Inverse Design of Ultralow Lattice Thermal Conductivity Materials Via Lone Pair Cation Coordination Environment

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Abstract

The presence of lone pair (LP) electrons is strongly associated with the disruption of lattice heat transport, which is a critical component of strategies to achieve efficient thermoelectric energy conversion. By exploiting an empirical relationship between lattice thermal conductivity \( \kappa_L \) and the bond angles of pnictogen group LP cation coordination environments, we develop an inverse design strategy based on a materials database screening to identify chalcogenide materials with ultralow \( \kappa_L \) for thermoelectrics. Screening the \( \sim 635,000 \) real and hypothetical inorganic crystals of the Open Quantum Materials Database based on the constituent elements, nominal electron counting, LP cation coordination environment, and synthesizability, we identify 189 compounds expected to exhibit ultralow \( \kappa_L \). As a validation, we explicitly compute the lattice dynamical properties of two of the compounds (\( \text{Cu}_2\text{AgBiPbS}_4 \) and \( \text{MnTl}_2\text{As}_2\text{S}_5 \)) using first-principles calculations and successfully find both achieve ultralow \( \kappa_L \) values at room temperature of \( \sim 0.3–0.4 \) W/(m·K) corresponding to the amorphous limit. Our data-driven approach provides promising candidates for thermoelectric materials and opens new avenues for the design of phononic properties of materials.

Graphical TOC Entry
Minimizing lattice thermal transport is critical for thermoelectric heat-to-electricity conversion, in which such heat flow acts as a loss mechanism. This can be seen in the dimensionless thermoelectric figure of merit to be maximized

$$ZT = \frac{\sigma S^2}{\kappa_L + \kappa_e} T,$$

in which the lattice thermal conductivity $\kappa_L$ appears in the denominator. Here, $\sigma$ is electrical conductivity, $\kappa_e$ is electronic thermal conductivity (typically small in semiconductors), $S$ is thermopower, and $T$ is temperature. Achieving ultralow values of $\kappa_L$ [i.e., $\lesssim 1\, \text{W/(m-K)}$] is an integral component of successful strategies to design high-performance thermoelectric materials.\(^2\)

While there exist various strategies to extrinsically reduce $\kappa_L$, such as nanostructuring, alloying, and doping (see, e.g., Refs.\(^3\)\(^\text{[13]}\)), a conceptually appealing alternative approach is to instead utilize materials with intrinsically ultralow $\kappa_L$.\(^4\) One characteristic related to ultralow $\kappa_L$ in certain materials is the presence of a lone pair (LP), a pair of valence electrons localized on a single atom.\(^5\) A LP is typically achieved via a cation (called a LP cation) whose two valence $s$ electrons remain localized on or near the cation. For example, given Sn’s electronic configuration of [Kr] $4d^{10}\,5s^2\,5p^2$, Sn$^{2+}$ (as in SnSe) is a LP cation, whereas Sn$^{4+}$ (as in SnSe$_2$) is not. Elements commonly forming LP cations include elements in group III (Tl; 1+ oxidation state), group IV (Ge, Sn, Pb; 2+ oxidation state), and the pnictogen group (P, As, Sb, Bi; 3+ oxidation state) of the periodic table.\(^6\)\(^7\)\(^8\)

