electrical match to other device components, potentially allowing this to be balanced with other properties if required. In a similar vein, the entropic stabilisation obtained by alloying may reduce or prevent undesirable chemical reactions at interfaces with contact materials.

Our calculations support the experimental observations that Pnma Sn(S₁₋ₓSeₓ) solid solutions with high Se content can improve the thermoelectric properties over the champion SnSe material, through a mixture of enhancing the electrical conductivity by reducing the bandgap and reducing the thermal conductivity through enhanced phonon scattering. Similar trends in the phonon spectra of the other Snₓ(S₁₋ₓSeₓ)ₙ phases with composition suggest that the thermal transport in these systems could also be controlled by alloying.

The predicted metastability of the majority of the Snₓ(S₁₋ₓSeₓ)ₙ and all of the rocksalt Sn(S₁₋ₓSeₓ) compositions implies that preparing and working with these materials in bulk would be challenging. On the other hand, both are at some compositions close enough to the convex hull that they may be of concern for phase purity. We consider it unlikely that either of these will find widespread applications in the near future.

Finally, from a methodological standpoint, our study shows that first-principles modelling of the structural and electrical properties of relatively complex solid solutions is within reach of modern quantum-chemical techniques and can provide valuable information to guide experimental syntheses. Moreover, given the importance of alloying in the optimisation of thermoelectric materials, future developments towards quantitative modelling of the composition dependence of the lattice dynamics and thermal transport will make this a valuable addition to the growing capabilities of computational materials design.

ASSOCIATED CONTENT

Electronic supporting information includes: breakdown of the Gibbs free energies of mixing into enthalpy and entropy terms and calculated reaction energies for the conversion of rocksalt Sn(S₁₋ₓSeₓ) to the Pnma phase and the decomposition of Sn(S₁₋ₓSeₓ)₃ to Sn(S₁₋ₓSeₓ) and Sn(SₓSeₓ)₃; averaged lattice parameters as a function of composition for each of the four solid solutions and calculated pair-distribution functions for the Pnma and rocksalt Sn(S₁₋ₓSeₓ) and Sn(SₓSeₓ)₃ systems; full details of the electronic-structure calculations including the selection of an appropriate exchange-correlation functional for calculating bandgaps, a comparison of SCAN and HSE 06 calculations on selected structures from each solid solution, and a full set of averaged bandgaps, electronic density-of-states curves and optical properties; additional data from the lattice-dynamics calculations including the selection of structures and calculated phonon spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

DATA ACCESS

The Python library used to prepare the solid-solution models and analyse the results, Transformer, is open source and available from GitHub at https://github.com/JMSkelton/Transformer/. A full set of data from this study, including optimized structures, calculated properties, and sample input files for the VASP code, is available free of charge in an online repository at http://dx.doi.org/10.17632/bwhjg65xvd.1.

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Author Contributions
* DG and JS contributed equally to this work. Both authors provided scientific input and contributed to writing the manuscript, and have given approval to the final version.

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ABBREVIATIONS

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DFT, density-functional theory.


Solid solutions of *Pnma* and rocksalt Sn(S$_{1-x}$Se$_x$), Sn(S$_{1-x}$Se$_x$)$_2$ and Sn$_2$(S$_{1-x}$Se$_x$)$_3$ are studied using high-throughput computational modelling, revealing facile, homogenous mixing and controlled tuning of the electronic structure, optical absorption and vibrational properties with composition.
Thermodynamics, electronic structure and vibrational properties of Sn$_n$(S$_{1-x}$Se$_x$)$_m$ solid solutions for energy applications

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1. Mixing Energies

![Graph showing breakdown of Gibbs free energies of mixing](image)

**Figure S1.1** Breakdown of the Gibbs free energies of mixing $G_{\text{mix}} = H_{\text{mix}} - T S_{\text{mix}}$ of Pnma and rocksalt Sn(S$_{1-x}$Se$_x$), Sn(S$_{1-x}$Se$_x$)$_2$ and Sn(S$_{1-x}$Se$_x$)$_3$ solid solutions (left column; as shown in Fig. 2 in the text) into enthalpy ($H_{\text{mix}}$; centre) and entropy ($-T S_{\text{mix}}$; right) terms. The line colours indicate formation temperatures from 300 K (blue) to 1100 K (orange).
Figure S1.2 Calculated free energies as a function of Se fraction $x_{Se}$ for the conversion of $Pnma$ Sn($S_{1-x}Se_x$) solid solutions to the rocksalt phase (a) and for the conversion of Sn$_2$($S_{1-x}Se_x$)$_3$ solid solutions to $Pnma$ Sn($S_{1-x}Se_x$) and Sn($S_{1-x}Se_x$)$_2$ phases with equivalent composition (b). We note that we do not consider the possibility of decomposition into phases with different composition (e.g. Sn$_2$($S_{0.33}Se_{0.66}$) $\rightarrow$ SnS + SnSe$_2$), since the mixing energies in Fig. S1.1/Fig. 2 in the text predict that both the Sn($S_{1-x}Se_x$) and Sn($S_{1-x}Se_x$)$_2$ products should readily form solid solutions. As in Fig. S1.1, the line colours denote synthesis temperatures from 300 K (blue) to 1100 K (orange).
2. Structural properties

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Table S2.1 Fit parameters for the variation of the cell volume as a function of Se fraction $x_{\text{Se}}$ to the model function in Eq. 6 in the text. All parameters are given with respect to the primitive unit cell used to build the supercells when forming the solid solution; note that for rocksalt Sn(S$_{1-x}$Se$_x$) this is the two-atom primitive rather than the eight-atom conventional cell.
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Table S2.2 Thermodynamically averaged lattice parameters for \( Pnma \) \( Sn(S_1-xSe_x) \) solid solutions as a function of Se fraction \( x_{\text{Se}} \). For each of the averaged unit-cell parameters \( \bar{a} \), \( \bar{b} \), \( \bar{c} \), \( \bar{\alpha} \), \( \bar{\beta} \) and \( \bar{\gamma} \), we also report the weighted standard deviation \( \sigma \) as a measure of the expected spread.
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Table S2.3 Thermodynamically averaged lattice parameters for rocksalt Sn(S$_{1-x}$Se$_x$) solid solutions as a function of Se fraction $x_{\text{Se}}$. Note that the averaged lattice constants $\bar{a}$, $\bar{b}$ and $\bar{c}$ and the cell angles $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$ are reported with respect to the primitive rocksalt cell with $a = b = c = a_0/\sqrt{2}$ and $\alpha = \beta = \gamma = 60^\circ$. For each of the averaged unit-cell parameters, we report the weighted standard deviation $\sigma$ as a measure of the expected spread.
For each of the averaged unit-cell parameters $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$, we also report the weighted standard deviation $\sigma$ as a measure of the expected spread.

