Showcasing research from a collaboration between the School of Materials Science and Engineering, Nanyang Technological University, the Institute of High Performance Computing (IHPC) and the Institute of Materials Research and Engineering (IMRE), the Agency for Science Technology and Research (A*STAR) along with the University of Tokyo.

Electronic transport descriptors for the rapid screening of thermoelectric materials

Our team focuses on materials-by-design. Using machine learning, computational science and experimental synthesis and validation, we endeavour to create new functional materials. In this work, we show that for degenerately doped inorganic semiconductors, considering polar optical phonon scattering is critical, along with impurity scattering, both of which depend strongly on the material’s dielectric constant. We come up with a new materials descriptor that is easy to calculate from first principles Density Functional Theory, to guide the search for earth-abundant thermoelectric materials.

See Junichiro Shiomi, Shuo-Wang Yang, Kedar Hippalgaonkar et al., Mater. Horiz., 2021, 8, 2463.
Electronic transport descriptors for the rapid screening of thermoelectric materials†

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The discovery of novel materials for thermoelectric energy conversion has potential to be accelerated by data-driven screening combined with high-throughput calculations. One way to increase the efficacy of successfully choosing a candidate material is through its evaluation using transport descriptors. Using a data-driven screening, we selected 12 potential candidates in the trigonal ABX₂ family, followed by charge transport property simulations from first principles. The results suggest that carrier scattering processes in these materials are dominated by ionised impurities and polar optical phonons, contrary to the oft-assumed acoustic-phonon-dominated scattering. Using these data, we further derive ground-state transport descriptors for the carrier mobility and the thermoelectric powerfactor. In addition to low carrier mass, high dielectric constant was found to be an important factor towards high carrier mobility. A quadratic correlation between dielectric constant and transport performance was established and further validated with literature. Looking ahead, dielectric constant can potentially be exploited as an independent criterion towards improved thermoelectric performance. Combined with calculations of thermal conductivity including Peierls and criterion towards improved thermoelectric performance. Combined with calculations of hard-to-calculate conductivity and inter-branch coherent contributions, we conclude that the trigonal ABX₂ family has potential as high performance thermoelectrics in the intermediate temperature range for low grade waste heat harvesting.

New concepts

In this work, we show for the first time with the aid of first principles thermoelectric simulations of charge scattering in highly doped semiconductors polar optical phonon scattering plays a substantial role. Then, we utilize the scattering time calculations in the emerging class of ABX₂ compounds to discover transport descriptors for both charge mobility and thermoelectric powerfactor that we expect to be widely utilized for screening of potential new thermoelectric materials, especially with the availability of calculated databases. We believe that this significantly advances the state-of-the-art: while general principles in terms of band structure of promising thermoelectric materials are known (band degeneracy, lower effective masses etc.), the role of hard-to-calculate carrier relaxation times is often ignored, largely because of a lack of accurate, yet rapid calculations of scattering times. Our work not only introduces a framework for such calculations, but can be broadly applied to functional inorganic materials design, beyond thermoelectrics in photovoltaics and high-power electronics.

Introduction

The advent of machine learning (ML) and high-throughput (HT) density functional theory (DFT) computation has shifted the scientific process from a time consuming Edisonian approach to a more efficient, in silico approach. The deployment of these tools has led to multiple advancements: prediction of novel compounds, either by HT-DFT or ML, that were later on realized experimentally resulting in a knock-on effect of an acceleration of materials diagnosis, and the fast screening of promising material...
candidates using materials descriptors, i.e. features that are inherent to the material, easily calculated and have a direct relationship with a functional property.

One widely used method for \textit{ab initio} calculation of charge transport properties is the Boltzmann transport equation (BTE). The commonly adopted constant scattering time approximation (CSTA), where a single, constant scattering time ($\tau_0$) is assigned to all charge carriers, is well-known for its simplicity. However, such an inherent assumption is not always accurate in reality and depends on the arbitrary choice of $\tau_0$. To bypass CSTA's shortcomings, researchers have employed the deformation potential theory (DPT)\textsuperscript{16} that adequately describes the electron–acoustic–phonon interactions.\textsuperscript{15,17–19} More recently, an electron–phonon averaged (EPA) approximation has been introduced as an alternative approximation, which includes both acoustic and optical phonon scattering and was applied to half-Heusler alloys.\textsuperscript{14} Nonetheless, the long-range Frohlich-type scattering by polar optical phonons (POP), which is particularly important for polar compound semiconductors,\textsuperscript{20} is not included in DPT or EPA approximations. Graziosi et al. have shown that inclusion of different electron–phonon and ionized impurity scattering mechanisms could significantly alter the predicted thermoelectric performance.\textsuperscript{21,22} A recently developed approach, Energy-dependent Phonon- and Impurity-limited Carrier Scattering Time AppRoximation (EPIC STAR), achieves good accuracy for polar materials at lower computational cost and is therefore suitable for HT screening of such materials.\textsuperscript{23} The Wannier interpolation technique\textsuperscript{24,25} enables accurate electron–phonon calculations as the state-of-the-art method for phonon-limited charge transport properties predictions.\textsuperscript{4,26–29} Yet it remains computationally expensive due to the large number of Brillouin zone sampling points needed for numerical integration,\textsuperscript{26,27} which is even more difficult for polar materials.\textsuperscript{30–32} Therefore, an easy-to-compute descriptor could facilitate rapid initial screening without performing complex computation for materials with lower predicted potential.

