

Remarkably Weak Anisotropy in Thermal Conductivity of Two-Dimensional Hybrid Perovskite Butylammonium Lead Iodide Crystals

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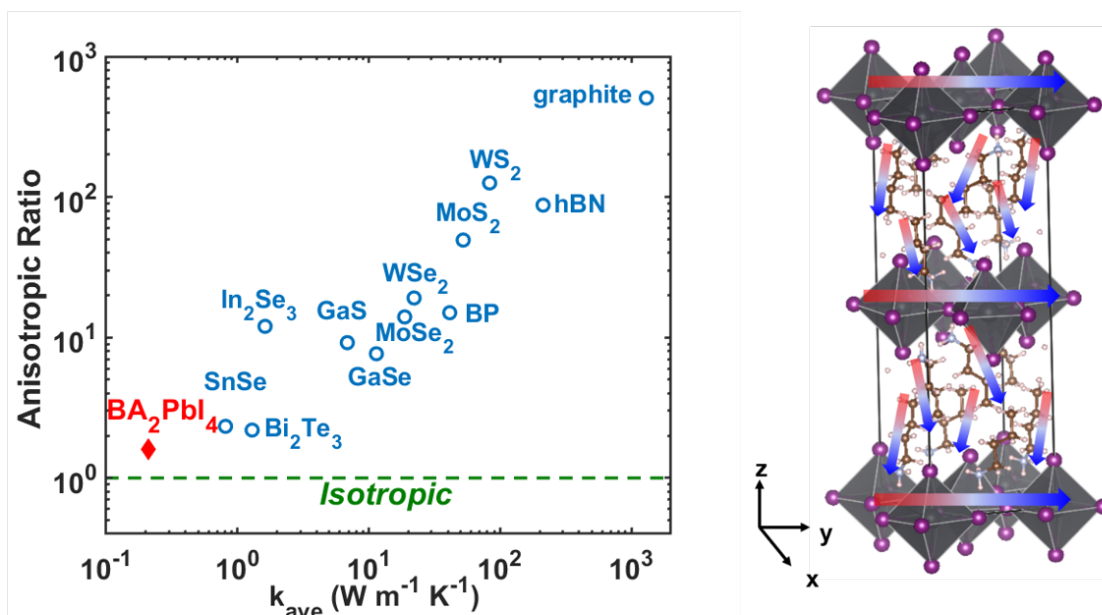
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ABSTRACT

Two-dimensional (2D) hybrid organic-inorganic perovskites consisting of alternating organic and inorganic layers are a new class of layered structures. They have attracted increasing interest for photovoltaic, optoelectronic, and thermoelectric applications, where knowing their thermal transport properties is critical. We carry out both experimental and computational studies on thermal transport properties of 2D butylammonium lead iodide crystals and find their thermal conductivity is ultralow (below $0.3 \text{ W m}^{-1} \text{ K}^{-1}$) with very weak anisotropy (around 1.5) among layered crystals. Further analysis reveals that the unique structure with the preferential alignment of organic chains and complicated energy landscape leads to moderately smaller phonon lifetimes in the out-of-plane direction and comparable phonon group velocities in in-plane and out-of-plane directions. These new findings may guide the future design of novel hybrid materials with desired thermal conductivity for various applications.



KEYWORDS

2D hybrid perovskite, anisotropic thermal conductivity, transient thermal grating, inelastic x-ray scattering, molecular dynamics

MAIN TEXT

Two-dimensional (2D) hybrid organic-inorganic perovskites have emerged as promising candidates for solar cells¹, light-emitting diodes², and photodetectors³, and thermoelectrics⁴, due to their significantly improved ambient stability⁵, remarkable structural flexibility, and tunability of physical properties⁶ compared with their three-dimensional (3D) counterparts. Understanding the thermal transport in 2D hybrid perovskites is important for the thermal management and energy conversion efficiency in optoelectronic and thermoelectric applications. The unique 2D-layered structures with alternating organic and inorganic layers could potentially differentiate their thermal

transport properties from other conventional 2D-layered structures. Despite very recent reports⁷⁻⁹ on the ultralow out-of-plane thermal conductivity ($k_{\perp}$), our knowledge about thermal transport in 2D hybrid perovskites is scarce. The anisotropy in the thermal conductivity remains unknown due to the lack of in-plane thermal conductivity ($k_{\parallel}$). Moreover, to obtain deep insights into underlying mechanisms, a close look at lattice dynamics and phonon properties in 2D hybrid perovskites is needed but difficult to obtain, given the complex crystal structure and complicated energy landscape.