It has been long known that the presence of LP cations is related to low thermal conductivity. In 1961, Petrov and Shtrum observed that thermal conductivity values of A$^1$B$^4$X$^6$\(^1\) compounds (whose B$^{3+}$ is a LP cation) are significantly lower than those of A$^1$B$^{11}$X$^6$\(^2\) compounds (whose B$^{3+}$ is not a LP cation), where A$^1$, B$^{11}$, and B$^4$ are monovalent, trivalent, and pentavalent elements, respectively, and X$^6$ is a chalcogen.\(^2\) For example, room-temperature $\kappa_L$ for AgSbSe$_2$ is only 0.7 W/(m-K), as compared to 1.8 W/(m-K) for AgInSe$_2$.\(^2\) Similarly, room-temperature $\kappa_L$ for Cu$_3$SbSe$_4$ (whose Sb$^{5+}$ is not a LP cation) is 2.5–3.5 W/(m-K), much larger than the corresponding 0.7–1.0 W/(m-K) for Cu$_3$SbSe$_3$ (whose Sb$^{3+}$ is a LP cation), despite the two compounds containing the same elements and having similar stoichiometry.\(^2\)\(^3\)\(^4\) Therefore, it is not surprising that several of the most promising thermoelectrics (e.g., PbTe, Bi$_2$Te$_3$, and SnSe) contain LP cations and that many other compounds containing LP cations have also been under investigation.\(^9\)\(^10\)

Empirically, the coordination environment of a LP cation was found by Skoug and Morelli to be intimately related to lattice thermal transport.\(^11\) In particular, within a set of compounds containing pnictogen group lone pair cations (L) coordinated to a given number of chalcogens (X), e.g., compounds whose L have 3 nearest neighbor X atoms, they observed a strong negative correlation between measured room-temperature $\kappa_L$ and a local structural parameter related to the bond angles $\angle$X–L–X of the LP cation’s coordination cage. This parameter $\bar{\alpha}(s)$ can be defined as

$$\bar{\alpha}(s) = \frac{1}{N_{\text{ang}}(s)} \sum_i \alpha_i(s) \theta(\alpha_{\text{max}}(s) - \alpha_i(s)),$$

where $\alpha_i(s)$ is the $i^{th}$ $\angle$X–L–X for the $s^{th}$ LP cation site, $\theta$ is the Heaviside step function, $\alpha_{\text{max}}(s)$ is cos$^{-1}(-\frac{1}{3}) \approx 109.5^\circ$ (bond angle for ideal tetrahedral coordination), and $N_{\text{ang}}(s) = \sum_i \theta(\alpha_{\text{max}}(s) - \alpha_i(s))$. In words, $\bar{\alpha}(s)$ is simply the average of the $N_{\text{ang}}(s)$ bond angles no larger than 109.5$^\circ$ for the $s^{th}$ LP cation site. The quantity $\bar{\alpha}(s)$, which originates from a study of Sb chalcogenides using the bond valence sum concept, was found to relate to the effective valence of the LP cation (i.e., between the nominal 3+ and 5+ common oxidation states for Sb) and was interpreted as describing the retraction of the LP from the LP cation.\(^15\) In general, the work of Skoug and Morelli (and others)\(^16\) strongly suggests the importance of the LP cation environment and spatial distribution of the LP in influencing lattice dynamics.
In this Letter, we exploit the connection between LP cation coordination environment and lattice heat transport with the goal of designing ultralow $\kappa$ materials. We develop an inverse design approach based on a materials database screening, which can be considered the so-called “second modality” of inverse design and is related to our previous works on inverse design for electronic band structure. Searching for synthesizable compounds containing pnictogen group LP cations coordinated to chalcogens with large $\alpha (s)$ (corresponding to low $\kappa$), we identify 189 compounds. As a validation, we explicitly compute the lattice dynamical properties for two of the identified compounds, Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$, and successfully find ultralow $\kappa$ values of $\sim 0.3$–0.4 W/(m·K) at room temperature. In addition to providing promising ultralow $\kappa$ materials, our data-driven approach opens up new avenues for inverse design of lattice dynamical properties.

Our design space consists of the materials within the Open Quantum Materials Database (OQMD), which contains electronic structure calculations based on density functional theory (DFT) for $\sim 635,000$ (as of November 2019) known and hypothetical inorganic crystals derived from the Inorganic Crystal Structure Database (ICSD) and structural prototypes. Our initial screening, before taking into account $\alpha (s)$, is based on several criteria that must be simultaneously satisfied:

1. **Chemical elements** – Compound must contain one or more of the pnictogen group elements that commonly occur with a 3+ oxidation state (As, Sb, Bi), one or more chalcogen elements (S, Se, Te), and (for practicality) no radioactive elements.