One of the earliest HT-DFT study using first principles transport calculations was reported in 2008 by Yang et al., where they proposed LaPdBi as a new n-type thermoelectric material after screening potential half-Heusler candidates with thermoelectric properties computed in CSTA. Similar methods were also conducted by Raghuvanshi et al. to study the same class of materials. Later on, based on the work reported by Gautier et al., Zhou et al. conducted accurate electron–phonon calculations on 15 half-Heusler compounds, which led them to explain the large powerfactor in NbFeSb and ZnNiSn. They also concluded that optical phonons are the dominant scattering mechanism for charges in many half-Heuslers, in good agreement with available experimental data. Zhu et al. performed stability studies on half-Heuslers and predicted six stable compounds including TaFeSb, which is experimentally synthesized and optimized to achieve a peak $zT$ of $\sim 1.52$ at 973 K. Other material families have also been searched, such as doped metals, clathrates, Chevrel phases and transition metal dichalcogenides.\textsuperscript{36–38}

Xi and co-workers\textsuperscript{15} screened the Materials Informatics Platform (MIP) database and computed the electrical transport properties of 161 potential chalcogenides using DPT. One of the candidates: CdIn$_2$Te$_4$, and its variations, experimentally showed $zT \sim 1$ at approximately 900 K.\textsuperscript{15} Li et al. also screened the MIP for diamond-like ABX$_2$ compounds, and out of 41 candidates with bandgap of 0.1–2.5 eV they predicted that 12 have high figure of merit ($zT$). And some of them were experimentally realized, demonstrating the potential of these approaches.\textsuperscript{39} These studies demonstrated that incorporating a relevant scattering mechanism in charge transport calculations is necessary for reliably predicting the electrical transport properties. However, such high-throughput scattering calculations are computationally demanding, and there is a long-standing lack of easy-to-compute, general transport property descriptors as an alternative for materials screening.

Herein, we leverage upon the richness of the Materials Project (MP) Database,\textsuperscript{40} screening for high symmetry, low band gap\textsuperscript{41} chalcogenide compounds. From the MP Database, we focus on the trigonal (space group number 166, R3m) ABX$_2$ family where A and B are elements of alkali, transition metals and group III and V, and X are chalcogens(S, Se, Te). ABX$_2$ compounds were chosen due to their tendency to have low thermal conductivity, with the possibility of ns$^2$ lone pair electrons,\textsuperscript{42} which enabled us to narrow down our focus on charge transport properties. Our findings reveal that in this family, polar optical phonon scattering, which has been neglected often in literature, is significant even with heavy doping. We proposed charge transport descriptors based on ground state properties and easy-to-obtain parameters. The descriptors described herein qualify themselves as robust first level thermoelectric screening parameters, which obviate the need for computationally expensive calculations. We expect this strategy to be widely implemented in the quest for high-performance inorganic TE materials.

Materials informatics and candidate screening

We establish a screening strategy for the identification of unexplored potential TE candidates. To do so, we first make use of appropriate material descriptors for the rapid assessment of key properties directly correlated to the performance.\textsuperscript{33} First, we screen for compounds with bandgaps lower than 4 eV, as it relates to the maximum Seebeck coefficient that can be achieved at a particular temperature $\left( S_{\text{max}} \sim \frac{E_g}{2eT_{\text{max}}} \right)$.\textsuperscript{44} The thermodynamic stability as indicated by the energy above convex Hull is evaluated at 0 K. At finite temperature ($T > 0$ K), however, the contribution from configurational entropy has been reported to stabilize compounds with $E_{\text{Hull}} > 0$. In other words, a small, non-zero $E_{\text{Hull}}$ at 0 K does not necessarily render experimental synthesis impossible ($E_{\text{Hull}} < 80$ meV).\textsuperscript{45,46} This is confirmed by looking at the most recent entry for trigonal AgBiS$_2$ in the MP database (mp-29678), which shows $E_{\text{Hull}} \sim 20$ meV and has been
experimentally realized.47 Next, the number of charge carrying valleys, or the valley degeneracy \( N_v \) is key to achieve high Seebeck coefficient and electrical conductivity simultaneously, and is preferentially found in high symmetry structures.48 We set a threshold for compounds with more than four symmetry operations, thus increasing the probability of having compounds with high \( N_v \) present in the dataset. Finally, to ensure data sufficiency, we screened for binary, ternary and quaternary chalcogenides. Domain knowledge motivates the choice of chalcogenide materials: traditionally, chalcogenides are good TE materials.49–55 Our screening resulted in nearly 600 compounds (combining binary, ternary and quaternary), from which we focused on ternary chalcogenides, as they represent the majority fraction in the mined data. Among all potentially stable, high symmetry chalcogenide compounds, we focus on a subset of the screened compounds, while keeping the space group fixed. In the end, the initial dataset was comprised of 146 ternary chalcogenides with chemical formula \( \text{ABX}_2 \) and trigonal structure (space group \( \text{R}3\text{m} \)). This initial dataset was reduced to 12 compounds after filtering out the low performing candidates based on previously calculated CSTA powerfactors from Ricci et al.,56 to compare CSTA with our detailed scattering time calculations. In addition, it is noteworthy to mention that TE properties have only been experimentally reported for 3 out of 12 compounds from our dataset (trigonal \( \text{TlBiTe}_2 \), trigonal \( \text{TlSbTe}_2 \) and a different symmetry, cubic \( \text{AgBiS}_2 \)), leaving an unexplored chemical space.57–61 While \( \text{AgBiS}_2 \) with space group \( \text{R}3\text{m} \) has not been demonstrated, this intermediate phase has been experimentally realized in \( \text{AgBiSe}_2 \).62,63 Hence, it could be possible to achieve trigonal \( \text{AgBiS}_2 \) in a similar fashion.