In this work, we perform a comprehensive study on the thermal conductivity and phonon properties in butylammonium lead iodide BA_2PbI_4 ($\text{BA} = \text{C}_4\text{H}_9\text{NH}_3^+$) at room temperature. The 2D BA_2PbI_4 hybrid perovskite consists of bilayers of interdigitated $\text{C}_4\text{H}_9\text{NH}_3^+$ cations alternating with inorganic PbI_4^{2-} layers.¹⁰ The 2D layers are held together by weak vdW/electrostatic interactions. We choose BA_2PbI_4 as the example material because it has a surge in popularity with studies on its mechanical¹¹, electrical¹², and optical¹³ properties. Despite challenges in measuring $k_{\parallel}$ of small thin crystals, we are able to measure $k_{\parallel}$ by transient thermal grating (TTG) technique. The measured $k_{\parallel}$'s of two independent sets of BA_2PbI_4 crystals are $0.28 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.29 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The $k_{\perp}$ of BA_2PbI_4 crystalline thin films was found to be $0.18 \pm 0.04 \text{ W m}^{-1} \text{ K}^{-1}$ by time-domain thermoreflectance (TDTR) measurement at the room temperature⁷. A slightly lower value of $k_{\perp} = 0.125 \pm 0.089 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained for BA_2PbI_4 single crystal by TDTR at 330 K⁸, probably due to the laser heating induced structural rearrangements at 325 K. Using molecular dynamics (MD), our calculated $k_{\parallel}$ and $k_{\perp}$ of $0.27 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.18 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$ at the room temperature agree very well with the experimental data. Most strikingly, the 2D layered BA_2PbI_4 crystals exhibit incredibly weak

anisotropy in their thermal conductivity. The anisotropic ratio ($k_{\parallel}/k_{\perp}$) is exceptionally small compared to other layered crystals and even approaches the isotropic limit. To gain a microscopic picture, we further map out the phonon dispersion of BA_2PbI_4 using inelastic x-ray (IXS) measurements and the spectral energy density (SED) calculations. This is the first study on phonon dispersion of a 2D hybrid material. We build the relationship between the crystal structure features and the phonon characteristics to understand its weak anisotropy in the thermal conductivity. The weak vdW/electrostatic interactions among organic chains and at organic-inorganic interfaces lead to moderately smaller phonon lifetimes in the out-of-plane direction and the preferential orientation of the organic chains results in comparable phonon group velocities, giving slightly smaller $k_{\perp}$.

Results

Crystal characterization

We carefully prepare two sets of high-quality BA_2PbI_4 crystals (sample #1 and #2, Figure 1a) using a slow cooling method¹⁴ (see Supporting Information (SI) for details) in two independent groups to cross-check the results. Sample #1 has a crystal size up to 5 mm in the in-plane direction and an out-of-plane thickness around 200 μm , while sample #2 has a crystal size up to 2.5 mm in the in-plane direction and an out-of-plane thickness ranging from 200 μm to 550 μm . The x-ray diffraction (XRD) measurements of samples #1 and #2 (Figure 1b) show sharp (00l) peaks equidistant in 2θ , which demonstrates the high degree of crystallinity along the out-of-plane direction. The crystal structure obtained from single-crystal XRD (SC-XRD) can be found in SI. In order to create smooth sample surfaces for TTG measurement, we exfoliate the samples using Scotch tape. The sample roughness can be significantly reduced through exfoliation as

demonstrated by atomic force microscopy (AFM) examination (Figure 1c). The scanning electron microscope (SEM) images in Figure 1d further verify the smooth surface after exfoliation and show the clear layered features at the sample edges. The SEM images with a larger scale bar can be found in SI and no obvious grains are observed in large areas along the in-plane direction.

