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Low thermal conductivity in a modular inorganic material with bonding anisotropy and mismatch

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Abstract: The thermal conductivity of crystalline materials cannot be arbitrarily low as the intrinsic limit depends on the phonon dispersion. We used complementary strategies to suppress the contribution of the longitudinal and transverse phonons to heat transport in layered materials containing different types of intrinsic chemical interface. BiOCl and

$\text{Bi}_2\text{O}_2\text{Se}$ encapsulate these design principles for longitudinal and transverse modes respectively, and the bulk superlattice material $\text{Bi}_4\text{O}_4\text{SeCl}_2$ combines these effects by ordering both interface types within its unit cell to reach an extremely low thermal conductivity of $0.1 \text{ W}\cdot\text{K}^{-1}\text{m}^{-1}$ at room temperature along its stacking direction. This value comes within a factor of four of air. We demonstrated that chemical control of the spatial arrangement of distinct interfaces can synergically modify vibrational modes to minimize thermal conductivity.

One Sentence Summary: Two different interfaces in a single bulk material produce low thermal conductivity.

Main Text: Lattice thermal conductivity, κ , is a property inherent to all solids, with important technological impact that has driven materials design concepts to maximize the range of values accessible. Electronic devices require high κ to reduce thermal load (1) and allotropes of carbon (2, 3) are materials of choice, with isotope control key to suppress scattering of the lattice vibrations (phonons) that carry heat (4). Thermoelectric modules for energy harvesting and thermal barrier coatings for turbine blades require low κ to maintain temperature gradients (5). Materials with thermal conductivities lower than that of silica glass ($0.9 \text{ W}\cdot\text{K}^{-1}\text{m}^{-1}$), used for everyday thermal insulation, are of special interest. The lower limits of κ have been investigated since theoretical work by Einstein (6). The thermal physics is generally understood to become qualitatively different at low κ , with numerous mechanisms appearing in this regime (7-12). Investigating new materials uncovers interesting physics where the effect of unexplored atomic arrangements and the arising bonding patterns on κ can be better understood.

Phonon heat transport can be reduced by decreasing either the phonon scattering length or the phonon group velocity, the long wavelength limit of which is the speed of sound of the material. The scattering length is determined both by intrinsic (phonon-phonon scattering, which is enhanced by anharmonicity) and extrinsic (*e.g.*, defect or boundary scattering) mechanisms, while the group velocity is controlled by the phonon dispersion, which is intrinsic to a material as it is defined by the structure and composition. Hence, much research has addressed reducing phonon scattering lengths extrinsically via nanostructuring and defect engineering of materials that are known to have intrinsically low thermal conductivities (*13, 14*). However, the phonon scattering length has a lower limit of half of the wavelength, below which the vibration can no longer be considered a phonon. This sets an asymptotic high temperature limit for the thermal conductivity that many materials approach in the high scattering regime. This limit is determined intrinsically by the whole phonon dispersion regardless of the heat conduction mechanism (*15*), and sets the scale of accessible κ at all temperatures (*16*). A successful materials design strategy would then reduce this asymptotic limit of κ through engineering the total phonon dispersion defined by the structure at the unit cell level (*17, 18*).

The modularity in the build-up of layered crystals offers the opportunity to control the materials properties by careful selection of the interfacial interaction between layers. Analytical models have been developed to describe the impact of the anisotropic bonding strength in layered compounds on their thermal conductivities (*19,20*) and provided a framework to understand how their asymptotic high temperature limit falls below the expected isotropic limit through a combination of phonon focusing and first Brillouin Zone truncation effects (*16*). We show how different layer sequences can be designed to selectively target longitudinal and transverse phonons and reduce their contribution to the thermal

conductivity by generating imbalances in chemical bonding and ion size. The imbalance in chemical bonding drastically modifies the phonon dispersion to reduce heat transport, and is structurally compatible with imbalances in ion size that further decrease the thermal conductivity. Designed combination of these interfaces at the unit cell level in a bulk superlattice material then allows these effects to synergize and affect all transport-active phonon modes along the stacking axis, leading to an extremely low thermal conductivity of $0.10(2) \text{ W.K}^{-1}\text{m}^{-1}$ at room temperature in $\text{Bi}_4\text{O}_4\text{SeCl}_2$, which is among the lowest for any bulk inorganic material and only four times the thermal conductivity of air.

Longitudinal phonons have atomic displacements along the direction of wave propagation, and are thus related to compression and expansion modes of the structure, while transverse modes have atomic displacements perpendicular to the propagation direction, and are related to shear modes. Because these modes originate from different types of atomic displacement, they require distinct design motifs to produce a phonon dispersion that confers low thermal conductivity. In materials with more than one atom per unit cell, phonons have both acoustic (all atoms in the unit cell share a displacement direction) and optical (atoms in the unit cell displace in opposite directions) branches. This leads to transverse acoustic (TA), transverse optical (TO), longitudinal acoustic (LA) and longitudinal optical (LO) phonons. Each acoustic branch has a speed of sound v defined by the group velocity or slope of the dispersion close to the center of the Brillouin zone (Fig. 1A). Because many properties, including thermal conductivity, depend most strongly on the low frequency regime, the Debye approximation to the dispersion, $\omega(k) = vk$, where k is the phonon wavevector and ω is the phonon frequency, is often used to derive models describing these quantities. This approximation results in the Debye-Callaway model for the thermal conductivity (21), which we refer to as $\kappa_1(T)$ (eq. S14), because a single phonon velocity is used, and its associated

high temperature asymptotic limit, or the minimum thermal conductivity, defined by Cahill and Pohl (22), referred to as $\kappa_{1\min}$.