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Table S2.4 Thermodynamically averaged lattice parameters for Sn(S$_{1-x}$Se$_x$)$_2$ solid solutions as a function of Se fraction $x_{\text{Se}}$. For each of the averaged unit-cell parameters $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$, we also report the weighted standard deviation $\sigma$ as a measure of the expected spread.
Thermodynamically averaged lattice parameters for Sn$_2$(S$_1$-xSe$_x$)$_3$ solid solutions as a function of Se fraction $x_{Se}$. For each of the averaged unit-cell parameters $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$, we also report the weighted standard deviation $\sigma$ as a measure of the expected spread.

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Figure S2.1 Calculated total (black) and Sn-S (orange)/Sn-Se (green) partial pair-distribution functions $g(r)$ for $Pnma$ Sn$_{(1-x)Se_x}$ solid solutions with compositions $x_{Se} = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The partial correlation functions have been rescaled so that they represent the area under the total $g(r)$ from all the Sn-S and Sn-Se bond lengths within a coordination sphere of radius $r$. The histograms of interatomic distances were generated with a bin width $\Delta r = 0.01$ Å and broadened with a Gaussian function of width $\sigma = 0.05$ Å.
Figure S2.2 Calculated total (black) and Sn-S (orange)/Sn-Se (green) partial pair-distribution functions $g(r)$ for rocksalt Sn(S$_{1-x}$Se$_x$) solid solutions with compositions $x_{Se} = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The partial correlation functions have been rescaled so that they represent the area under the total $g(r)$ from all the Sn-S and Sn-Se bond lengths within a coordination sphere of radius $r$. The histograms of interatomic distances were generated with a bin width $\Delta r = 0.01$ Å and broadened with a Gaussian function of width $\sigma = 0.05$ Å.
Figure S2.3 Calculated total (black) and Sn-S (orange)/Sn-Se (green) partial pair-distribution functions $g(r)$ for Sn(S1, Se)2 solid solutions with compositions $x_{Se} = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The partial correlation functions have been rescaled so that they represent the area under the total $g(r)$ from all the Sn-S and Sn-Se bond lengths within a coordination sphere of radius $r$. The histograms of interatomic distances were generated with a bin width $\Delta r = 0.01$ Å and broadened with a Gaussian function of width $\sigma = 0.05$ Å.
3. Electronic structure and optical properties

As noted in the text, accurate electronic-structure calculations pose a technical challenge to high-throughput modelling studies, since density-functional theory (DFT) with semi-local generalised-gradient approximation (GGA) functionals tend to underestimate the electronic bandgap\(^1\) and incorrectly predict related properties such as the dielectric function and optical-absorption coefficient. In practice, this deficiency is usually mitigated with so-called hybrid functionals that incorporate a fraction of the non-local exact exchange energy and yield more accurate electronic structures, but at a much higher cost and less favourable scaling with system size.

Since it is not practical to perform hybrid calculations on the 1000s of structures in our four solid solution models, we examined the possibility of selecting a smaller subset of representative low-energy structures. However, plotting the distribution of the occurrence probabilities \(P_n\) over the structures in each system/composition (Fig. S3.1) showed a small difference of just an order of magnitude between largest and smallest occurrence probabilities, which we do not consider sufficient to justify excluding a significant fraction of the structures from the thermodynamic averages.

In a bid to balance accuracy and computational cost, we tested the predictive capabilities of five electronic-structure methods on the primitive cells of the sulphide and selenide endpoints of each system (i.e. \(Pnma\) and rocksalt \(\text{SnS}/\text{SnSe}, \text{SnS}_2/\text{SnSe}_2\) and \(\text{Sn}_2\text{S}_3/\text{Sn}_2\text{Se}_3\)). Taking structures optimised with PBEsol+D3, we compared the band gaps obtained with the PBEsol GGA,\(^3\) the SCAN\(^4\) and mBJ\(^5\) meta-GGA functionals and the HSE 06 hybrid functional.\(^7\) We note in passing that the empirical DFT-D3 dispersion correction\(^8\) does not correct the electronic structure, and thus the band energies from “bare” PBEsol and PBEsol-D3 calculations on a given structure are equivalent. We also tested the \(G_0W_0\) method,\(^9,10\) which gives a non-self-consistent perturbative correction to the energy levels obtained with another method, in our case either PBEsol or SCAN. In principle, hybrid functionals can also be used in a similar non-self-consistent manner, i.e. by taking self-consistent wavefunctions obtained with a less demanding functional and recalculating the band energies with the hybrid. Although not common, this approach has been shown to be suitable for high-throughput or screening calculations,\(^11,12\) so we included it in our testing.

\(\Gamma\)-centred Monkhorst-Pack meshes with \(8\times4\times8, 8\times8\times8, 8\times8\times4\) and \(4\times8\times3\) subdivisions were employed in the calculations on the primitive cells of \(Pnma\) and rocksalt \(\text{SnS}/\text{SnSe}, \text{SnS}_2/\text{SnSe}_2\) and \(\text{Sn}_2\text{S}_3/\text{Sn}_2\text{Se}_3\) respectively. For the HSE 06 calculations, the plane-wave cutoff was reduced to 300 eV, a reduced FFT grid was used to evaluate the Hartree-Fock exchange (the FPRECFOCK = Fast setting in VASP\(^13\)), and the exact exchange was evaluated at a subset of the \(k\)-points in the sampling meshes (EVENONLY = .TRUE.). From extensive testing, we found that these substantially reduced the computational requirements of the calculations without significant loss of accuracy. Similarly, we found that in the \(G_0W_0\) calculations the cutoff for the basis used to represent the response functions could be reduced to 200 eV and the exact-exchange contribution could be evaluated with a reduced FFT grid; however, attempting to reduce the \(k\)-point mesh led to a notable loss of accuracy, so we did not do so. We found that the convergence of the bandgap with respect to the number of virtual states (empty bands) was somewhat slow, so a total of 528, 480, 504 and 240 bands were included in the \(Pnma\) and rocksalt \(\text{SnS}/\text{SnSe}, \text{SnS}_2/\text{SnSe}_2\) and \(\text{Sn}_2\text{S}_3/\text{Sn}_2\text{Se}_3\) calculations, respectively, of which the quasiparticle corrections were computed for the first 48, 24, 24 and 120 bands, respectively, covering the valence and low-lying conduction bands.

\(\text{Sn}_2\) is a wide-bandgap semiconductor with an extrapolated 0 K indirect gap of 2.28 eV.\(^14\) The PBEsol gap of 1.24 eV is a significant underestimate, while SCAN and mBJ yield improved predictions of 1.62 and 2.15 eV.
respectively. HSE 06 gives a near-quantitative estimate of 2.21 eV, as does $G_0W_0$ with 2.25/2.45 eV with the PBEsol/SCAN wavefunctions), albeit at the cost of a 50-60× increase in the required computing resources. Interestingly, non-self-consistent HSE 06 calculations performed with the PBEsol and SCAN wavefunctions yield bandgaps within 20 meV of the self-consistent result (2.21 and 2.19 eV respectively) and reduce the computational cost by a factor of 10, indicating that this approach does indeed have some merit.