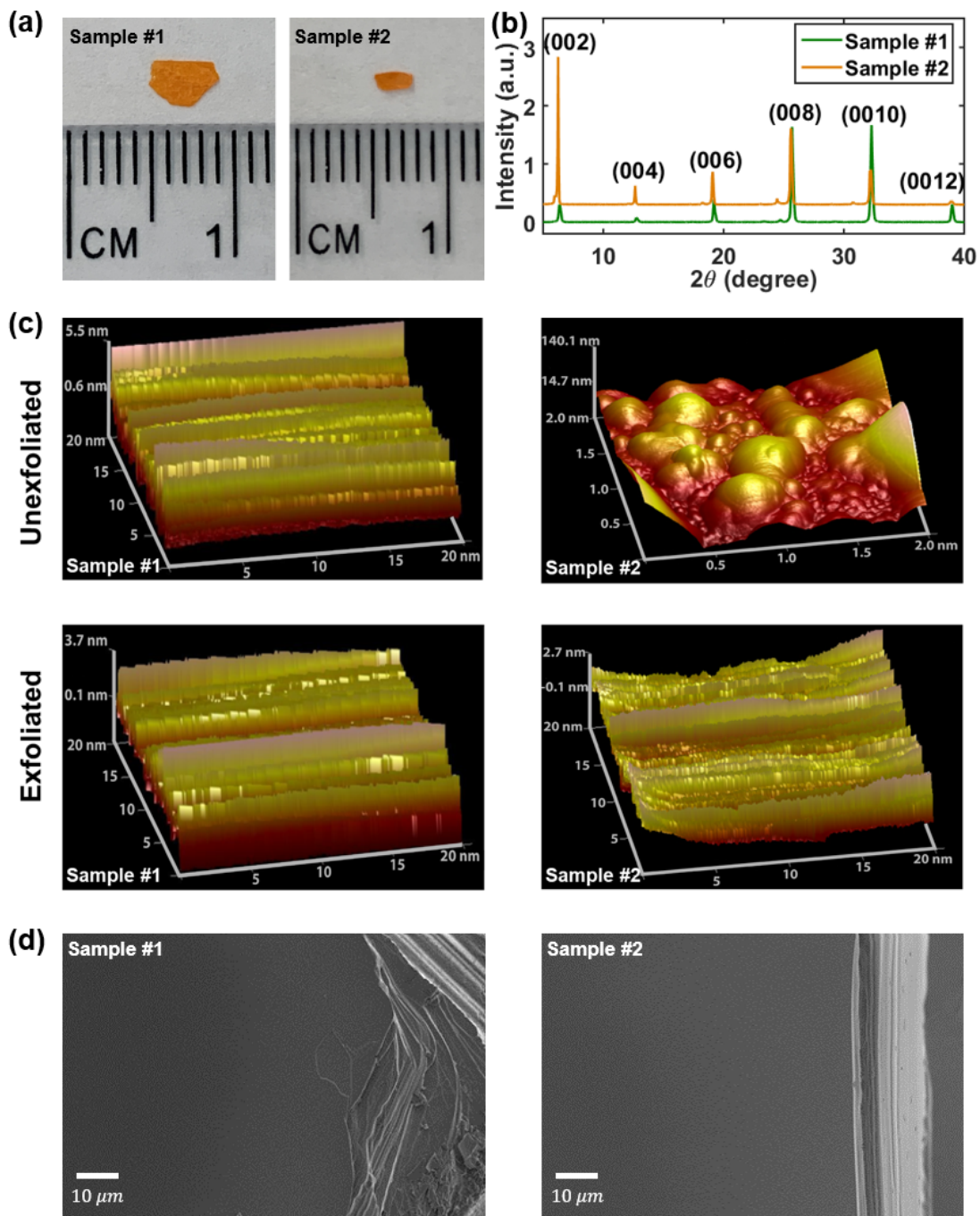


Figure 1 (a) Images of synthesized samples #1 and sample #2. (b) the XRD pattern of samples #1 and #2 measured by using Cu K α radiation. (c) AFM image of unexfoliated and exfoliated samples. The surface roughness of sample #1 is reduced from $R_q=1.51$ nm to $R_q=0.89$ nm, and the surface

roughness of sample #2 from $R_q=33.60$ nm to $R_q=0.77$ nm after exfoliation. Note that R_q is the root mean square average of height deviations taken from the mean image data plane. The difference in initial surface roughness between samples #1 and #2 results from the different synthesis parameters. (d) SEM images of the top surface for exfoliated samples.