We considered the effect of bond contrast at an interface in a layered material, in order to capture the effect of weak interlayer bonds, for example, at a van der Waals (vdW) gap, on the longitudinal phonons that propagate in the out-of-plane (stacking) direction (Fig. 1A). We build a Born von Karman (BvK) model (fig. S1) to describe the longitudinal phonon dispersion based on nearest-neighbor bonding with anisotropic bond contrast, where the weak bonds between the layers with force constant C_1 alternate along the stacking direction with the strong bonds of force constant C_2 ($C_1 < C_2$) that describe the bonds within the layers both in- and out-of-plane. This is a similar model and resulting phonon dispersion to that in (19) – here we use this phonon dispersion and its parameterization with respect to the bonding interactions to connect the thermal conductivity directly to the bonding via a simple parameterized Debye-Callaway formalism. The in-plane thermal conductivity of the material is described by the κ_1 and $\kappa_{1\min}$ models at any C_1/C_2 ratio as the in-plane phonon dispersion is entirely determined by C_2 .

Out-of-plane, the LA phonon involves primarily interlayer displacements and its maximum frequency is determined solely by C_1 , while the LO dispersion depends on both C_1 and C_2 , as this phonon involves both intra- and interlayer displacements (fig. S1). As C_1/C_2 decreases, the LA mode becomes more anisotropic with a larger energy gap to the LO mode, which decreases in velocity. The out-of-plane direction then requires a different thermal conductivity model $\kappa_2(T)$ (eq. S24) with two components that describe the LA and LO modes separately to account for their markedly different velocities. The use of two components corrects for the overestimation of the heat transfer along the weak interlayer bonds due to

phonon focusing (16,19,20) and reflects the importance of considering the entire phonon dispersion to describe thermal transport (15). To obtain the associated asymptotic high temperature limit $\kappa_{2\min}$ in the out-of-plane direction, we assume the minimum mean free path is equal to half the phonon wavelength and use a modified Debye approximation (fig. S22), similar in construction to the Debye-Snyder approximation (18). $\kappa_{2\min}$ is controlled by C_1/C_2 , the out-of-plane speed of sound v_{\perp} and the atomic number density N , and is below $\kappa_{1\min}$ when C_1/C_2 is below 1 (23); as C_1/C_2 decreases, so does $\kappa_{2\min}$ (fig. S2). This suggests that anisotropic bond contrast at vdW interfaces in a layered structure can minimize the contribution of longitudinal phonons to thermal transport in the out-of-plane direction.

An alternative strategy can be employed to reduce the contribution of the transverse phonons to the thermal conductivity (Fig. 1B). Materials that are prone to a static distortion producing a structural phase transition often have soft, nonlinear anharmonic TA modes (24-27). The interface between the undersized Mg layer and the Mg_2Sb_2 layer in Mg_3Sb_2 creates soft anharmonic shear modes (28), and the ferroelectric-like incipient lattice distortion that softens phonons in SnSe contributes to its low lattice thermal conductivity (27). In a layered material with the stacking axis perpendicular to the basal plane, the out-of-plane transverse phonons exhibit only in-plane displacements. As the chemistry is tuned to vary the energy profile of the in-plane distortion, *e.g.*, by varying the mismatch of size and bonding at the interface between an interstitial ion and a layered building unit, the out-of-plane TA dispersion evolves from linear at small k when there is no distortion to displaying imaginary frequency at the k corresponding to the static displacement of a dynamically stable distortion (25), with a softening effect on the transverse phonons in the case of an incipient phase transition (Fig. 1B). The resulting anharmonicity of the out-of-plane TA modes in the latter case will reduce the out-of-plane thermal conductivity by increasing the intrinsic phonon

scattering rate. The anharmonicity also leads to a lower velocity for the out-of-plane TA modes ($v_{T\perp}$), which reduces the asymptotic limit of the out-of-plane thermal conductivity.

Combining structurally compatible layered building units that display anisotropic bond contrast and are close to in-plane displacive shearing transitions should integrate their effects on the phonon thermal transport. This requires appropriate chemistry that orders at least three interfaces - a weak and a strong interlayer bonding interface, and an interface that is prone to in-plane distortion. A schematic of such a material is shown in Figure 1C, together with the targeted phonon dispersion that combines the anisotropic LA mode softening (Fig. 1A) with anisotropic TA mode softening and anharmonicity (Fig. 1B). This highlights the challenge of identifying bonding motifs that allow these characteristic phonon dispersion features of the individual modules to be combined without degradation.