2. **Electron count** – The pnictogen must have an oxidation state of 3+ (so it is a LP cation) and all other elements must have integer oxidation states (to focus on possible semiconductors/insulators).

3. **Crystal structure** – Each pnictogen atom must be coordinated solely by chalcogen atoms and must have a coordination number $\geq 3$.

4. **Synthesizability** – The compound formation energy must be at most 25 meV/atom above that of the thermodynamic ground state determined by convex hull analysis (consistent with the overall scale of metastability for experimentally observed chalcogenides and/or reported experimentally). This criterion is chosen to focus on synthesizable compounds.

The criteria are based on pnictogen group LP cations (as opposed to others like Pb$^{2+}$ and Tl$^+$ and chalcogens since the data in work of Skoug and Morelli pertain to such chemistries. Further details about the screening criteria are included in the Supporting Information.

352 compounds pass the initial screening criteria. Although we have characterized these compounds in terms of chemical composition, crystal structure, electronic properties, and synthesizability (see the Supporting Information), we focus here on the local coordination environment of the LP cations. Fig. 1(a) shows the coordination number and $\overline{\alpha}(s)$ of each pnictogen LP cation element in the 352 compounds. For atomic sites with complex, low-symmetry coordination environments (often the case for LP cations), defining coordination number can be challenging. Therefore, to avoid ambiguity, we employ the well-defined effective coordination number of Hoppe, a continuous quantity that includes contributions (smoothly and rapidly decaying with increasing distance) from all other atoms. For compounds containing multiple sites of a LP cation element with distinct environments, we show the average values of coordination number and $\overline{\alpha}(s)$ (which we call $\langle \text{CN} \rangle$ and $\langle \overline{\alpha} \rangle$, respectively), with the ranges indicated by the “error bars.” The coordination number generally increases as the LP cation element goes down the pnictogen group of the periodic table (As → Sb → Bi). In addition, consistent with the work of Skoug and Morelli, we generally find smaller $\overline{\alpha}(s)$ values for larger coordination number. Notably, many of the 352 compounds exhibit large $\overline{\alpha}(s)$ values $\sim 90$–100°.

To search for the most promising compounds, we further screen based on $\overline{\alpha}(s)$. Since the
as2se3 as2te3 tI3sBse3

FeBiSbS4

The majority of the compounds occur in two regions: (1) the red region of smaller coordination number (containing many Bi compounds) and (2) the cyan region of larger coordination number (containing many As compounds). The 189 compounds we have identified should be considered promising candidates for ultralow $\kappa_L$, and possibly thermoelectric applications. Indeed, among the 189 are various systems that have been explored previously for thermoelectricity and exhibit low $\kappa_L$, such as AgBiS2, AgBiS3, Bi2Se3, K2Bi8Se13, AgBiSe2, Bi2Te3, Bi2Te2Se, AgBiTe2, GeBi5Te4, GeBi4Te7, PbBi2Te4, PbBi4Te7, Tl9BiTe6, Cu3SbSe3, AgSbTe2, TlSbTe2, and Tl9SbTe6.

In order to validate our approach, we explicitly compute the lattice thermal transport behavior for two of the identified compounds. We choose one compound from the cyan region (CuAgBiPbS4) and one from the red region (MnTl2As2S5) of Fig. 1(b). Both compounds exist (i.e., they are experimental structures from the ICSD), but they have not been explored for thermoelectricity. We note that they are metastable compounds within the OQMD whose formation energies are a small amount (13–14 meV/atom) above the convex hull.