Ab initio transport property simulations were then performed for these 12 compounds, and a pictorial representation of the computational framework deployed in this work can be found in Fig. 1. It is to be noted that while we use these 12 compounds to analyse and produce transport descriptors, the methodology is expected to be generally applied to a larger class of inorganic semiconductors; we restricted it only for the purposes of this work.

Results and discussion

Fig. 2(a) shows the crystal structure for \( \text{ABX}_2 \) compounds, with space group \( \text{R}3\text{m} \) (No. 166). The layered structure is comprised of \( \text{B}–\text{X} \) slabs in the \( b–c \) plane with \( \text{A} \) cations orthogonal to this plane (along the \( c \)-axis). The atoms \( \text{A} \) and \( \text{B} \) occupy octahedral positions and interact with \( \text{X} \) with dissimilar strength, depending on the ion charge and specific position they occupy in the slab. On the other hand, the \( \text{X} \) atoms are octahedrally coordinated with respect to \( \text{AB} \). To illustrate the bonding nature and crystal symmetry, Fig. 2(b) shows the DFT band structure for \( \text{AgBiS}_2 \), which has an indirect bandgap of \( \sim 0.65 \text{ eV} \), where the valence band maxima is between the \( \Gamma \) and \( \text{X} \) high symmetry points and the conduction band minima is centred at the \( \text{Z} \) point. According to the partial density of states (PDOS), the valence band maxima is comprised of sulphur p-states with modest contribution from silver d-states, whilst the conduction band minima is mainly bismuth p-states, with minor contributions from silver and sulphur. The phonon dispersion shown in Fig. 2(c) is comprised of three acoustic branches and nine optical branches, with the lowest optical phonon located at \( \text{ca.} 50 \text{ cm}^{-1} \). The proximity of the optical branches to the acoustic branches is expected to lead to a
decreased lattice thermal conductivity near room temperature, due to increased scattering phase space and higher likelihood of phonon–phonon scattering. The phonon density of states in Fig. 2(c) shows the optical branches at low energy mainly comprised of vibrations of Ag atoms, followed by vibrations of Bi atoms. Additional verification is given by the atomic participation ratio (APR), which quantifies the degree of participation of different atoms in a specific phonon mode.\(^6\)\(^5\) We observe that Ag and Bi have a large participation ratio (red colour) in the phonon modes of the lowest optical branches. In addition, these low-lying optical branches are flat and avoid crossing the acoustic branches at certain high symmetry points of the Brillouin zone (for instance at the \(\Gamma\) and \(L\) points). The combination of high participation ratio, flat low energy optical branches and avoided crossing with acoustic branches hints at localized phonon vibration which would potentially decrease the lattice thermal conductivity.\(^6\)\(^6\) Further, ABX\(_2\) compounds have attracted interest due to the presence of lone-pair electrons, which are expected to result in softened phonon modes. Note that experimentally synthesized AgBiS\(_2\) results in the rock-salt disordered cubic \(Fm\text{3}m\) space group, different from our study of the \(R\text{3}m\) space group. In rock-salt compounds with the ABX\(_2\) formula, the presence of ns\(^2\)-orbitals\(^6\)\(^7\) induces structural instabilities that translate into an increase of anharmonicity in the bonding, ultimately resulting in strong phonon–phonon interactions that can potentially reduce the lattice thermal conductivity as low as the amorphous limit.\(^4\)\(^2\) Fig. 2(d) shows a bar plot representing the theoretical thermoelectric performance for a range of temperatures, from 300 K to 900 K, for six out of the twelve n- and p-type ABX\(_2\) chalcogenides, (note that thermal conductivity calculations are more computationally expensive, hence were not performed on all 12 compounds). The thermoelectric figure-of-merit \(zT\)\(_{\text{max}}\) was calculated using lattice thermal conductivity in the amorphous limit, while \(zT\)\(_{\text{cryst}}\) was calculated using lattice thermal conductivity corresponding to perfectly crystalline samples (Fig. S1(a), ESI\(^\dagger\)). In addition, we also calculated \(zT\) using the lattice thermal conductivity for polycrystalline samples with grain size of 1 \(\mu\)m (Fig. S1(a), ESI\(^\dagger\)) and the resulting \(zT\) border the values of the single crystal samples \((zT\)\(_{\text{cryst}}\)). This is because the phonon mean free path is much smaller than 1 \(\mu\)m (see Fig. S1(b), ESI\(^\dagger\)), so the impact of grain boundaries becomes less relevant. In many cases, p-type ABX\(_2\) compounds show higher thermoelectric performance than their n-type counterpart, due to a high band degeneracy which is attributed to their complex valence band structure.\(^9\)