To realize this phonon dispersion in a bulk material, we considered the family of layered $(\text{Bi}_2\text{O}_2)_m\text{X}_n$ materials. These materials feature strongly bonded $\text{Bi}_2\text{O}_2^{2+}$ cationic layers stacked alternately with a wide range of anionic X layers that offer different interfaces resulting in distinct bonding dimensionalities. Fig. 2A shows the crystal structure of BiOCl where the layers are terminated by strong Bi-Cl bonds, such that discrete strongly bonded $\text{Bi}_2\text{O}_2\text{Cl}_2$ layers are weakly bonded to each other along the c direction by a Cl...Cl vdW interaction (29), which can be described as a weak interlayer bond. BiOCl thus has both strong and weak bonding interfaces, and should exhibit large anisotropic bond contrast. We measured the thermal conductivities parallel and perpendicular to the plane of a densified pellet of BiOCl (Fig. 2B), which is highly (001) textured (fig. S3) perpendicular to the pellet plane, *i.e.*, in the pressing direction. In this and all materials presented here, the measured thermal conductivity is dominated by the lattice contribution due to the low electronic

conductivities (23). The temperature dependence is consistent with crystalline conduction, with a low temperature peak observed in both directions followed by an inverse temperature dependence towards the asymptotic high temperature limit. The thermal conductivity we measured parallel to the pellet plane is above $\kappa_{1\min}$ and its temperature dependence is well-described by $\kappa_1(T)$ (Fig. 2B) with appropriate scattering parameters (Table S4). Testing other models confirmed that the thermal conductivity should be described in terms of phonon transport (fig. S19). The thermal conductivity we measured perpendicular to the pellet plane is strikingly different, as the room temperature value of $0.15(2) \text{ W.K}^{-1}\text{m}^{-1}$ is well below $\kappa_{1\min}$ of $0.5 \text{ W.K}^{-1}\text{m}^{-1}$ and continues to decrease on heating (fig. S7). The thermal conductivity perpendicular to the pellet plane is described well by the two-component model, $\kappa_2(T)$ (Fig. 2B), introduced to describe systems with the bonding shown in Fig. 1A, with appropriate scattering parameters (Table S3) and $\kappa_{2\min}$ of $0.125 \text{ W.K}^{-1}\text{m}^{-1}$. As the two component model was needed for the *c*-axis-dominated direction but not the *ab*-plane-dominated direction, this suggests that anisotropic bond contrast in BiOCl induces strong deviation of the longitudinal modes from the Debye model in the out-of-plane direction that suppresses their contribution to the thermal conductivity.

To test the validity of this hypothesis, we calculated the phonon dispersion for BiOCl with first-principles DFT (shown up to 100 cm^{-1} , Fig. 2C). The low frequency dispersion closely resembles that arising from the bonding scheme (Fig. 1A). The predicted anisotropy of the LA mode is evident in the computed speeds of sound (Tables S1-2) where $v_{L//}/v_{L\perp} = 1.61$. This LA anisotropy and the large anisotropic energy gap (104 cm^{-1} out-of-plane) between the LA and first LO phonons in BiOCl show good agreement with the BvK model when $C_1/C_2 = 0.054$ (fig. S20), and arise from the anisotropic bond contrast between the inter- and intralayer displacements that differentiate the LA and LO modes propagating out-of-plane

(fig. S13). This value of C_1/C_2 is far below 1, confirming that the low value of κ and applicability of the $\kappa_{2\min}$ and κ_2 models is due to the structural control of the longitudinal phonons leading to a large anisotropic deviation from the linear Debye model. The transverse modes propagating out-of-plane contain only in-plane displacements, and thus to first order are not affected by the anisotropic bond contrast, suggesting there is scope to reduce both κ and $\kappa_{2\min}$ further by modifying the phonon dispersion through chemical bonding control beyond the longitudinal modes.

Targeting these out-of-plane transverse phonons requires the introduction of an in-plane structural instability (Fig. 1B) associated with chemical and structural motifs that are compatible with BiOCl. Amongst chemically compatible materials with $\text{Bi}_2\text{O}_2^{2+}$ layers, $\text{Bi}_2\text{O}_2\text{Se}$ has the appropriate bonding (Fig. 3A) to control the transverse modes. A single layer of Se^{2-} anions symmetrically bridges the same $\text{Bi}_2\text{O}_2^{2+}$ layers to form the anti- ThCr_2Si_2 structure, where there is no vdW gap and therefore no associated strong anisotropic bond contrast (30). The AM_2X_2 (here $\text{A} = \text{Se}$, $\text{M} = \text{Bi}$, $\text{X} = \text{O}$) structure field radius ratio (31) $f = (r_A)/(r_X + 0.2r_M) = 1.14$ places $\text{Bi}_2\text{O}_2\text{Se}$ in the stability region of the hexagonal anti- CaAl_2Si_2 structure adopted by $\text{La}_2\text{O}_2\text{Se}$, suggesting Se is undersized in its 8-coordinate environment (with a long 3.4\AA Bi-Se bond), through mismatch to the Bi_2O_2 layer dimensions. The internal lattice strain from this bonding frustration at the bridging Bi_2O_2 -Se interface positions the tetragonal structure near a distorted phase (32) that is realized through in-plane static displacements in orthorhombic ultrathin, freestanding $\text{Bi}_2\text{O}_2\text{Se}$ nanosheets (33). Therefore, $\text{Bi}_2\text{O}_2\text{Se}$ can be considered to have both a strong bonding interface (within the $\text{Bi}_2\text{O}_2^{2+}$ unit) and a distortion-prone interface (between the $\text{Bi}_2\text{O}_2^{2+}$ and Se^{2-} layers).