Fig. 2 shows the crystal structures of...
Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$. Cu$_2$AgBiPbS$_4$, a mineral, is orthorhombic (Pnma space group) with a complex 3D bonding network. In Cu$_2$AgBiPbS$_4$, Bi$^{3+}$ is octahedral with $\langle \alpha \rangle = 89.98^\circ$ and $\langle \text{CN} \rangle = 5.61$, whereas Cu$^+$ exists in linear and trigonal planar coordinations, Ag$^+$ is trigonal pyramidal, and Pb$^{2+}$ (also a LP cation) is capped trigonal prismatic. MnTl$_2$As$_2$S$_5$, which has been synthesized hydrothermally, also crystallizes with an orthorhombic (Cmce) space group, and it can be considered a layered structure.

Table 1: Group velocity $v$ at $\Gamma$ (in km/s), Debye temperature $\Theta$ (in K), and root-mean-square Grüneisen parameter for each acoustic branch in each direction.

We focus on lattice dynamical properties, but
details on the electronic properties are included in the Supporting Information for completeness. The low-frequency phonon dispersions for Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$ are shown in Fig. 3. Due to partial occupancy of the trigonal planar Cu site (not considered in the OQMD), we employ a unit cell doubled along the $x$ direction to study Cu$_2$AgBiPbS$_4$, as discussed in detail in the Supporting Information. Both materials exhibit acoustic and optical phonons that are quite low in frequency. In the case of Cu$_2$AgBiPbS$_4$, vibrations of all four cations contribute appreciably to these modes, with Cu vibrations contributing the most. For MnTl$_2$As$_2$S$_5$, Tl vibrations are dominant. The computed sound velocities and Debye temperatures (taken to be the zone boundary frequencies) for each acoustic branch and direction are shown in Table 1. Both exhibit sound velocities of $\sim 1$–$3$ km/s and, due in part to the complexity of the unit cell, Debye temperatures of only $\sim 15$–$40$ K. Therefore, both Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$ are very soft in terms of elastic (harmonic) properties.

To measure the anharmonicity in Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$, we compute the mode Grüneisen parameter. Defined as $\gamma = -\frac{\partial \ln \omega}{\partial \ln V}$, where $\omega$ is phonon frequency and $V$ is crystal volume, the Grüneisen parameter provides a measure of the strength of the phonon–phonon scattering, which limits lattice heat transport. As shown in Fig. 3 and Table 1, both compounds exhibit large Grüneisen parameter for the acoustic and especially the low-lying optical modes. For example, for the optical modes, we find values of $\sim -15$ for Cu$_2$AgBiPbS$_4$ and $\sim 20$ for MnTl$_2$As$_2$S$_5$. For the MnTl$_2$As$_2$S$_5$ case, the lowest optical mode at the zone center contains substantial Tl motion. Therefore, especially given the large experimental atomic displacement parameters for Tl ($28$–$36 \times 10^{-3}$ Å$^2$), the concept of “rattler” Tl atoms may be relevant to MnTl$_2$As$_2$S$_5$. In contrast, for the Cu$_2$AgBiPbS$_4$ case, the lowest optical mode at the zone center corresponds to a collective motion of all atom types. Visualizations of various phonon modes are included in the Supporting Information.

Determining a highly accurate prediction of $\kappa_L$ for complex crystals is a significant challenge and is outside the scope of this work. However, to establish a baseline estimate for the magnitude, we employ the Debye-Callaway model \cite{debye1912,callaway1951}, which has been used to provide a good qualitative picture for a variety of low-$\kappa_L$ materials. In this approach, for which the data in Table 1 serve as input, only acoustic phonon scattering is considered. Due to the soft elastic properties, complex unit cell, and substantial anharmonicity, the computed Debye-Callaway model $\kappa_L$ values are only 0.01–0.03 W/(m·K) for Cu$_2$AgBiPbS$_4$ and 0.01–0.07 W/(m·K) for MnTl$_2$As$_2$S$_5$. Such low values, which can only result since the Debye-Callaway model does not consider that the interatomic distance is a lower bound to the phonon mean
free path, are below the minimum possible (amorphous limit) $\kappa_L$. Therefore, we take the minimum $\kappa_L$, via the Cahill model, $^{32}$ as our best expectation for the measured lattice thermal conductivity. We find minimum $\kappa_L$ of 0.44, 0.40, and 0.38 W/m-K in the x, y, and z directions, respectively, for Cu$_2$AgBiPbS$_4$. Similarly, we find minimum $\kappa_L$ of 0.31, 0.38, and 0.29 W/m-K in the x, y, and z directions, respectively, for MnTl$_2$As$_2$S$_5$. Both compounds thus are expected to successfully achieve the desired ultralow $\kappa_L$, validating our approach.