SnSe$_2$ has direct and indirect gaps of 1.7 and 0.9 eV, respectively. The PBEsol values of 0.71 and 0.42 are again substantial underestimates, while the SCAN and mBJ predictions of 1.13/0.70 and 1.50/1.05 eV are significant improvements. The HSE 06 values of 1.56/1.13 eV and the $G_0W_0$ estimates of 1.36/0.97 and 1.57/1.13 eV based on the PBEsol and SCAN wavefunctions are reasonably accurate, although neither method appears to be able to reproduce the values of the direct and indirect gap simultaneously. We again find that the non-self-consistent HSE 06 calculations are a very good approximation to the more expensive self-consistent result, underestimating the gaps by 30-60 meV. Comparison of the SnS$_2$ and SnSe$_2$ results suggests that there are no fundamental differences in the performance of the various functionals between the sulphide and selenide systems, although the smaller gap of the selenide appears to result in a larger relative error.

Sn$_2$Se$_3$ is a more interesting case, because the PBEsol functional predicts a near-metallic electronic structure with a gap of just 67 meV. Since there are not yet any experimental reports of Sn$_2$Se$_3$, we do not have an experimental reference, but the (self-consistent) HSE 06 calculation predicts a narrow-gap semiconductor with a bandgap of 0.38 eV. Given the small PBEsol gap, non-self-consistent HSE 06 and $G_0W_0$ calculations using the PBEsol wavefunctions do not come close to reproducing the self-consistent HSE 06 result, in both cases yielding gaps close to zero. However, SCAN predicts a wider 0.16 eV gap, and non-self-consistent calculations using the SCAN wavefunctions yield far more reasonable non-self-consistent HSE 06 and $G_0W_0$ gaps of 0.33 and 0.40 eV, respectively.

A full set of calculated bandgaps and a comparison to experimental measurements where available is given in Tables S3.1-S3.8 and Figs. S3.2-S3.9.

Returning to the questions of the optimum choice of functional for high-throughput calculations, based on the five compounds for which experimental bandgaps are available, the accuracy of the electronic-structure methods falls in the order $G_0W_0 \approx$ HSE 06 > mBJ > SCAN > PBEsol. Barring Sn$_2$Se$_3$, the non-self-consistent HSE 06 results are typically very good, with average and maximum absolute errors of 27 and 64 meV, or 3 and 12.5 % of the gap, in exchange for a typical 10× reduction in computational cost compared to a full self-consistent calculation. In addition to predicting a similar bandgap, we also found that the non-self-consistent calculations gave a quantitative reproduction of the valence and conduction band density of states (DoS) of SnS$_2$ (Fig. S3.10), indicating them to be suitable for calculating e.g. band dispersions and optical properties.

Although mBJ was designed to predict accurate bandgaps, and typically produces results close to the HSE 06 values at a much smaller cost, it does not appear to reproduce the shape of the band dispersion as well; a comparison of the calculated Sn$_2$ DoS between functionals shows that the smaller PBEsol and SCAN gaps result primarily from a uniform shift of the valence and conduction bands compared to the HSE 06 calculations (Fig. S3.11), whereas mBJ predicts a markedly different shape to the conduction-band edge.
Based on all these considerations, we opted to perform a full set of electronic-structure calculations using SCAN, and to perform non-self-consistent calculations on a subset of structures to obtain an estimate of the error.

Finally, to simulate optical properties we used the SCAN electronic-structure calculations to obtain the complex dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ within the independent-particle approximation using the linear-optics routines in the Vienna \textit{Ab initio} Simulation Package code.\(^\text{16}\) The calculated wavelength-dependent refractive index $n(\lambda)$, extinction coefficient $\kappa(\lambda)$ and absorption coefficient $\alpha(\lambda)$ were then calculated as:

$$n(\lambda) = \sqrt{\varepsilon(\lambda) + \varepsilon_{\text{Re}}(\lambda)}$$ \hspace{1cm} (3.1)

$$\kappa(\lambda) = \sqrt{\varepsilon(\lambda) - \varepsilon_{\text{Re}}(\lambda)}$$ \hspace{1cm} (3.2)

$$\alpha(\lambda) = 4\pi \frac{\kappa(\lambda)}{\lambda}$$ \hspace{1cm} (3.3)

where $|\varepsilon(\lambda)| = \sqrt{\varepsilon_{\text{Re}}^2 + \varepsilon_{\text{Im}}^2}$ in Eq. 3.1 and 3.2 is the complex modulus.
Figure S3.1 Cumulative distribution of occurrence probabilities $P_n$ over the structures in each composition $x_{Se}$ of Pnma (a) and rocksalt (b) Sn(S$_{1-x}$Se$_x$), Sn(S$_{1-x}$Se$_x$)$_2$ (c) and Sn$_3$(S$_{1-x}$Se$_x$)$_3$ (d) solid solutions. The lines are colour coded by Se content from blue (dark; $x_{Se} = 0$) to cyan (light; $x_{Se} = 1$).
Figure S3.2 Calculated bandgap of \textit{Pnma} SnS using the electronic-structure methods described above. Non-self-consistent HSE 06 and \textit{G}\textsubscript{0}\textit{W}\textsubscript{0} calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For comparison, the experimentally-measured bandgap from Ref.\textsuperscript{14} is overlaid as a dashed black line.

Table S3.1 Calculated direct and minimum bandgaps ($E_{g,\text{dir}}$/$E_{g,\text{min}}$) of \textit{Pnma} SnS using the electronic-structure methods described above. Non-self-consistent HSE 06 and \textit{G}\textsubscript{0}\textit{W}\textsubscript{0} calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.2.
Figure S3.3 Calculated bandgap of \textit{Pnma} SnSe using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For comparison, the experimentally-measured bandgap from Ref. 15 is overlaid as a dashed black line.

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<td>HSE 06 (PBEsol)</td>
<td>1.329</td>
<td>38</td>
<td>0.959</td>
<td>64</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>1.305</td>
<td>14</td>
<td>0.905</td>
<td>10</td>
</tr>
<tr>
<td>$G_0W_0$ (PBEsol)</td>
<td>1.165</td>
<td>-</td>
<td>0.789</td>
<td>-</td>
</tr>
<tr>
<td>$G_0W_0$ (SCAN)</td>
<td>1.277</td>
<td>-</td>
<td>0.853</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S3.2 Calculated direct and minimum bandgaps ($E_{\text{g,dir}}$/$E_{\text{g,min}}$) of \textit{Pnma} SnSe using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.3.
**Figure S3.4** Calculated bandgap of rocksalt SnS using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{g,\text{dir}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEsol</td>
<td>0.827</td>
<td>-</td>
<td>0.713</td>
<td>-</td>
</tr>
<tr>
<td>SCAN</td>
<td>0.711</td>
<td>-</td>
<td>0.666</td>
<td>-</td>
</tr>
<tr>
<td>mBJ</td>
<td>0.456</td>
<td>-</td>
<td>0.456</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06</td>
<td>0.684</td>
<td>-</td>
<td>0.684</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06 (PBEsol)</td>
<td>0.677</td>
<td>-7</td>
<td>0.677</td>
<td>-7</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>0.667</td>
<td>-17</td>
<td>0.667</td>
<td>-17</td>
</tr>
<tr>
<td>$G_0W_0$ (PBEsol)</td>
<td>0.742</td>
<td>-</td>
<td>0.710</td>
<td>-</td>
</tr>
<tr>
<td>$G_0W_0$ (SCAN)</td>
<td>0.619</td>
<td>-</td>
<td>0.619</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table S3.3** Calculated direct and minimum bandgaps ($E_{g,\text{dir}}/E_{g,\text{min}}$) of rocksalt SnS using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.4.
Figure S3.5 Calculated bandgap of rocksalt SnSe using the electronic-structure methods described above. Non-self-consistent HSE 06 and \( G_0W_0 \) calculations performed using the PBESol and SCAN wavefunctions are denoted with the base functional in parentheses.