Among these, the p-type AgBiS\(_2\) and TlBiTe\(_2\) compounds could reach a \(zT\) above 1 at room temperature. Especially, the predicted value for n-type AgBiS\(_2\) is higher than the experimental results obtained by Rathore \(\text{et al.}\)\(^4\)\(^7\) This mismatch is likely because the optimal carrier concentration \((1.48 \times 10^{19} \text{ cm}^{-3}\) for n-type AgBiS\(_2\) at room temperature) was not experimentally realized, and their synthesis resulted in the cation-disordered cubic rock salt structure.\(^4\)\(^7\) Their analysis also concluded that further optimization of the carrier concentration through doping in n-type AgBiS\(_2\) was required to achieve better
performance. Interestingly, our calculations show the p-type TlBiTe$_2$ compound is expected to achieve a maximum $zT$ of $\sim 1.9$ at 900 K, which is much larger than previously reported experimental values for the material (0.15 at 760 K), signifying the potential for further optimization.$^5$ Within the ABX$_2$ family, the best performance is attained experimentally by the cubic p-type alloy AgSbTe$_{1.85}$Se$_{0.15}$, with $zT \sim 2$ in the temperature range 550–600 K, mainly due to further reduction in the thermal conductivity from point defects and stacking faults.$^6$ Recently, Roy Chowdhury et al. have developed a strategy based on atomic disorder engineering in Cd-doped AgSbTe$_2$, reporting an ultrahigh $zT$ of $\sim 1.5$ near-room temperature.$^7$ In fact, this material is also cubic (space group $Fd\bar{3}m$) as opposed to the trigonal (space group $R\bar{3}m$) ABX$_2$ compounds studied here, and it is not currently contained in the Materials Project database, which explains its absence from the potential candidate dataset resultant from the screening.$^6$

We also study in detail the representative charge scattering mechanism that makes these compounds good prospects for mid-temperature thermoelectric applications. Fig. 3 shows the energy dependence of the scattering rate for both n- and p-type AgBiS$_2$ and TlBiTe$_2$ at 300 K for the optimal doping condition (determined from the peak of the powerfactor, $S^2\sigma$ as a function of carrier concentration). In general, the same scattering phenomena are dominant, from the energy dependencies, for both n-type and p-type materials at 300 K. For these optimally doped materials, ionised impurities dominate the charge scattering around the Fermi level (blue dash-dotted lines in Fig. 3). Interestingly, even in such a heavily doped regime where charge carrier scattering arising from polar optical phonons is partially screened by the free carriers, we still observed a strong contribution from optical phonons, that surpasses the acoustic phonon contribution. The contribution from optical phonons is especially significant for n-type TlBiTe$_2$ [Fig. 3(c)], comparable to that from ionised impurities. Moreover, for high-energy carriers the optical phonon scattering even dominates over ionized impurities. Similar trends are observed for the p-type materials, as shown in Fig. 3(b) and (d). This emphasizes the importance of polar optical phonon scattering, even in the heavily doped case where free-carrier screening is strong. In fact, in both n-type and p-type AgBiS$_2$ and TlBiTe$_2$, the overall scattering rate has a higher contribution from the optical phonons as compared to the acoustic phonons, which is in stark contrast to the widely used assumption of acoustic-phonon-dominated scattering in the literature.$^{70,71}$ This signifies the importance of including the polar optical phonon (POP) scattering contribution for polar materials, as this could potentially indicate the dominance of POP despite high temperature and doping. Consequently, using acoustic phonon limited assumption in analyzing the charge transport properties can result in substantial error, particularly in ABX$_2$ as well as half-Heusler class of compounds.$^8$

In light of this understanding, and to facilitate the rapid screening and identification of potential high-performance thermoelectric materials, key descriptors that account for these

Fig. 3 Room temperature scattering rate for optimally doped (a) n-type and (b) p-type AgBiS$_2$ and (c) n-type and (d) p-type TlBiTe$_2$. The vertical blue line indicates the Fermi level at optimal doping level.
scattering mechanisms can be deduced. Previously the quality factor $B$ proposed by Wang et al. has been adopted in the screening for high performance thermoelectrics.\textsuperscript{72} Nevertheless, this requires one key assumption: the scattering is dominated by acoustic phonons throughout the doping and temperature range under study. However, in our case of ABX$_2$ compounds, and possibly in other potential thermoelectric materials, the $B$-factor would not qualify as a reasonable descriptor, as from Fig. 3 we observed that the charge scattering events are controlled by polar optical phonons and ionized impurities.