Our inverse design strategy is successful in that we have identified materials (fully listed in the Supporting Information) very likely to exhibit the desired ultralow $\kappa_L$. A natural question is whether this success stems from solely a correlation between the properties of the LP and $\kappa_L$, or whether the relationship is causal. Previously, it has been proposed that the large polarizability of the LP does cause anharmonicity due to electrostatic interaction between the LP and the bonding states. $^{21,24,33,83}$ As evidence, Zhang et al. observed that anharmonic phonon modes in Cu$_5$SbSe$_5$ involve motion of the Sb$^{3+}$ in the direction of the LP. $^{24}$ and Nielsen et al. found that the Sb$^{3+}$ LP is encompassed by the polarization response to Se atomic motion associated with anharmonic modes in NaSbSe$_2$. $^{33}$ In addition, it has been argued that the further spatial removal of the LP from the LP cation in particular, as represented by large $\langle \pi \rangle$, enhances the anharmonicity. $^{33}$

Isolating the specific role of the LP in producing low $\kappa_L$ remains a significant challenge. $^{34}$ To investigate this role for Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$, we perform calculations to assess the coupling of the LP to the anharmonic phonon modes. As discussed in the Supporting Information, based on our analysis of the electronic localization function and electronic density of states, we do not find evidence for an especially strong coupling. In particular, we find no dramatic change in either the spatial location or the energy of the LP (which is far below the valence band edge in our case) as a result of the anharmonic phonons. As such, for the compounds in this study, we are unable to claim that the presence of the LP, or the specific LP cation coordination environment or spatial distribution of the LP, directly causes the ultralow $\kappa_L$. In any case, our data-driven inverse design approach based on the established correlation between LP cation properties is capable of providing promising materials with ultralow $\kappa_L$, and opens the door to future strategies for inverse design of phononic properties.

### Computational Methods

DFT calculations using a plane-wave basis set and the projector augmented wave method $^{85,87}$ are performed using vasp. $^{88}$ We employ the generalized gradient approximation of Perdew, Burke, and Ernzerhof, $^{59}$ a 500 eV plane wave energy cutoff, and uniform k-meshes with k-point density $\geq 700$ k-points/Å$^3$. The energy and ionic forces are converged to within $10^{-6}$ eV and 0.01 eV/Å, respectively. Lattice dynamical properties are computed using PHONOPY $^{80}$ with approximately cubic supercells $^{91,92}$ of 216 atoms for Cu$_2$AgBiPbS$_4$ and 200 atoms for MnTl$_2$As$_2$S$_5$. We use atomic displacements of 0.005 Å to compute the phonons and volume differences of $\pm 1.5\%$ to compute the mode Grüneisen parameter. $\kappa_L$ is computed via the Debye-Callaway model $^{77,79}$ and compared to the minimum (amorphous limit) values. $^{82}$ The reciprocal space high-symmetry paths are based on Ref. $^{93}$

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Supporting Information Available

The following files are available free of charge. Full list and characterization of the identified compounds, screening criteria details, results and discussion of dynamical instability in Cu$_2$AgBiPbS$_4$, acoustic branch definitions and visualization of phonon modes of Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$, and calculations of electronic properties and coupling with anharmonic phonons of Cu$_2$AgBiPbS$_4$ and MnTl$_2$As$_2$S$_5$.

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