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_{\text{g,dir}} ) [eV]</th>
<th>( \Delta_{\text{SCF}} ) [meV]</th>
<th>( E_{\text{g,min}} ) [eV]</th>
<th>( \Delta_{\text{SCF}} ) [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBESol</td>
<td>0.893</td>
<td>0.771</td>
<td>0.771</td>
<td>0.771</td>
</tr>
<tr>
<td>SCAN</td>
<td>0.692</td>
<td>0.692</td>
<td>0.692</td>
<td>0.692</td>
</tr>
<tr>
<td>mBJ</td>
<td>0.507</td>
<td>0.507</td>
<td>0.507</td>
<td>0.507</td>
</tr>
<tr>
<td>HSE 06</td>
<td>0.640</td>
<td>0.640</td>
<td>0.640</td>
<td>0.640</td>
</tr>
<tr>
<td>HSE 06 (PBESol)</td>
<td>0.658</td>
<td>18</td>
<td>0.658</td>
<td>18</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>0.657</td>
<td>17</td>
<td>0.657</td>
<td>17</td>
</tr>
<tr>
<td>( G_0W_0 ) (PBESol)</td>
<td>0.711</td>
<td>0.711</td>
<td>0.711</td>
<td>0.711</td>
</tr>
<tr>
<td>( G_0W_0 ) (SCAN)</td>
<td>0.621</td>
<td>0.621</td>
<td>0.621</td>
<td>0.621</td>
</tr>
</tbody>
</table>

Table S3.4 Calculated direct and minimum bandgaps (\( E_{\text{g,dir}}/E_{\text{g,min}} \)) of rocksalt SnSe using the electronic-structure methods described above. Non-self-consistent HSE 06 and \( G_0W_0 \) calculations performed using the PBESol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.5.
Figure S3.6 Calculated bandgap of SnS$_2$ using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For comparison, the experimentally-measured bandgap from Ref. 14 is overlaid as a dashed black line.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{g,\text{dir}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEsol</td>
<td>1.718</td>
<td>-</td>
<td>1.244</td>
<td>-</td>
</tr>
<tr>
<td>SCAN</td>
<td>2.224</td>
<td>-</td>
<td>1.615</td>
<td>-</td>
</tr>
<tr>
<td>mBJ</td>
<td>2.679</td>
<td>-</td>
<td>2.145</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06</td>
<td>2.811</td>
<td>-</td>
<td>2.212</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06 (PBEsol)</td>
<td>2.786</td>
<td>-25</td>
<td>2.210</td>
<td>-2</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>2.795</td>
<td>-16</td>
<td>2.192</td>
<td>-20</td>
</tr>
<tr>
<td>$G_0W_0$ (PBEsol)</td>
<td>2.668</td>
<td>-</td>
<td>2.242</td>
<td>-</td>
</tr>
<tr>
<td>$G_0W_0$ (SCAN)</td>
<td>2.930</td>
<td>-</td>
<td>2.453</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S3.5 Calculated direct and minimum bandgaps ($E_{g,\text{dir}}/E_{g,\text{min}}$) of SnS$_2$ using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.6.
Figure S3.7 Calculated bandgap of SnSe$_2$ using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For comparison, the experimentally-measured bandgap from Ref. 15 is overlaid as a dashed black line.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{g,\text{dir}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEsol</td>
<td>0.711</td>
<td>-</td>
<td>0.421</td>
<td>-</td>
</tr>
<tr>
<td>SCAN</td>
<td>1.128</td>
<td>-</td>
<td>0.704</td>
<td>-</td>
</tr>
<tr>
<td>mBJ</td>
<td>1.497</td>
<td>-</td>
<td>1.045</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06</td>
<td>1.559</td>
<td>-</td>
<td>1.125</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06 (PBEsol)</td>
<td>1.502</td>
<td>-57</td>
<td>1.081</td>
<td>-44</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>1.527</td>
<td>-32</td>
<td>1.084</td>
<td>-4.1</td>
</tr>
<tr>
<td>$G_0W_0$ (PBEsol)</td>
<td>1.361</td>
<td>-</td>
<td>0.965</td>
<td>-</td>
</tr>
<tr>
<td>$G_0W_0$ (SCAN)</td>
<td>1.570</td>
<td>-</td>
<td>1.130</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S3.6 Calculated direct and minimum bandgaps ($E_{g,\text{dir}}/E_{g,\text{min}}$) of SnSe$_2$ using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.7.
**Figure S3.8** Calculated bandgap of Sn$_2$S$_3$ using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For comparison, the experimentally-measured bandgap from Ref. 14 is overlaid as a dashed black line.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{g,\text{dir}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEsol</td>
<td>0.382</td>
<td>-</td>
<td>0.382</td>
<td>-</td>
</tr>
<tr>
<td>SCAN</td>
<td>0.625</td>
<td>-</td>
<td>0.625</td>
<td>-</td>
</tr>
<tr>
<td>mBJ</td>
<td>0.770</td>
<td>-</td>
<td>0.770</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06</td>
<td>0.947</td>
<td>-</td>
<td>0.947</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06 (PBEsol)</td>
<td>0.899</td>
<td>-48</td>
<td>0.899</td>
<td>-48</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>0.918</td>
<td>-29</td>
<td>0.918</td>
<td>-29</td>
</tr>
<tr>
<td>$G_0W_0$ (PBEsol)</td>
<td>0.936</td>
<td>-29</td>
<td>0.914</td>
<td>-29</td>
</tr>
<tr>
<td>$G_0W_0$ (SCAN)</td>
<td>1.117</td>
<td>-</td>
<td>1.090</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table S3.7** Calculated direct and minimum bandgaps ($E_{g,\text{dir}}/E_{g,\text{min}}$) of Sn$_2$S$_3$ using the electronic-structure methods described above. Non-self-consistent HSE 06 and $G_0W_0$ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.8.
Figure S3.9 Calculated bandgap of Sn₂Se₃ using the electronic-structure methods described above. Non-self-consistent HSE 06 and G₀W₀ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{g,\text{dir}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$\Delta_{\text{SCF}}$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEsol</td>
<td>0.124</td>
<td>-</td>
<td>0.067</td>
<td>-</td>
</tr>
<tr>
<td>SCAN</td>
<td>0.185</td>
<td>-</td>
<td>0.161</td>
<td>-</td>
</tr>
<tr>
<td>mBJ</td>
<td>0.252</td>
<td>-</td>
<td>0.249</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06</td>
<td>0.377</td>
<td>-</td>
<td>0.376</td>
<td>-</td>
</tr>
<tr>
<td>HSE 06 (PBEsol)</td>
<td>0.002</td>
<td>-1375</td>
<td>0.002</td>
<td>-374</td>
</tr>
<tr>
<td>HSE 06 (SCAN)</td>
<td>0.329</td>
<td>-48</td>
<td>0.329</td>
<td>-47</td>
</tr>
<tr>
<td>G₀W₀ (PBEsol)</td>
<td>0.047</td>
<td>-</td>
<td>0.047</td>
<td>-</td>
</tr>
<tr>
<td>G₀W₀ (SCAN)</td>
<td>0.399</td>
<td>0.399</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S3.8 Calculated direct and minimum bandgaps ($E_{g,\text{dir}}/E_{g,\text{min}}$) of Sn₂Se₃ using the electronic-structure methods described above. Non-self-consistent HSE 06 and G₀W₀ calculations performed using the PBEsol and SCAN wavefunctions are denoted with the base functional in parentheses. For the non-self-consistent HSE 06 calculations, the differences with respect to the self-consistent result are shown in the third and fifth columns. The minimum gaps correspond to those plotted in Fig. S3.9.
Figure S3.10 Comparison of the electronic density of states $n(E)$ of SnS$_2$ obtained with self-consistent HSE 06 and “single-shot” (non-self-consistent) calculations starting from the PBEsol and SCAN wavefunctions. The energy zero is set to the valence-band maximum (VBM). We note that the shape of the DoS differs slightly from Fig. 6 in the text and Fig. S3.29 below due to differences in $k$-point sampling from the use of a supercell rather than a primitive and the use of the tetrahedron method to integrate the Brillouin zone; however, the bandgaps of the two are near identical.