To derive such descriptors, we first observe that the POP scattering rate is proportional to the Fröhlich coupling strength \( \tau_{\text{POP}}(E) \propto |C_{\text{POP}}|^2 \), which in turn can be written as a function of Born effective charge, phonon displacement and dielectric constant. Importantly, it is inversely proportional to the dielectric constant via \( C_{\text{POP}} \propto \frac{1}{\varepsilon} \). Therefore, the POP scattering time should also be proportional to dielectric constant squared \( \tau_{\text{POP}}(E) \propto \varepsilon^2 \). Similarly, the ionized impurity scattering strength also depends on the dielectric constant as the charges also experience electrostatic screening.\textsuperscript{23,74} In the Brooks-Herring model, the scattering rate from ionized impurity is also inversely proportional to dielectric constant squared \( \tau_{\text{IIS}}(E) \propto \varepsilon^2 \). Since the dielectric constant determines the overall electrostatic interaction, we conjecture that the interaction strength for other phonons may also be inversely correlated to \( \varepsilon \). Furthermore, this assumption is advantageous, since a small reduction in accuracy is traded for a simpler, easy-to-calculate descriptor. Hence, we focus on the role of dielectric constant and hypothesize that the overall scattering rate should be strongly correlated to \( \varepsilon^2 \) (further details in Section S1, ESI\textsuperscript{†}). Thus, we propose a general transport descriptor by considering mixed scattering contribution from ionized impurities and polar optical phonons. The descriptor for the carrier mobility is obtained by applying the relation \( \mu = \frac{e \tau}{m_c} \) considering that the total scattering time is proportional to \( \varepsilon^2 \):

$$\mu \propto \varepsilon^2 m_c^{-1}$$

where \( \mu \) is the direction averaged mobility at optimal carrier concentration, \( m_c \) is the conductivity effective mass, and \( \varepsilon \) is the dielectric constant and \( T \) is the absolute temperature in K.

Fig. 4(a) shows the correlation between the transport descriptor and the direction averaged mobility for our calculated ABX$_2$ compounds. We benchmarked our data together with experimental values from the literature, in order to validate the descriptor.\textsuperscript{49–53,55,75} The temperature dependent effective masses, conductivity effective masses and the dielectric constant were used when reported,\textsuperscript{50,52,53} whereas for other compounds we used values reported in the Landolt–Börnstein database, e.g. for effective mass for PbTe,\textsuperscript{76} or other literature e.g. for the dielectric constant of PbTe.\textsuperscript{77} Interestingly, materials of different crystal systems (e.g. cubic PbTe and orthorhombic SnSe) follow

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Transport descriptors for ABX$_2$ materials. (a) Direction averaged mobility transport descriptor at optimal doping. (b) Optimal carrier concentration \( n_{\text{opt}} \) descriptor.\textsuperscript{78} (c) Seebeck coefficient for each material (x-axis, ABX$_2$ materials are listed in alphabetical order) versus theoretical criteria (Ioffe's criterion\textsuperscript{79} and golden range\textsuperscript{80}). (d) Direction averaged powerfactor transport descriptor at optimal doping. The benchmark corresponds to experimental data.\textsuperscript{49–53,75,81–86} The data was taken from the respective references and averaged using the method described by Parker et al.\textsuperscript{87} The blue area in (a), (b) and (d) corresponds to the prediction band calculated for ABX$_2$ compounds. It corresponds to the range of values that are likely to contain the value of a new observation, with a 95% confidence.
}\end{figure}
the same trend, hinting that the descriptor could be generally applicable.

In addition to the carrier mobility, another key quantity in optimizing the thermoelectric performance is the carrier concentration. Assuming a single carrier type, the optimal carrier concentration \((n_{\text{opt}})\) should be proportional to the Seebeck effective mass and the temperature, \(n_{\text{opt}} \propto (m_{e} T)^{1.5} \) \(^{78}\). In Fig. 4(b), this trend is plotted for n- and p-type ABX₂ compounds as well as for the literature values used for benchmark, at their corresponding carrier concentration. We observe that, as expected, our compounds follow the trend whilst some literature values deviate from this ideal relationship, indicating that the reported carrier concentration may not be at the optimal level.