A pellet of $\text{Bi}_2\text{O}_2\text{Se}$, which is highly (001) textured (fig. S4), shows low thermal conductivity in both directions ($1.0(2) \text{ W}\cdot\text{K}^{-1}\text{m}^{-1}$ at room temperature, consistent with previous reports (34)) that has the temperature dependence expected for a crystalline material but is, unlike BiOCl , above $\kappa_{1\text{min}}$ (Fig. 3B). It can thus be described by the one component Debye-Callaway model $\kappa_1(T)$, indicating weak anisotropic bond contrast ($C_1/C_2 \approx 1$) compared to BiOCl , arising from Se as a bridging ligand in place of terminal Cl. This description is confirmed in the calculated phonon dispersion (Fig. 3C) by the much more isotropic ($v_{L//}/v_{L\perp} = 1.10$) and higher velocity out-of-plane LA mode in $\text{Bi}_2\text{O}_2\text{Se}$ ($3844 \text{ m}\cdot\text{s}^{-1}$) than in BiOCl ($2593 \text{ m}\cdot\text{s}^{-1}$). The TA modes are controlled by the shear motion of Bi_2O_2 planes against the Se plane, and the small (0.7 cm^{-1}) imaginary frequency in their dispersion (fig. S12) shows the proximity of $\text{Bi}_2\text{O}_2\text{Se}$ to a static in-plane distortion, resulting in low velocity, anharmonic TA modes propagating out-of-plane, with the velocity increasing at low frequencies before going to zero at the Brillouin Zone edge, leading to an inflection point at 0.025 \AA^{-1} (where the second derivative of the dispersion is zero, Fig. 3C). The anharmonicity of the TA phonons is demonstrated by the non-linearity in the $\omega(k)$ dispersion at low k (35-37). The second derivative of the dispersion of BiOCl (Fig. 2C) indicates that the dispersion shows little deviation from linearity. Because the LA modes are nearly isotropic, the difference in the temperature dependence of the measured κ between the two directions is attributed to the anharmonicity of the out-of-plane TA modes. The $\kappa_1(T)$ model for both directions could be described using identical values for the extrinsic scattering parameters (Table S4). The flattening we observed of the low temperature peak in the thermal conductivity measured perpendicular to the pellet plane requires an additional intrinsic phonon-phonon scattering term at low frequencies that we ascribed to out-of-plane TA anharmonicity. This anharmonicity also leads to a much lower calculated out-of-plane TA mode velocity in $\text{Bi}_2\text{O}_2\text{Se}$ ($836 \text{ m}\cdot\text{s}^{-1}$) than in BiOCl ($1678 \text{ m}\cdot\text{s}^{-1}$). These observations emphasize that the TA

modes in $\text{Bi}_2\text{O}_2\text{Se}$ show the key features of Fig. 1B, leading to a different shape of $\kappa(T)$ out-of-plane than in-plane, through mechanisms distinct from, and thus potentially complementary to, the longitudinal mode control achieved in BiOCl .

In order to create a material where thermal transport by both longitudinal and transverse modes is suppressed through combination of anisotropic bond contrast with layer dimension mismatch, we considered the $\text{Bi}_2\text{O}_2^{2+}$ -derived phase $\text{Bi}_4\text{O}_4\text{SeCl}_2$ (Fig. 4A). $\text{Bi}_4\text{O}_4\text{SeCl}_2$ can be described as a bulk superlattice of BiOCl , with contrasting strong and weak bonding interfaces, and $\text{Bi}_2\text{O}_2\text{Se}$ containing an undersized bridging Se layer, with its associated distortion-prone interface arising from the in-plane structural instability, experimentally stabilized by Se/Cl site mixing (38). This extended structure should therefore combine the ingredients of Figs. 1A and 1B to achieve the schematic phonon dispersion presented in Fig. 1C. To evaluate this hypothesis, we calculated the phonon dispersion for $\text{Bi}_4\text{O}_4\text{SeCl}_2$ without site mixing (fig. S11). The low frequency region of the dispersion (Fig. 4B) displays both the effect of anisotropic bond contrast at the terminally bonded van der Waals interface on the longitudinal phonons, and the creation of soft anharmonic TA phonons through proximity to an in-plane structural instability driven by structural mismatch at the bridging interface (fig. S12), demonstrating the targeted combination of phonon dispersion effects. This integration of both transverse and longitudinal mode control in $\text{Bi}_4\text{O}_4\text{SeCl}_2$ results in a lower average out-of-plane speed of sound than in either BiOCl or $\text{Bi}_2\text{O}_2\text{Se}$, with an average speed of sound reduction of 25% compared to BiOCl . In contrast to either end-member, the phonon dispersion features both significantly anisotropic LA modes ($v_{L//}/v_{L\perp} = 1.46$) and anharmonic, low velocity ($896 \text{ m}\cdot\text{s}^{-1}$) out-of-plane TA modes. This reflects the interface synergy in phonon dispersion realized by the combination of terminal and bridging chemistries in the layer sequence of $\text{Bi}_4\text{O}_4\text{SeCl}_2$.