Figure S3.11 Comparison of the electronic density of states $n(E)$ of SnS$_2$ obtained with the PBEsol, SCAN, mBJ and HSE 06 functionals. The energy zero is set to the valence-band maximum (VBM). We note that the shape of the DoS differs from Fig. 6 in the text and Fig. S3.29 below due to differences in $k$-point sampling from the use of a supercell rather than a primitive and the use of the tetrahedron method to integrate the Brillouin zone; however, the bandgaps of the two are near identical.
<table>
<thead>
<tr>
<th>$x_{\text{Se}}$</th>
<th>$E_g$ [eV]</th>
<th>$\pm \sigma$ [eV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$E_{g,\text{max}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.846</td>
<td>0.000</td>
<td>0.846</td>
<td>0.846</td>
</tr>
<tr>
<td>0.063</td>
<td>0.809</td>
<td>0.000</td>
<td>0.809</td>
<td>0.809</td>
</tr>
<tr>
<td>0.125</td>
<td>0.802</td>
<td>0.021</td>
<td>0.774</td>
<td>0.829</td>
</tr>
<tr>
<td>0.188</td>
<td>0.789</td>
<td>0.018</td>
<td>0.751</td>
<td>0.808</td>
</tr>
<tr>
<td>0.250</td>
<td>0.786</td>
<td>0.024</td>
<td>0.733</td>
<td>0.843</td>
</tr>
<tr>
<td>0.313</td>
<td>0.775</td>
<td>0.022</td>
<td>0.713</td>
<td>0.821</td>
</tr>
<tr>
<td>0.375</td>
<td>0.768</td>
<td>0.025</td>
<td>0.692</td>
<td>0.839</td>
</tr>
<tr>
<td>0.438</td>
<td>0.760</td>
<td>0.024</td>
<td>0.674</td>
<td>0.822</td>
</tr>
<tr>
<td>0.500</td>
<td>0.754</td>
<td>0.026</td>
<td>0.638</td>
<td>0.850</td>
</tr>
<tr>
<td>0.563</td>
<td>0.751</td>
<td>0.025</td>
<td>0.645</td>
<td>0.799</td>
</tr>
<tr>
<td>0.625</td>
<td>0.746</td>
<td>0.024</td>
<td>0.663</td>
<td>0.800</td>
</tr>
<tr>
<td>0.688</td>
<td>0.744</td>
<td>0.024</td>
<td>0.682</td>
<td>0.779</td>
</tr>
<tr>
<td>0.750</td>
<td>0.737</td>
<td>0.017</td>
<td>0.688</td>
<td>0.768</td>
</tr>
<tr>
<td>0.813</td>
<td>0.726</td>
<td>0.011</td>
<td>0.710</td>
<td>0.744</td>
</tr>
<tr>
<td>0.875</td>
<td>0.714</td>
<td>0.007</td>
<td>0.705</td>
<td>0.724</td>
</tr>
<tr>
<td>0.938</td>
<td>0.683</td>
<td>0.000</td>
<td>0.683</td>
<td>0.683</td>
</tr>
<tr>
<td>1.000</td>
<td>0.658</td>
<td>0.000</td>
<td>0.658</td>
<td>0.658</td>
</tr>
</tbody>
</table>

Table S3.9 Averaged bandgap $\bar{E}_g$ as a function of Se fraction $x_{\text{Se}}$ for $Pnma$ Sn($S_{1-x}Se_x$) solid solutions, together with the standard deviation $\sigma$ and minimum and maximum values ($E_{g,\text{min}}/E_{g,\text{max}}$) observed across the set of structures associated with each composition.

<table>
<thead>
<tr>
<th>$x_{\text{Se}}$</th>
<th>$E_g$ [eV]</th>
<th>$\pm \sigma$ [eV]</th>
<th>$E_{g,\text{min}}$ [eV]</th>
<th>$E_{g,\text{max}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.666</td>
<td>0.000</td>
<td>0.666</td>
<td>0.666</td>
</tr>
<tr>
<td>0.063</td>
<td>0.606</td>
<td>0.000</td>
<td>0.606</td>
<td>0.606</td>
</tr>
<tr>
<td>0.125</td>
<td>0.601</td>
<td>0.016</td>
<td>0.555</td>
<td>0.610</td>
</tr>
<tr>
<td>0.188</td>
<td>0.599</td>
<td>0.026</td>
<td>0.517</td>
<td>0.634</td>
</tr>
<tr>
<td>0.250</td>
<td>0.590</td>
<td>0.023</td>
<td>0.470</td>
<td>0.646</td>
</tr>
<tr>
<td>0.313</td>
<td>0.588</td>
<td>0.018</td>
<td>0.492</td>
<td>0.614</td>
</tr>
<tr>
<td>0.375</td>
<td>0.591</td>
<td>0.020</td>
<td>0.510</td>
<td>0.634</td>
</tr>
<tr>
<td>0.438</td>
<td>0.594</td>
<td>0.020</td>
<td>0.523</td>
<td>0.648</td>
</tr>
<tr>
<td>0.500</td>
<td>0.598</td>
<td>0.019</td>
<td>0.535</td>
<td>0.673</td>
</tr>
<tr>
<td>0.563</td>
<td>0.604</td>
<td>0.016</td>
<td>0.551</td>
<td>0.640</td>
</tr>
<tr>
<td>0.625</td>
<td>0.613</td>
<td>0.018</td>
<td>0.568</td>
<td>0.643</td>
</tr>
<tr>
<td>0.688</td>
<td>0.622</td>
<td>0.021</td>
<td>0.589</td>
<td>0.661</td>
</tr>
<tr>
<td>0.750</td>
<td>0.628</td>
<td>0.018</td>
<td>0.597</td>
<td>0.671</td>
</tr>
<tr>
<td>0.813</td>
<td>0.634</td>
<td>0.007</td>
<td>0.620</td>
<td>0.644</td>
</tr>
<tr>
<td>0.875</td>
<td>0.645</td>
<td>0.005</td>
<td>0.642</td>
<td>0.660</td>
</tr>
<tr>
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</tr>
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</table>