Thermal conductivity measurements and calculations

We then perform TTG measurements (see SI for experimental details) on those two sets of samples. TTG is a non-contact optical technique¹⁵⁻¹⁷, allowing highly accurate in-plane measurements of thin films. The in-plane thermal diffusivity is determined by fitting the thermal decay data as in Figure 2a. Using a specific heat capacity of $0.48 \text{ J g}^{-1} \text{ K}^{-1}$ measured by differential scanning calorimetry (DSC) method and a density of 2.68 g cm^{-3} determined by SC-XRD (see SI for details), we extract the in-plane thermal conductivity of samples #1 and #2 to be $0.28 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.29 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, at 300 K. We are unable to reliably extract the out-of-plane thermal conductivity of these single crystals using frequency domain thermoreflectance (FDTR) mainly due to the low sensitivity and laser heating, as also confirmed by a latest publication⁹. Therefore, we compare the in-plane thermal conductivity of BA_2PbI_4 crystals measured by TTG with the out-of-plane thermal conductivity of BA_2PbI_4 thin film measured by TDTR⁷. Although TDTR and TTG are two different techniques, the measured samples in both experiments are fully crystalline, and the measured results agree well with calculation. We think the comparison between the in-plane and out-of-plane thermal conductivities is fair and the best we could do with the existing techniques.

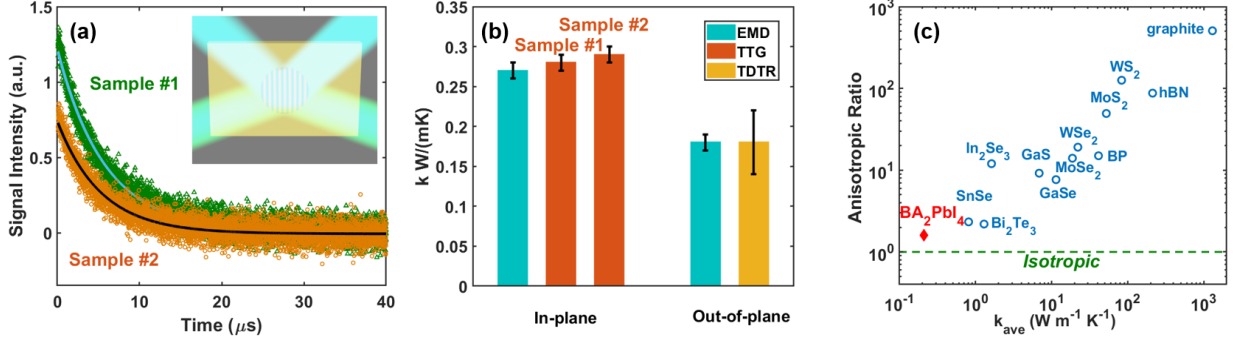


Figure 2 (a) The obtained thermal decay data from TTG measurements. Green triangles and orange circles denote samples #1 and #2, respectively. Blue and black curves denote the fittings from the theoretical thermal model of samples #1 and #2, respectively. Inset is a schematic of the pump beams (blue) forming thermal gratings on samples and the probe beam (green) diffracting from the thermal gratings and overlapping with a reference beam (green) in TTG measurement. (b) In-plane ($k_{\parallel}$) and out-of-plane ($k_{\perp}$) thermal conductivity of 2D BA₂PbI₄ hybrid perovskite crystals at 300 K. Orange, yellow and blue denote the thermal conductivity of crystals measured by TTG in this study, crystalline thin films measured using TDTR⁷, and single crystal calculated from EMD simulations in this study, respectively. (c) The anisotropic ratio ($k_{\parallel}/k_{\perp}$) vs. average thermal conductivity (k_{ave}) of BA₂PbI₄ crystals and other layered single crystals^{18–23}.

We calculate the thermal conductivity of 2D BA₂PbI₄ using equilibrium MD (EMD) simulations with a classical model potential for the hybrid perovskite (MYP) force field²⁴. We choose the MYP force field because it successfully reproduced the structural, elastic, vibrational properties²⁵, and thermal conductivity²⁶ of 3D MAPbI₃ (MA = CH₃NH₃⁺). In addition, the MYP force field was applied to calculate the molar heat capacity of BA₂PbI₄⁷ and the result agrees well with our DSC measurements. The predicted $k_{\parallel}$ and $k_{\perp}$ of BA₂PbI₄ are 0.27 ± 0.01 W m⁻¹ K⁻¹ and 0.18 ± 0.01

$\text{W m}^{-1} \text{K}^{-1}$ at 300 K, respectively. The in-plane and out-of-plane thermal conductivities of BA_2PbI_4 predicted by EMD simulations with MYP force field are in good agreement with the TTG and TDTR measurements, respectively (Figure 2b).