We measured the neutron-weighted generalized phonon density of states (DOS) of $\text{Bi}_4\text{O}_4\text{SeCl}_2$ with inelastic neutron scattering (INS) and it compares well with the calculated neutron-weighted phonon DOS both with and without site-mixing (Fig. 4C). The calculated DOS for all materials studied here also agrees well with the thermodynamic parameters extracted from the experimental heat capacity (fig. S18). The Se/Cl site mixing has only a small effect on the calculated DOS with small changes appearing on optical phonons above 100 cm^{-1} , leaving the low-frequency modes relatively unaffected. Site mixing can lead to increased point defect scattering, as seen in the increased computed phonon localization in $\text{Bi}_4\text{O}_4\text{SeCl}_2$ with Se/Cl site mixing compared to BiOCl , $\text{Bi}_2\text{O}_2\text{Se}$ or $\text{Bi}_4\text{O}_4\text{SeCl}_2$ without site mixing (fig. S14); the effect of Se/Cl site mixing is therefore expected to be mostly extrinsic. These observations indicate good qualitative agreement between the calculated and experimental phonon DOS for $\text{Bi}_4\text{O}_4\text{SeCl}_2$, showing that the essential features of the component module phonon dispersions are conserved in the bulk superlattice and should further reduce its thermal conductivity below those of the component motifs.

A pressed, highly (001) textured pellet (figs. S5-S6) and a single crystal of $\text{Bi}_4\text{O}_4\text{SeCl}_2$ indeed show extremely low and anisotropic thermal conductivity (Fig. 4D) with a characteristic glass-like temperature dependence. We did not observe a low temperature peak and instead, rather than an inverse decrease, we observed a monotonic increase at high temperature towards the asymptotic limit. This suggests that the heat transport cannot be described using a semi-classical framework but requires consideration of inter-branch tunneling and decoherence between vibrational eigenstates (15). This transition from crystal to glass-like thermal transport has previously been observed in compounds presenting phonon localization due to site mixing (39) and is phenomenologically implemented here by the

suppression of the Umklapp scattering contribution in the one- and two-component models. Thus, it does not affect the high temperature asymptotic limit (as represented by $\kappa_{1\min}$ and $\kappa_{2\min}$) of these models, as this is governed by intrinsic materials properties controlled by the phonon dispersion. The in-plane thermal conductivity of a $\text{Bi}_4\text{O}_4\text{SeCl}_2$ single crystal is $1.0(1) \text{ W.K}^{-1}\text{m}^{-1}$ at room temperature, remains above $\kappa_{1\min}$ ($0.6 \text{ W.K}^{-1}\text{m}^{-1}$) and can be described with the $\kappa_1(T)$ model with its associated scattering mechanisms (Table S4). The thermal conductivity of the textured pellet measured parallel to the pellet plane is very low ($0.4(1) \text{ W.K}^{-1}\text{m}^{-1}$) at room temperature, and slightly lower than the $\kappa_{1\min}$ for that direction because of the contribution of the out-of-plane component from incomplete texturing. The thermal conductivity at room temperature perpendicular to the pellet plane of $0.10(2) \text{ W.K}^{-1}\text{m}^{-1}$ is well below $\kappa_{1\min}$, and may be compared with the $0.026 \text{ W.K}^{-1}\text{m}^{-1}$ thermal conductivity of air. This extremely low value is consistent with the longitudinal phonon dispersion, where the anisotropic bond contrast effect (Fig. 1A) requires modelling the temperature dependence with the two-component $\kappa_2(T)$ model, as in BiOCl . The complementarity of the transverse phonon mode dispersions through structural mismatch at the bridging interface is highlighted by the further lowering of $\kappa_{2\min}$ compared to BiOCl . The measured asymptotic high temperature limit of the thermal conductivity for $\text{Bi}_4\text{O}_4\text{SeCl}_2$ is about 30% lower than that for BiOCl (fig. S7), which is very close to the difference in average speed of sound due to the anharmonic TA mode softening in $\text{Bi}_4\text{O}_4\text{SeCl}_2$ (Table S1). The thermal conductivity of $\text{Bi}_4\text{O}_4\text{SeCl}_2$ at room temperature is thus amongst the lowest reported for any bulk inorganic solid (Fig. 4D), achieved by control of the phonon dispersion at the unit cell level. The distinct bonding motifs in BiOCl and $\text{Bi}_2\text{O}_2\text{Se}$ create low velocity longitudinal and transverse phonons, respectively. Their complementary chemistries then allow their integration as modules to afford the single phase superlattice $\text{Bi}_4\text{O}_4\text{SeCl}_2$, where their individual properties are compatibly combined to enhance performance.

These two modules represent the broad classes of van der Waals materials and materials close to electronically-driven structural instabilities, indicating diverse functional opportunities through combination of two or more such units. For example, the single property of thermal conductivity is addressed in $\text{Bi}_4\text{O}_4\text{SeCl}_2$, whereas introduction of electronic carriers complementary to these phonons in a module selected to optimise power factor (40-42) would enhance thermoelectric performance, while appropriate electron-phonon coupling across modules might open access to superconductivity. This potential for multiple property optimisation illustrates how synergy between modular units with compatible bonding can enable chemical generation and control of function.

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Author contributions: QDG, JA and MJR developed the concept and wrote the first and final drafts. QDG synthesized the materials. LMD carried out materials processing. QDG, LMD, SH, RD and JA carried out physical property measurements. HCW performed the INS measurements. MZ performed the scanning electron microscopy. QDG and JA analyzed and modeled the physical properties. TQ, BS and FC carried out the computational work. All authors were involved in discussions and evaluation of drafts during the writing process. MJR directed the research. **Competing interests:** Authors declare no competing interests. **Data and materials availability:** All underlying data is available at (45).