Table S3.10 Averaged bandgap $\bar{E}_g$ as a function of Se fraction $x_{\text{Se}}$ for rocksalt Sn($S_{1-x}Se_x$) solid solutions, together with the standard deviation $\sigma$ and minimum and maximum values ($E_{g,\text{min}}/E_{g,\text{max}}$) observed across the set of structures associated with each composition.
<table>
<thead>
<tr>
<th>$x_{Se}$</th>
<th>$E_g$ [eV]</th>
<th>$\pm \sigma$ [eV]</th>
<th>$E_{g,\min}$ [eV]</th>
<th>$E_{g,\max}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.599</td>
<td>0.000</td>
<td>1.599</td>
<td>1.599</td>
</tr>
<tr>
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<td>1.524</td>
<td>0.000</td>
<td>1.524</td>
<td>1.524</td>
</tr>
<tr>
<td>0.125</td>
<td>1.435</td>
<td>0.024</td>
<td>1.393</td>
<td>1.469</td>
</tr>
<tr>
<td>0.188</td>
<td>1.339</td>
<td>0.027</td>
<td>1.292</td>
<td>1.373</td>
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<tr>
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<td>0.024</td>
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<td>1.332</td>
</tr>
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<td>0.910</td>
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<td>0.851</td>
<td>1.016</td>
</tr>
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<td>0.862</td>
<td>0.034</td>
<td>0.811</td>
<td>0.938</td>
</tr>
<tr>
<td>0.750</td>
<td>0.815</td>
<td>0.035</td>
<td>0.761</td>
<td>0.909</td>
</tr>
<tr>
<td>0.813</td>
<td>0.780</td>
<td>0.036</td>
<td>0.715</td>
<td>0.839</td>
</tr>
<tr>
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<td>0.759</td>
<td>0.025</td>
<td>0.676</td>
<td>0.765</td>
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<td>0.000</td>
<td>0.705</td>
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</table>

Table S3.11 Averaged bandgap $\overline{E}_g$ as a function of Se fraction $x_{Se}$ for Sn$_{(1-x)Se_x}$ solid solutions, together with the standard deviation $\sigma$ and minimum and maximum values ($E_{g,\min}$/$E_{g,\max}$) observed across the set of structures associated with each composition.

<table>
<thead>
<tr>
<th>$x_{Se}$</th>
<th>$E_g$ [eV]</th>
<th>$\pm \sigma$ [eV]</th>
<th>$E_{g,\min}$ [eV]</th>
<th>$E_{g,\max}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.634</td>
<td>0.000</td>
<td>0.634</td>
<td>0.634</td>
</tr>
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<td>0.083</td>
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<td>0.059</td>
<td>0.440</td>
<td>0.560</td>
</tr>
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<td>0.443</td>
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<td>0.390</td>
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<td>0.241</td>
<td>0.556</td>
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<tr>
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<td>0.342</td>
<td>0.076</td>
<td>0.190</td>
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<td>0.309</td>
<td>0.070</td>
<td>0.164</td>
<td>0.506</td>
</tr>
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<td>0.065</td>
<td>0.059</td>
<td>0.492</td>
</tr>
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<td>0.251</td>
<td>0.054</td>
<td>0.140</td>
<td>0.415</td>
</tr>
<tr>
<td>0.667</td>
<td>0.232</td>
<td>0.047</td>
<td>0.114</td>
<td>0.393</td>
</tr>
<tr>
<td>0.750</td>
<td>0.215</td>
<td>0.042</td>
<td>0.136</td>
<td>0.327</td>
</tr>
<tr>
<td>0.833</td>
<td>0.192</td>
<td>0.056</td>
<td>0.037</td>
<td>0.326</td>
</tr>
<tr>
<td>0.917</td>
<td>0.180</td>
<td>0.034</td>
<td>0.155</td>
<td>0.233</td>
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<td>0.185</td>
<td>0.000</td>
<td>0.185</td>
<td>0.185</td>
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</table>

Table S3.12 Averaged bandgap $\overline{E}_g$ as a function of Se fraction $x_{Se}$ for Sn$_{2}$(S$_1$$_x$Se$_x$)$_3$ solid solutions, together with the standard deviation $\sigma$ and minimum and maximum values ($E_{g,\min}$/$E_{g,\max}$) observed across the set of structures associated with each composition.
<table>
<thead>
<tr>
<th>$x_{\text{Se}}$</th>
<th>S. G. #</th>
<th>Str. #</th>
<th>$E_g$ [eV]</th>
<th>SCAN</th>
<th>HSE 06</th>
<th>$\Delta$ [meV]</th>
<th>$\Delta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>62</td>
<td>1</td>
<td>0.846</td>
<td>1.055</td>
<td>-209</td>
<td>-19.81</td>
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</tr>
<tr>
<td>0.25</td>
<td>2</td>
<td>5</td>
<td>0.742</td>
<td>0.941</td>
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<td>-21.15</td>
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</tr>
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<td>14</td>
<td>1</td>
<td>0.789</td>
<td>0.979</td>
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</tr>
<tr>
<td>0.75</td>
<td>4</td>
<td>5</td>
<td>0.718</td>
<td>0.917</td>
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<td>0.658</td>
<td>0.904</td>
<td>-246</td>
<td>-27.21</td>
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Table S3.13 Comparison of the bandgaps $E_g$ of five structures in the $Pnma$ Sn($S_{1-x}$Se$_x$) solid solution model obtained with the SCAN meta-GGA and from a single-shot non-self-consistent HSE 06 hybrid calculation based on the SCAN wavefunctions (see Section 3c in the text). For each structure, the first three columns give the Se fraction $x_{\text{Se}}$, spacegroup (S. G.) and structure number in the composition/spacegroup set, the fourth and fifth columns give the calculated bandgaps, and the last two columns give the absolute and percentage differences.