Next, a descriptor for the powerfactor \((PF = S^2 \sigma; PF \propto S^2 m_{n})\) is derived, where the mobility descriptor is given by Equation 1 and a descriptor for optimal carrier concentration is given by \(n_{\text{opt}} \propto (m_{e} T)^{1.5} \) \(^{78}\). However, a descriptor for the Seebeck coefficient is not as readily available. The underlying difficulty of finding a descriptor for the Seebeck coefficient resides in the fact that theoretically, the Seebeck coefficient at optimal doping should be a constant \(^{88}\). This originates from the steady-state solution to the BTE, that states that the optimal Seebeck coefficient only depends on reduced Fermi potential and scattering exponent and thus, is independent of effective masses, the valley degeneracy and scattering strength. \(^{74}\) Hence, under the parabolic band approximation, the powerfactor will be maximized at a single value of Seebeck coefficient, \(S_{\text{opt}}\). This was first proposed by Ioffe, who reported that the optimized value for Seebeck coefficient is 172 \(\mu\text{V K}^{-1}\). \(^{79}\) Later, Pichanusakorn and Bandaru showed that \(S_{\text{opt}}\) can be found in a range of 130–187 \(\mu\text{V K}^{-1}\) and that the most frequent value was 167 \(\mu\text{V K}^{-1}\). \(^{49}\)

Recently, Hong et al. expanded on this issue by reporting that the optimized Seebeck coefficient is not a single value but a range that changes depending on whether we are optimizing \(zT\) or the powerfactor. The authors reported that to achieve maximum powerfactor, the Seebeck values range from 195 \(\mu\text{V K}^{-1}\) to 202 \(\mu\text{V K}^{-1}\). \(^{80}\) The Seebeck tendency to accumulate around a range of values has also been noted by Zhang et al. \(^{90}\). Fig. 4(c) shows the Seebeck coefficient of our ABX₂ compounds along with the Seebeck coefficient of the literatures. Deviations from the optimal value may be indicative of non-optimal doping. However, we observe that while the majority of theoretical and experimental values of \(S\) approach the theoretically predicted limits, they still span a wider range.

Nevertheless, we introduce a transport descriptor for the direction averaged powerfactor at optimal doping (PF), shown in eqn (3). They key assumption is that the carrier concentration is given by its optimal value \((n = n_{\text{opt}} \propto (m_{e} T)^{1.5})\), while the Seebeck coefficient is around an optimal constant \((S \sim S_{\text{opt}} \sim \text{constant})\):

\[
PF \propto e^2 m_{c}^{-1} m_{s}^{1.5} T^{4.5}
\]  

The comparison between PF and the descriptor are shown in Fig. 4(d). We indeed observe an increasing trend of PF with respect to the transport descriptor for both simulated n- and p-type ABX₂ compounds as well as for the literature, with some literature values deviating from the general trend. This is a consequence of assuming optimal doping during the derivation of the PF descriptor: the powerfactor of materials with non-optimal doping will be lower than the maximal powerfactor that can be achieved. This also provides a theoretical guidance for experimental optimization of thermoelectric performance via tuning the carrier concentration towards optimal doping level. The good correlation between the transport descriptors and the transport properties potentially enables a facile method for first-level screening of potential TE candidates from easy to calculate parameters. In order to compare to the CSTA derived descriptors in Ricci et al., we also observed that another descriptor for the powerfactor, the Fermi surface complexity factor \((N_{f}^{1/2} K^*)\) \(^{9}\) indeed also captures the trend. Importantly, our descriptor is related to \(N_{f}^{1/2} K^*\), as it captures the band features, but contains more information regarding the scattering rate, which is absent in \(N_{f}^{1/2} K^*\) due to the CSTA assumption.

In addition, we also analyze phonon properties of these ABX₂ compounds to gain insights into their phonon anharmonicity and instability, which lead to low thermal conductivities (Fig. S3(a), ESI†). In order to explore anharmonicity, Nielsen et al. \(^{42}\) used an applied electric field and displacement of atoms, that significantly deform the lone-pair charge density of the group V element, resulting in the structural instability and strong phonon anharmonicity of ABX₂ compounds. For materials composed of guest atoms and a framework such as skutterudites \(^{91,92}\) and clathrates, \(^{93}\) effects of phonon anharmonicity can be analyzed by comparing phonon properties of the pristine structure and structure excluding the guest atoms. One, however, cannot employ this approach for ABX₂ compounds because removing the group V elements breaks the structure. In this analysis, we have applied hydrostatic strains to ABX₂ compounds to tune its phonon anharmonicity.