Supplementary Materials:

Materials and Methods

Supplementary Text

Figures S1-S22

Tables S1-S4

References 46-59

Figure 1. Chemically compatible interfaces allow synergic phonon dispersion

modification and combination driven by bond anisotropy and mismatch **A** Schematic of a material with anisotropic bond contrast produced by stacking of strong and weak bonding interfaces. In the in-plane directions denoted by //, there are only strong bonds (force constant C_2 denoted by springs). In the out-of-plane direction denoted by \perp , strong and weak (force constant C_1 denoted by orange shading; $C_1 < C_2$) bonds alternate. The resulting phonon dispersion is shown below, with the LA modes in orange computed from the BvK model ($C_1/C_2 = 0.15$) and a schematic of the TA modes in blue. The slopes are their respective velocities. The red dashed line is the LA mode along k_{\perp} in the isotropic case where $C_1 = C_2$. The full model for the longitudinal modes is shown in Figure S1. **B** Schematic of a material with an incipient in-plane distortion due to an undersized ion layer creating layer mismatch strain, denoted by the blue shading, and a strong bonding interface, denoted by springs. The resulting schematic phonon dispersion is shown below, with the LA modes in red. The TA modes are in blue, and their line thickness represents the second derivative and thus the anharmonicity, which arises from the proximity to a static distortion. The blue dashed line represents the TA modes in the case with no tendency towards distortion, and the light blue line in the case with a static, dynamically stable in-plane distortion. **C** Schematic of a material that combines both anisotropic bond contrast from alternating strong and weak bonding interfaces with an incipient in-plane distortion from layer mismatch strain. The resulting qualitative phonon dispersion is shown below, demonstrating the integrated effects of all three interfaces in the k_{\perp} direction.

Figure 2. Longitudinal phonon softening at a van der Waals interface in BiOCl lowers the out-of-plane thermal conductivity **A** Crystal structure of BiOCl, shows the strong bonding and weak van der Waals bonding (orange shading) interfaces (fig. S21 for an alternative view). **B** Total thermal conductivity of a pressed pellet of BiOCl both parallel (top) and perpendicular (bottom) to the pellet plane. The inset shows the orientation of the measurement direction in comparison to the direction of $\langle 001 \rangle$ preferred orientation. Fits to the one component model $\kappa_1(T)$ are shown in solid red and the two component model $\kappa_2(T)$ in orange. The intrinsic asymptotic high temperature limits $\kappa_{1\min}$ and $\kappa_{2\min}$ are shown by red and orange arrows, respectively. **C** Calculated low frequency phonon dispersion of BiOCl in the in-plane ($k_{//}$) and out-of-plane (k_{\perp}) directions, highlighting the LA (orange) and TA (blue) modes (the full dispersion is shown in Figure S9). The dashed red line qualitatively illustrates the LA mode along k_{\perp} in the isotropic case. The LA mode quantitatively matches the BvK model (Fig. 1A), when $C_1/C_2 = 0.054$ (fig. S20). The shading of the TA mode along k_{\perp} is proportional to the second derivative, and therefore the anharmonicity.

Figure 3. Transverse phonon anharmonicity at a distortion-prone interface in Bi₂O₂Se

A Crystal structure of Bi₂O₂Se, showing distortion-prone (due to layer mismatch strain; blue shading) and strong bonding interfaces. **B** Total thermal conductivity of a pressed pellet of Bi₂O₂Se both parallel (top) and perpendicular (bottom) to the pellet plane. Fits to the one component model $\kappa_1(T)$ are shown in solid red lines. **C** Calculated low frequency phonon dispersion of Bi₂O₂Se in the in-plane ($k_{//}$) and out-of-plane (k_{\perp}) directions, highlighting the LA (red) and TA (blue) modes (the full dispersion is shown in Figure S10). The line shading of the TA mode along k_{\perp} is proportional to the second derivative, and thus the anharmonicity. The dashed blue line qualitatively illustrates the TA dispersion in the case without the tendency towards in-plane distortion.

Figure 4. Extremely low thermal conductivity in Bi₄O₄SeCl₂ **A** Crystal structure of Bi₄O₄SeCl₂, highlighting the three types of interface present; strong bonding, weak van der Waals bonding and distortion-prone (fig. S21 for an alternative view). **B** Calculated low frequency phonon dispersion of Bi₄O₄SeCl₂ without Se/Cl site mixing, highlighting the LA and TA modes (full dispersion in fig. S11). **C** A comparison of the measured inelastic neutron scattering (black circles) with the neutron-weighted generalized phonon density of states (DOS) calculated for Bi₄O₄SeCl₂ both with (blue line) and without (magenta line) Se/Cl site mixing. The calculated neutron-weighted phonon DOS does not include the multiple phonon scattering contribution to the experimental data. **D** Total thermal conductivity of a pressed pellet of Bi₄O₄SeCl₂ parallel (left, also including the in-plane single crystal thermal conductivity) and perpendicular (right) to the pellet plane. In the left panel, the single crystal in-plane data are shown as stars, with the parallel to pellet plane data shown as circles. The fits to the one component model $\kappa_1(T)$ and the two component model $\kappa_2(T)$ are shown in red and green, respectively. The thermal conductivity is plotted logarithmically for easier comparison both with $\kappa_{1\min}$ and with other low thermal conductivity bulk inorganic materials (7, 8, 43, 44) and air.