<table>
<thead>
<tr>
<th>$x_{\text{Se}}$</th>
<th>S. G. #</th>
<th>Str. #</th>
<th>$E_g$ [eV]</th>
<th>SCAN</th>
<th>HSE 06</th>
<th>$\Delta$ [meV]</th>
<th>$\Delta$ [%]</th>
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</thead>
<tbody>
<tr>
<td>0.00</td>
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<td>0.666</td>
<td>0.670</td>
<td>-4</td>
<td>-0.60</td>
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</tr>
<tr>
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<td>166</td>
<td>2</td>
<td>0.646</td>
<td>0.661</td>
<td>-15</td>
<td>-2.27</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>166</td>
<td>3</td>
<td>0.628</td>
<td>0.649</td>
<td>-21</td>
<td>-3.24</td>
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</tr>
<tr>
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<td>2</td>
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<td>0.691</td>
<td>0.656</td>
<td>35</td>
<td>5.34</td>
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Table S3.14 Comparison of the bandgaps $E_g$ of five structures in the rocksalt Sn($S_{1-x}$Se$_x$) solid model solution obtained with the SCAN meta-GGA and from a single-shot non-self-consistent HSE 06 hybrid calculation based on the SCAN wavefunctions (see Section 3c in the text). For each structure, the first three columns give the Se fraction $x_{\text{Se}}$, spacegroup (S. G.) and structure number in the composition/spacegroup set, the fourth and fifth columns give the calculated bandgaps, and the last two columns give the absolute and percentage differences.

<table>
<thead>
<tr>
<th>$x_{\text{Se}}$</th>
<th>S. G. #</th>
<th>Str. #</th>
<th>$E_g$ [eV]</th>
<th>SCAN</th>
<th>HSE 06</th>
<th>$\Delta$ [meV]</th>
<th>$\Delta$ [%]</th>
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<tr>
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<td>12</td>
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<tr>
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<td>12</td>
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<td>1.179</td>
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</tr>
<tr>
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<td>164</td>
<td>0.705</td>
<td>1.082</td>
<td>-377</td>
<td>-34.84</td>
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</table>

Table S3.15 Comparison of the bandgaps $E_g$ of five structures in the Sn($S_{1-x}$Se$_x$)$_2$ solid model solution obtained with the SCAN meta-GGA and from a single-shot non-self-consistent HSE 06 hybrid calculation based on the SCAN wavefunctions (see Section 3c in the text). For each structure, the first three columns give the Se fraction $x_{\text{Se}}$, spacegroup (S. G.) and structure number in the composition/spacegroup set, the fourth and fifth columns give the calculated bandgaps, and the last two columns give the absolute and percentage differences.
<table>
<thead>
<tr>
<th>$x_{\text{Se}}$</th>
<th>S. G. #</th>
<th>Str. #</th>
<th>$E_g$ [eV]</th>
<th>SCAN</th>
<th>HSE 06</th>
<th>$\Delta$ [meV]</th>
<th>$\Delta$ [%]</th>
</tr>
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<tbody>
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</tr>
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<tr>
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<tr>
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**Table S3.16** Comparison of the bandgaps $E_g$ of five structures in the Sn$_2$(S$_{1-x}$Se$_x$)$_3$ solid model solution obtained with the SCAN meta-GGA and from a single-shot non-self-consistent HSE 06 hybrid calculation based on the SCAN wavefunctions (see Section 3c in the text). For each structure, the first three columns give the Se fraction $x_{\text{Se}}$, spacegroup (S. G.) and structure number in the composition/spacegroup set, the fourth and fifth columns give the calculated bandgaps, and the last two columns give the absolute and percentage differences.

**Figure S3.12** Electronic density of states (DoS) of the valence and conduction bands of $Pnma$ Sn(S$_{1-x}$Se$_x$)$_3$ solid solutions with Se fractions $x_{\text{Se}} = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The DoS curves are drawn as stacked area plots showing the projections onto Sn (blue), S (red) and Se (orange) atomic states. The energies are referenced to the average Sn 1s core-level eigenvalues and the zero is set to the valence-band maximum of the SnS endpoint ($x_{\text{Se}} = 0$; subplot a).
Figure S3.13  Electronic density of states (DoS) of the valence and conduction bands of rocksalt Sn(S$_{1-x}$Se$_x$) solid solutions with Se fractions $x_{Se} = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The DoS curves are drawn as stacked area plots showing the projections onto Sn (blue), S (red) and Se (orange) atomic states. The energies are referenced to the average Sn 1s core-level eigenvalues and the zero is set to the valence-band maximum of the SnS endpoint ($x_{Se} = 0$; subplot a).
Figure S3.14 Electronic density of states (DoS) of the valence and conduction bands of Sn$_2$(S$_{1-x}$Se$_x$)$_3$ solid solutions with Se fractions $x_{\text{Se}} = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e). The DoS curves are drawn as stacked area plots showing the projections onto Sn (blue), S (red) and Se (orange) atomic states. The energies are referenced to the average Sn 1s core-level eigenvalues and the zero is set to the valence-band maximum of the Sn$_2$S$_3$ endpoint ($x_{\text{Se}} = 0$; subplot a).
Figure S3.15 Composition dependence of the real ($\varepsilon_{\text{Re}}$, a) and imaginary ($\varepsilon_{\text{Im}}$, b) parts of the complex dielectric function of Pnma Sn(S$_{1-x}$Se$_x$) solid solutions together with the calculated wavelength-dependent refractive index and extinction coefficients $n(\lambda)$ (c) and $\kappa(\lambda)$ (d). The lines are colour coded by Se fraction $x_{\text{Se}}$ from blue (dark; $x_{\text{Se}} = 0$) to cyan (light; $x_{\text{Se}} = 1$).
Figure S3.16 Composition dependence of the real ($\epsilon_{\text{Re}}$, a) and imaginary ($\epsilon_{\text{Im}}$, b) parts of the complex dielectric function of rocksalt Sn(S$_{1-x}$Se$_x$) solid solutions together with the calculated wavelength-dependent refractive index and extinction coefficients $n(\lambda)$ (c) and $k(\lambda)$ (d). The lines are colour coded by Se fraction $x_{\text{Se}}$ from blue (dark; $x_{\text{Se}} = 0$) to cyan (light; $x_{\text{Se}} = 1$).
Figure S3.17 Composition dependence of the real ($\varepsilon_{\text{Re}}$, a) and imaginary ($\varepsilon_{\text{Im}}$, b) parts of the complex dielectric function of Sn(S$_{1-x}$Se$_x$)$_2$ solid solutions together with the calculated wavelength-dependent refractive index and extinction coefficients $n(\lambda)$ (c) and $\kappa(\lambda)$ (d). The lines are colour coded by Se fraction $x_{\text{Se}}$ from blue (dark; $x_{\text{Se}} = 0$) to cyan (light; $x_{\text{Se}} = 1$).
Figure S3.18 Composition dependence of the real ($\varepsilon_{\text{Re}}$, a) and imaginary ($\varepsilon_{\text{Im}}$, b) parts of the complex dielectric function of Sn$_2$(S$_{1-x}$Se$_x$)$_3$ solid solutions together with the calculated wavelength-dependent refractive index and extinction coefficients $n(\lambda)$ (c) and $\kappa(\lambda)$ (d). The lines are colour coded by Se fraction $x_{\text{Se}}$ from blue (dark; $x_{\text{Se}} = 0$) to cyan (light; $x_{\text{Se}} = 1$).
Figure S3.19 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of $Pnma$ SnS calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 based on the SCAN wavefunctions (red).