Because the three-phonon scattering is a complicated process, we have carefully analyzed change of harmonic and anharmonic terms on phonon relaxation times when such a strain was applied to the system. Here, we analyzed AgBiS₂, which exhibits promising electronic powerfactor. As shown in Fig. 2(c) and 5(a), ABX₂ compounds have flat bands at low frequency. The most intuitive effect of the flat band may be enhancement of Scattering Phase Space (SPS). SPSs of absorption (+) and emission (−) processes, \(P^{+}_{S}(q) = \frac{1}{N} \sum_{q_{1} q_{2}} \delta(\omega_{1} - \omega_{2}) \delta(q - q_{1} - q_{2} - G)\), have been computed with and without including the effect of the lowest optical branch, one of the flat bands around 60–80 \(\text{cm}^{-1}\) shown as a bold line in Fig. 5(a). This flat band increases SPS of absorption (emission) process at frequencies lower (higher) than its frequency as shown in Fig. 5(b). It is worth noting that while the lone-pair electrons result in whole features of atomic vibrations rather than only in flat bands, the flattening is one of the representative features of the lone-pairs resulting in weak bonding.

While the presence of flat bands may be related to the phonon anharmonicity and local distortions, SPS is a harmonic phonon property. We have, therefore, applied a hydrostatic
strain, a uniform expansion, to the compound to explore its phonon anharmonicity. As shown in Fig. 5(a), transverse acoustic (TA) modes around \( T \) point, \( q = (0.5, 0.5, 0.5) \), are significantly modified by the applied strain; their frequencies decrease and finally approach imaginary values, which are represented as negative values in Fig. 5(a). The instability of TA modes on \( G \)--\( X \) line can be clearly confirmed by the Grüneisen parameter, defined as the change in the frequency with the crystal volume, as shown in Fig. 5(c). Red markers in Fig. 5(c) show values for TA modes along \( q = (q, q, q) \), where \( q \) is an arbitrary number, corresponding to the \( G \)–\( T \) line and their maximum value corresponds to the \( T \) point. Inset shows data for the TA mode on \( G \)–\( T \) line with respect to \( q \). (d) Change in the \( |V_3|^2 \) term with the 0.5% strain for the TA mode at \( T \) point, which is marked with a cross (x) in the bottom panel.

Fig. 5 Phonon instability of AgBiS\(_2\). (a) Phonon dispersions under hydrostatic strains (0.0, 0.5, and 1.0%). The transverse acoustic (TA) mode at \( T \) point (\( q = (0.5, 0.5, 0.5) \)) becomes unstable under the applied strain. The bold line around 60–80 cm\(^{-1}\) shows the lowest optical mode that significantly enhances phonon scattering. (b) Contribution of the flat band to scattering phase space (SPS). Blue and red markers show data for absorption and emission processes while circles and crosses show, respectively, the total value and the value excluding the effect of the lowest optical mode. Black line shows phonon density of states (DOS). (c) Grüneisen parameters of the pristine structure (left) and the structure under 0.5% strain (right). Red crosses show data for the TA modes along \( q = (q, q, q) \), where \( q \) is an arbitrary number, corresponding to the \( G \)–\( T \) line and their maximum value corresponds to the \( T \) point. Inset shows data for the TA mode on \( G \)–\( T \) line with respect to \( q \). (d) Change in the \( |V_3|^2 \) term with the 0.5% strain for the TA mode at \( T \) point, which is marked with a cross (x) in the bottom panel.

Conclusions

Two novel transport descriptors for the rapid screening of potential thermoelectric materials with high mobility and powerfactor have been introduced. Pre-existing information in Materials Project database was used to filter out 12 potential
candidates, and their charge transport properties have been calculated and used to derive the descriptors. Inspection of the charge carrier scattering rates for this family of compounds reveals that in heavily doped regime, while ionised impurities have a dominant scattering contribution, polar optical phonon scattering is also important and non-negligible, and must be considered for screening of new thermoelectric materials. Transport descriptors for carrier mobility and powerfactor are proposed by including this new insight and validated with literature. In addition to effective mass, we propose that dielectric constant plays an important role in determining the carrier mobility and the maximum powerfactor. Excellent agreement with theoretical and experimental data is observed, hence validating its use as first-level screening parameter in the search of novel materials. In addition, the anharmonic scattering terms have been explicitly considered to study the phononic thermal conductivity and the ABX₃ class of compounds are observed to be promising candidates for intermediate temperature thermoelectrics.

Methods

The ab initio charge transport calculations were carried out using an Energy-dependent Phonon- and Impurity-limited Carrier Scattering Time AppRoximation (EPIC STAR), a fast and reliable first principles method based on density functional perturbation theory (DFPT) phonon calculation. QUANTUM ESPRESSO was used for DFPT calculation and the electron density of states and the charge carrier scattering rates for this family of compounds in their primitive cell calculations. The subscripts \( i \) correspond to the wavevector and \( o \), and \( q \) is the phonon frequency, \( n_l = 1/\exp(\beta/h\omega_l) - 1 \) is the Bose-Einstein distribution, \( \beta = k_BT \) with the Boltzmann constant \( k_B \), \( h \) is the reduced Planck constant, \( N \) is the number of \( q \) points, and \( -q = (-q \cdot s) \). The three-phonon matrix element \( V \) is given by:

\[
V(q, q_1, q_2) = \left( \frac{\hbar}{N\omega_{01}\omega_{2}} \right)^{1/2} \times \sum_{R_{ij}} u^{P\eta}_{00}(R_{ij}) f_{R_{ij}}(q_0) \\
\times \frac{\epsilon^2_{i}(q)\epsilon^2_{j}(q)\epsilon^2_{k}(q)}{\sqrt{M_0 M_1 M_2}} \\
\times \exp[i(q \cdot R_0 + q_1 \cdot R_1 + q_2 \cdot R_2)]
\]

where \( R_i \) is the position of the primitive cell, \( l_i \) is the atom site, \( p_i \) is the direction of the displacement of atom \( l_i \), \( M_i \) is the atomic mass, \( \Psi \) is the cubic IFCs, and \( g(q) \) is the eigenvector of the mode \( q \). The phonon relaxation time due to three-phonon scattering \( \tau_{pp} \) is given by \( \tau_{pp}(q) = 1/(2\Gamma(q)) \). The total phonon relaxation time is calculated with Mattheissens’s rule: \( \tau_{pp}^{-1} = \tau_{pp}^{-1} + \tau_{iso}^{-1} + \tau_{inst}^{-1} \), where \( \tau_{iso}^{-1} \) is the scattering rate due to natural isotopes, obtained with Tamura model, and \( \tau_{inst}^{-1} = 2|\nu|/\nu_\text{g} \) due to boundaries of grains with an effective diameter \( L_\text{g} \). Peierls contributions is calculated as \( \kappa_{c}^{\text{P}}(T) = (V_N)^{-1} \sum_{q} \epsilon_{q}(T) \epsilon_{q}(T) \epsilon_{q}(T) \tau_{q}(T) \), where \( V \) is the volume of the primitive unit cell, \( \epsilon \) is the mode specific heat, \( \nu \) is the group velocity, and \( x \) and \( \beta \) are the Cartesian directions. In this study, the averaged value of \( \kappa_{c}^{\text{P}}(T) = \kappa_{c}^{\text{P}}(2x, y, z) \) was used for the Peierls contribution. Note that ABX₃ compounds have slightly anisotropic lattice thermal conductivity. For example, \( \kappa_{c}^{\text{P}} \) was 17% smaller than \( \kappa_{c}^{\text{P}} \) for AgBiS₂ at 300 K.

The contribution of the wavelike coherent transport, which is associated with the off-diagonal term of the group velocity operator, was calculated with the unified theory as:

\[
\kappa_{c}^{\text{W}} = \frac{\hbar}{k_B^2 TVN} \sum_{q} \sum_{n_1,n_2} \frac{\omega_1 + \omega_2}{4} \Gamma_{12}^{\text{iso}}(q) \Gamma_{12}^{\text{iso}}(q) \\
\times \omega_1 n_1(n_1 + 1) + \omega_2 n_2(n_2 + 1) \\
\frac{(\omega_1 - \omega_2)^2 + (\Gamma_1 + \Gamma_2)^2}{(\Gamma_1 + \Gamma_2)^2} \Gamma_1 + \Gamma_2
\]

where \( V_{ij} \) is the generalized group velocity operator between eigenvector \( e_i \) and \( e_j \). The detailed documentation can be found also in elsewhere.

The structural optimization and computation of interatomic force constants (IFCs) were conducted with first-principles calculations using Vienna Ab initio Simulation Package (VASP). PBEsol exchange–correlation functional, which reproduced the lattice constant well, was employed for the phonon transport analysis. Because of strong structural instability of materials, the structural optimization of the primitive cell needed to be carefully performed with 40 × 40 × 40 k-points including Γ point; (a) the structural optimization was performed for structures with slightly different volumes, (b) the crystal volume was determined by a parabolic fitting with respect to the volume and minimized energy, and (c) the structural optimization was again performed for the structure with the optimal volume. The error of the finally-obtained minimum energy and the maximum force on the atoms were confirmed to be less than 0.01 meV and 0.01 meV Å⁻¹.
respectively. IFCs were computed with a $4 \times 4 \times 1$ supercell of rectangular conventional cell which contains 192 atoms with a finite-displacement method. We have confirmed that the phonon frequency took a positive value in the whole reciprocal space. Using the obtained IFCs, we have calculated phonon properties such as scattering phase space (SPS), relaxation time, and lattice thermal conductivities ($\kappa_{lat}$). Thermal conductivity was calculated with $16 \times 16 \times 16$ $q$-points.

**Author contributions**

K. H. and S.-W. Y conceived the idea. T. D. performed the charge transport calculations. J. R.-G. performed data mining. T. D. and J. R.-G. drafted the manuscript. M. O. and J. S. computed the lattice thermal conductivities. D. V. M. R. conducted the data analysis. T. D., J. R.-G., D. V. M. R., P. K. and A. S. derived the transport descriptors. All authors contributed to the discussions and manuscript revisions.

**Conflicts of interest**

The authors declare no competing interests.

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