References

1. A. L. Moore, L. Shi, Emerging challenges and materials for thermal management of electronics. *Mat. Today* **17**, 163-174 (2014).
2. S. Berber, Y.-K. Kwon, D. Tománek, Unusually high thermal conductivity of carbon nanotubes. *Phys. Rev. Lett.* **84**, 4613 (2000).
3. G. A. Slack, Nonmetallic crystals with high thermal conductivity. *J. Phys. Chem. Sol.* **34**, 321-335 (1973).

4. K. Chen *et al.*, Ultrahigh thermal conductivity in isotope-enriched cubic boron nitride. *Science* **367**, 555-559 (2020).
5. G. J. Snyder, M. T. Agne, R. Gurunathan, Thermal conductivity of complex materials. *Nat. Sci. Rev.* **6**, 380-381 (2019).
6. A. Einstein, Elementary observations on thermal molecular motion in solids. *Ann. Phys.* **35**, 679-694 (1911).
7. H. Lin *et al.*, Concerted rattling in CsAg₅Te₃ leading to ultralow thermal conductivity and high thermoelectric performance. *Angew. Chemie* **128**, 11603-11608 (2016).
8. S. Mukhopadhyay *et al.*, Two-channel model for ultralow thermal conductivity of crystalline Tl₃VSe₄. *Science* **360**, 1455-1458 (2018).
9. R. Pohl, Thermal conductivity and phonon resonance scattering. *Phys. Rev. Lett.* **8**, 481 (1962).
10. B. Taylor, H. Maris, C. Elbaum, Phonon focusing in solids. *Phys. Rev. Lett.* **23**, 416 (1969).
11. S. Lee *et al.*, Resonant bonding leads to low lattice thermal conductivity. *Nat. Commun.* **5**, 1-8 (2014).
12. M. T. Agne, R. Hanus, G. J. Snyder, Minimum thermal conductivity in the context of diffuson-mediated thermal transport. *Energy Environ. Sci.* **11**, 609-616 (2018).
13. X. Qian, J. Zhou, G. Chen, Phonon-engineered extreme thermal conductivity materials. *Nat. Mat.* 10.1038/s41563-021-00918-3 (2021).
14. C. Chiritescu *et al.*, Ultralow thermal conductivity in disordered, layered WSe₂ crystals. *Science* **315**, 351-353 (2007).
15. M. Simoncelli, N. Marzari, F. Mauri, Unified theory of thermal transport in crystals and glasses. *Nat. Phys.* **15**, 809-813 (2019)
16. Z. Chen, C. Dames, An anisotropic model for the minimum thermal conductivity. *Appl. Phys. Lett.* **107**, 193104 (2015).
17. Z. Chen, X. Zhang, S. Lin, L. Chen, Y. Pei, Rationalizing phonon dispersion for lattice thermal conductivity of solids. *Nat. Sci. Rev.* **5**, 888-894 (2018).
18. E. S. Toberer, A. Zevkink, G. J. Snyder, Phonon engineering through crystal chemistry. *J. Mat. Chem.* **21**, 15843-15852 (2011).
19. Z. Wei, Y. Chen, C. Dames, Negative correlation between in-plane bonding strength and cross-plane thermal conductivity in a model layered material. *Appl. Phys. Lett.* **102**, 011901 (2013).
20. A.J. Minnich, Phonon heat conduction in layered anisotropic crystals. *Phys. Rev. B* **91**, 085206 (2015).

21. J. Callaway, Model for lattice thermal conductivity at low temperatures. *Phys. Rev.* **113**, 1046 (1959).
22. D. G. Cahill, R. Pohl, Heat flow and lattice vibrations in glasses. *Solid State Commun.* **70**, 927-930 (1989).
23. Materials and Methods are available as Supplementary Materials on Science Online
24. D. J. Singh, Stability and phonons of KTaO_3 . *Phys. Rev. B* **53**, 176 (1996).
25. D. Sarkar *et al.*, Ferroelectric Instability Induced Ultralow Thermal Conductivity and High Thermoelectric Performance in Rhombohedral p-Type GeSe Crystal. *J. Am. Chem. Soc.* **142**, 12237-12244 (2020).
26. A. Tagantsev *et al.*, The origin of antiferroelectricity in PbZrO_3 . *Nat. Commun.* **4**, 1-8 (2013).
27. C. W. Li *et al.*, Orbitally driven giant phonon anharmonicity in SnSe . *Nat. Phys.* **11**, 1063-1069 (2015).
28. W. Peng, G. Petretto, G.-M. Rignanese, G. Hautier, A. Zevalkink, An unlikely route to low lattice thermal conductivity: Small atoms in a simple layered structure. *Joule* **2**, 1879-1893 (2018).
29. F.A. Bannister, Crystal structure of Bismuth Oxyhalides. *Mineral. Mag. J. Mineral. Soc.* **24**, 49-58 (1934).
30. H. Boller, Die Kristallstruktur von $\text{Bi}_2\text{O}_2\text{Se}$. *Monatsh. Chem.* **4**, 916-919 (1973).
31. W. Peng, S. Chanakian, A. Zevalkink, Crystal chemistry and thermoelectric transport of layered AM_2X_2 compounds. *Inorg. Chem. Front.* **5**, 1744-1759 (2018).
32. M. Wu, X. C. Zeng, Bismuth oxychalcogenides: a new class of ferroelectric/ferroelastic materials with ultra high mobility. *Nano Lett.* **17**, 6309-6314 (2017).
33. T. Ghosh *et al.*, Ultrathin free-standing nanosheets of $\text{Bi}_2\text{O}_2\text{Se}$: room temperature ferroelectricity in self-assembled charged layered heterostructure. *Nano Lett.* **19**, 5703-5709 (2019).
34. P. Ruleova *et al.*, Thermoelectric properties of $\text{Bi}_2\text{O}_2\text{Se}$. *Mat. Chem. Phys.* **119**, 299-302 (2010).
35. A. Askar, Dispersion relation and wave solution for anharmonic lattices and Korteweg De Vries continua. *Proc. R. Soc. A* **334**, 83-94 (1973).
36. R. Zivieri, F. Garesci, B. Azzarboni, M. Chiappini, G. Finocchio, Nonlinear dispersion relation in anharmonic periodic mass-spring and mass-in-mass systems. *J. Sound Vib.* **462**, 114929 (2019).
37. N. W. Ashcroft, N. David Mermin. Classical Theory of the Harmonic Crystal in *Sol. State Phys.* (New York, 1976) London: Holt, Rinehart and Winston. Vol. 2005.
38. Q. D. Gibson *et al.*, Modular Design via Multiple Anion Chemistry of the High Mobility van der Waals Semiconductor $\text{Bi}_4\text{O}_4\text{SeCl}_2$. *J. Am. Chem. Soc.* **142**, 847-856 (2019).