Figure S3.20 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of $Pnma$ SnS$_{0.75}$Se$_{0.25}$ (spacegroup no. 6, structure no. 55) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 based on the SCAN wavefunctions (red).
Figure S3.21 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of \textit{Pnma} $\text{Sn(S}_0.5\text{Se}_0.5\text{)}$ (spacegroup no. 11, structure no. 9) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 based on the SCAN wavefunctions (red).

Figure S3.22 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of \textit{Pnma} $\text{Sn(S}_0.25\text{S}_0.75\text{)}$ (spacegroup no. 4, structure no. 5) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 based on the SCAN wavefunctions (red).
Figure S3.23 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of Pnma SnSe calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.24 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of rocksalt SnS calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
Figure S3.25 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of rocksalt Sn(S$_{0.75}$Se$_{0.25}$) (spacegroup no. 166, structure no. 2) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.26 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of rocksalt Sn(S$_{0.5}$Se$_{0.5}$) (spacegroup no. 166, structure no. 3) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
Figure S3.27 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of rocksalt Sn(S$_{0.25}$Se$_{0.75}$) (spacegroup no. 166, structure no. 2) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.28 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of rocksalt SnSe calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
**Figure S3.29** Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of SnS$_2$ calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

**Figure S3.30** Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of Sn(S$_{0.75}$Se$_{0.25}$)$_2$ (spacegroup no. 5, structure no. 12) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
Figure S3.31 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of Sn(S$_{0.5}$Se$_{0.5}$)$_2$ (spacegroup no. 9, structure no. 12) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.32 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of Sn(S$_{0.25}$Se$_{0.75}$)$_2$ (spacegroup no. 13, structure no. 12) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
Figure S3.33 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of SnSe$_2$ calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.34 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of Sn$_2$S$_3$ calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
Figure S3.35 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of $\text{Sn}_2(\text{S}_{0.75}\text{Se}_{0.25})_3$ (spacegroup no. 6, structure no. 55) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.36 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of $\text{Sn}_2(\text{S}_{0.5}\text{Se}_{0.5})_3$ (spacegroup no. 11, structure no. 9) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
Figure S3.37 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of $\text{Sn}_2(\text{S}_{0.25}\text{Se}_{0.75})_3$ (spacegroup no. 6, structure no. 33) calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).

Figure S3.38 Comparison of the electronic density of states $n(E)$ and energy-dependent real and imaginary dielectric function $\varepsilon(E) = \varepsilon_{\text{Re}}(E) + i\varepsilon_{\text{Im}}(E)$ of $\text{Sn}_2\text{Se}_3$ calculated using the SCAN meta-GGA functional (blue) and “single-shot” (non-self-consistent) HSE 06 starting from the SCAN wavefunctions (red).
4. Lattice dynamics

**Figure S4.1** Cumulative occurrence probability $P_n$ and fraction of structures as a function of the cosine distance from the thermodynamically-averaged structural fingerprint $F$ (“centre of mass”; CoM) for *Pnma* (a) and rocksalt (b) Sn(S$_{1-x}$Se$_x$), Sn(S$_{1-x}$Se$_x$)$_2$ (c) and Sn$_2$(S$_{1-x}$Se$_x$)$_3$ solid solutions with composition $x_{\text{Se}} = 0.5$. 

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Figure S4.2 Heat maps of the cosine distances between pairs of structures in the Pnma (a) and rocksalt (b) Sn(S_{1-x}Se_x), Sn(S_{1-x}Se_x)_2 (c) and Sn_2(S_{1-x}Se_x)_3 solid solution models with composition x_{Se} = 0.5. The structures are ordered by occurrence probability P_n to emphasise the similarity of the most likely atomic arrangements in most of the systems.

Figure S4.3 Comparison of the calculated phonon density of states (DoS; g(ν)) of the “most average” structure in the Pnma Sn(S_{0.5}S_{0.5}) solid-solution model (blue; see text for an explanation of the structure selection) to a linear combination of the spectra of the SnS and SnSe endpoints (red).
Figure S4.4 Phonon density of states (DoS, $g(v)$) curves for rocksalt Sn(S$_{1-x}$Se$_x$) solid solutions with Se fractions $x_{Se} = 0$ (a), 0.5 (b), and 1 (c). The curves are drawn as stacked area plots showing the projections of phonon modes onto Sn (blue), S (red) and Se (orange) atoms. For the $x_{Se} = 0.5$ composition in (b), the main curve shows the phonon spectrum of the “most average” structure, and the dashed black lines show ± the difference to the spectrum of the “least average” structure to give an idea of the expected spread (see text).

Figure S4.5 Comparison of the calculated phonon density of states (DoS, $g(v)$) of the “most average” structure in the rocksalt Sn(S$_{0.5}$S$_{0.5}$) solid-solution model (blue; see text) to a linear combination of the spectra of the SnS and SnSe endpoints (red).
**Figure S4.6** Phonon density of states (DoS, \( g(v) \)) curves for Sn(S\(_{1-x}\)Se\(_x\))\(_2\) solid solutions with Se fractions \( x_{Se} = 0 \) (a), 0.5 (b), and 1 (c). The curves are drawn as stacked area plots showing the projections of phonon modes onto Sn (blue), S (red) and Se (orange) atoms. For the \( x_{Se} = 0.5 \) composition in (b), the main curve shows the phonon spectrum of the “most average” structure, and the dashed black lines show ± the difference to the spectrum of the “least average” structure to give an idea of the expected spread (see text).

**Figure S4.7** Comparison of the calculated phonon density of states (DoS, \( g(v) \)) of the “most average” structure in the rocksalt Sn(S\(_{0.5}\)Se\(_{0.5}\))\(_2\) solid-solution model (blue; see text) to a linear combination of the spectra of the SnS\(_2\) and SnSe\(_2\) endpoints (red).
Figure S4.8 Phonon density of states (DoS, $g(\nu)$) curves for Sn$_2$(S$_{1-x}$Se$_x$)$_3$ solid solutions with Se fractions $x_{Se} = 0$ (a), 0.5 (b), and 1 (c). The curves are drawn as stacked area plots showing the projections of phonon modes onto Sn (blue), S (red) and Se (orange) atoms. For the $x_{Se} = 0.5$ composition in (b), the main curve shows the phonon spectrum of the “most average” structure, and the dashed black lines show ± the difference to the spectrum of the “least average” structure to give an idea of the expected spread (see text).

Figure S4.9 Comparison of the calculated phonon density of states (DoS, $g(\nu)$) of the “most average” structure in the rocksalt Sn(S$_{0.5}$Se$_{0.5}$)$_3$ solid-solution model (blue; see text) to a linear combination of the spectra of the Sn$_2$S$_3$ and Sn$_2$Se$_3$ endpoints (red).
5. References