The average thermal conductivity of BA_2PbI_4 is $0.21 \text{ W m}^{-1} \text{K}^{-1}$, which is comparable to most amorphous polymers and much lower than other layered crystal structures (Figure 2c). Moreover, it is smaller than the thermal conductivity of 3D MAPbI_3 ($0.3 - 0.5 \text{ W m}^{-1} \text{K}^{-1}$)²⁷⁻²⁹, and comparable to that of “0D” $\text{MA}_3\text{Bi}_2\text{I}_9$ ($0.23 \text{ W m}^{-1} \text{K}^{-1}$)³⁰. This can be intuitively explained by the strength of interactions. MAPbI_3 has a 3D continuous inorganic framework of strong Pb-I ionic/covalent bonds, while $\text{MA}_3\text{Bi}_2\text{I}_9$ has discontinuous inorganic units separated by organic units and 2D BA_2PbI_4 has alternating inorganic/organic layers held together by weak long-range electrostatic and vdW interactions. Similar to other hybrid perovskites^{30,31}, the ultralow thermal conductivity of BA_2PbI_4 can be attributed to low phonon group velocities resulting from ultralow phonon frequencies and short phonon lifetimes originating from a significant overlap between acoustic and optical phonons as indicated by its phonon dispersion from IXS measurements (See SI for experimental details) and SED calculations in Figure 3a. The low phonon group velocities are further supported by ultralow indentation moduli from nanoindentation measurements and the speed of sound measurements by pulse echo technique. The detailed discussion can be found in SI.

Anisotropic thermal conductivity analysis

Most strikingly, the anisotropic ratio of BA_2PbI_4 crystal is only 1.50 from EMD calculations and 1.58 from experimental measurements, which are much lower than other layered crystals and approach the isotropic limit as shown in Figure 2c. To understand the exceptionally small

anisotropy, we take a close look at the structure and phonon properties. Note that the organic chains are preferentially aligned in the out-of-plane direction in BA_2PbI_4 (Figure 3b). In the in-plane direction, there are strong intraplanar Pb-I ionic/covalent bonds in the inorganic layers and weak vdW/electrostatic interchain interactions in the organic layers. In the out-of-plane direction, there are covalent bonds (C-C and C-N) within organic chains and weak vdW/electrostatic interactions between organic chains (there are two chains stacking vertically in each layer) and at organic-inorganic interfaces.

Thermal conductivity can be expressed as a function of the volumetric heat capacity C_v , average phonon group velocity $\bar{v}$, and phonon lifetime $\bar{\tau}$ as $\kappa = \frac{1}{3} C_v \bar{v}^2 \bar{\tau}$. We then connect their structure features to phonon lifetimes and group velocities. In the in-plane direction, the PbI_4^{2-} framework allows for continuous heat conduction pathways (Figure 3b). In other words, within the inorganic layers, phonons have relatively large lifetimes. In contrast, the heat conduction path along the out-of-plane direction is interrupted by the weak interchain interactions and organic-inorganic interfaces (Figure 3b), and phonons can be strongly scattered at those joints. Strong anharmonicity at the organic-inorganic interfaces also contributes to phonon scatterings and suppress phonon lifetimes in the out-of-plane direction^{26,32–34}. The smaller phonon lifetimes along the out-of-plane direction are supported by phonon dispersion using the SED method (see SI for details). The broader the phonon dispersion curves, the smaller the phonon lifetimes³⁵. As shown in Figure 3a, acoustic phonon branches in the $\Gamma\text{-Z}$ direction are more blurred than that in the $\Gamma\text{-X/Y}$ directions, indicating smaller phonon lifetimes along the out-of-plane direction. By further extracting the widths of SED peaks, we reach the same conclusion, as shown in Figure S11. This difference is not significant, though, due to the small volume fraction of the inorganic layers. In brief, the

phonon lifetimes are relatively anisotropic mainly because of the continuous heat conduction path in the inorganic framework along the in-plane direction vs. the disconnected pathways in the out-of-plane direction.