39. L.M. Daniels *et al.*, Phonon-glass electron-crystal behaviour by A site disorder in n-type thermoelectric oxides. *Energy Environ.* **10**, 1917-1922 (2017).
40. S. Roychowdhury, T. Ghosh, R. Arora, M. Samanta, L. Xie, N. K. Singh, A. Soni, J. He, U.V. Waghmare, K. Biswas. Enhanced atomic ordering leads to high thermoelectric performance in AgSbTe₂. *Science* **371**, 722-727 (2021).
41. J. R. Sootsman, H. Kong, C. Uher, J. J. D'Angelo, C.-I. Wu, T.P. Hogan, T. Caillat, M.G. Kanatzidis, Large enhancements in the thermoelectric power factor of bulk PbTe at high temperature by synergistic nanostructuring. *Angew. Chemie* **120**, 8746-8750 (2008).
42. L. Wu, X. Li, S. Wang, T. Zhang, J. Yang, W. Zhang, L. Chen, J. Yang, Resonant level-induced high thermoelectric response in indium-doped GeTe. *NPG Asia Mat.* **9**, e343-e343 (2017).
43. J.J. Freeman and A.C. Anderson. Thermal conductivity of amorphous solids. *Phys. Rev. B*, **34**, 5684 (1986).
44. L.-D. Zhao *et al.*, Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe. *Science* **351**, 141-144 (2016).
45. <https://datacat.liverpool.ac.uk/id/eprint/1239>
46. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mat. Sci.* **6**, 15-50 (1996).
47. G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*. **54**, 11169 (1996).
48. J. Klimeš, D. R. Bowler, A. Michaelides, Chemical accuracy for the van der Waals density functional. *J. Phys.: Condens. Matt.* **22**, 022201 (2009).
49. D. Cui *et al.*, Band-gap engineering of BiOCl with oxygen vacancies for efficient photooxidation properties under visible-light irradiation. *J. Mater. Chem. A* **6**, 2193-2199 (2018).
50. X. Tan *et al.*, Boosting the thermoelectric performance of Bi₂O₂Se by isovalent doping. *J. Am. Chem. Soc.* **101**, 4634-4644 (2018).
51. A. Togo, I. Tanaka, First principles phonon calculations in materials science. *Scr. Mater.* **108**, 1-5 (2015).
52. Gonze, X., Lee, C. Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Phys. Rev. B* **55**, 10355 (1997).

53. J. Hutter, M. Iannuzzi, F. Schiffmann, J. VandeVondele, cp2k: atomistic simulations of condensed matter systems. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **4**, 15-25 (2014).
54. S. Goedecker, M. Teter, J. Hutter, Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **54**, 1703 (1996).
55. R. Bewley *et al.*, MERLIN, a new high count rate spectrometer at ISIS. *Physica B: Cond. Matt.* **385**, 1029-1031 (2006).
56. M. Russina, F. Mezei, First implementation of repetition rate multiplication in neutron spectroscopy. *Nucl. Instrum. Methods Phys. Res., Sect. A* **604**, 624-631 (2009).
57. O. Arnold *et al.*, Mantid—Data analysis and visualization package for neutron scattering and μ SR experiments. *Nucl. Instrum. Methods Phys. Res., Sect. A* **764**, 156-166 (2014).
58. M. Tachibana, E. Takayama-Muromachi, Thermal conductivity and heat capacity of the relaxor ferroelectric $[\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3]_{1-x}[\text{PbTiO}_3]_x$. *Phys. Rev. B* **79**, 100104 (2009).
59. P. B. Allen, J. L. Feldman, Thermal conductivity of glasses: Theory and application to amorphous Si. *Phys. Rev. Lett.* **62**, 645 (1989).