For phonon group velocities, they are related to the strength of the interatomic interactions. The preferential alignment of the organic chain is the key factor that balances out the weak interlayered interactions. The orientation of the organic chains was reported to have a large effect on the out-of-plane thermal conductivity of 2D hybrids.⁷ Here, we pin down the orientational effects to phonon group velocities. Since stronger covalent bonds in one crystal axis result in higher group velocities in that axis³⁶, the group velocities along the organic chain direction are higher than those perpendicular to the chain direction. In the out-of-plane direction, the preferentially vertical alignment of organic chains leads to large phonon group velocities along the organic chains, compensating the weak interlayered interactions and resulting in similar phonon group velocities to the in-plane direction. In the in-plane direction, despite the strong intraplanar P-I ionic/covalent bonds in the inorganic PbI_4^{2-} framework, the organic layers have weak vdW/electrostatic interactions and take up a large volume fraction of 78%. This dwarfs the average bonding strength and, thus, the overall phonon group velocities. In brief, the interplay among different effects leads to comparable group velocities between in-plane and out-of-plane directions. This is supported by the group velocities obtained from the phonon dispersion in Figure 3a and our estimations on bond strength comparison between in-plane and out-of-plane directions (see details in SI). As a result, moderately smaller phonon lifetimes along the out-of-plane direction and the comparable group velocities between in-plane and out-of-plane directions give slightly smaller $k_{\perp}$ and thus remarkably weak anisotropy.

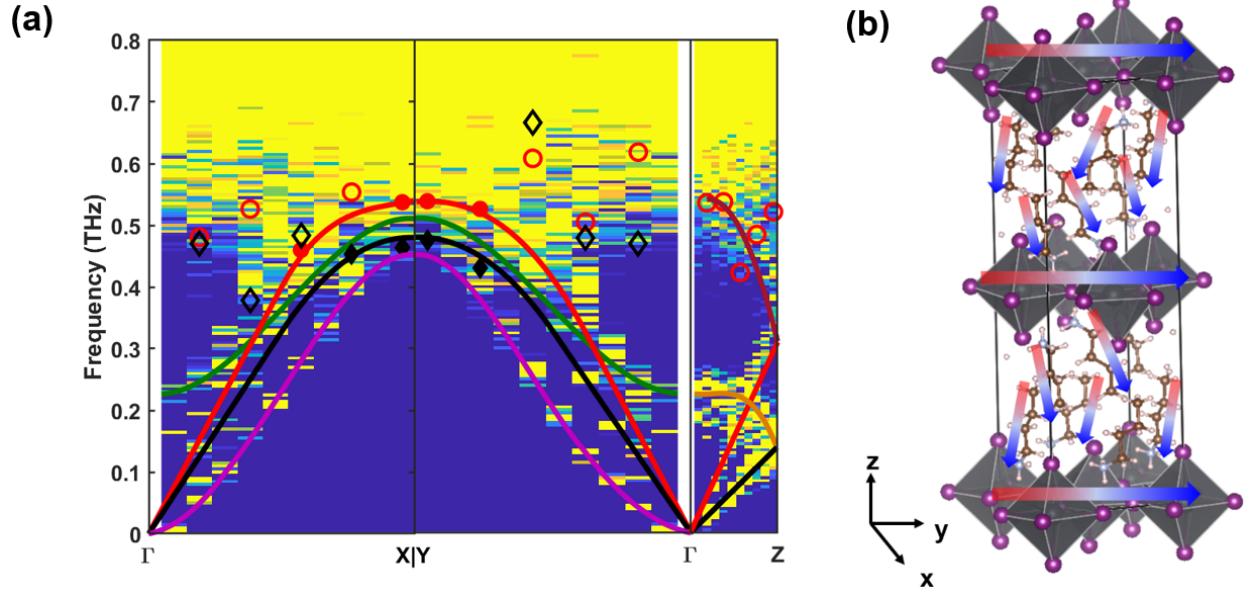


Figure 3 (a) Phonon dispersion of BA₂PbI₄ single crystal measured by IXS and calculated by SED at 300 K. The high symmetry points are chosen based on the first Brillouin zone of a simple orthorhombic lattice: Γ (0 0 0), X (0.5 0 0), Y (0 0.5 0), and Z (0 0 0.5) in the units of $\mathbf{b}_1 = (\frac{2\pi}{a}, 0, 0)$, $\mathbf{b}_2 = (0, \frac{2\pi}{b}, 0)$, $\mathbf{b}_3 = (0, 0, \frac{2\pi}{c})$. The markers represent phonons measured by IXS. Red solid circles, black solid diamonds, red circles, black diamonds denote longitudinal acoustic (LA) modes, transverse acoustic (TA) modes, longitudinal-optical (LO) modes, and transverse-optical (TO) modes, respectively. The red (LA), black (TA), magenta (ZA), green (ZO), orange (TO), and maroon (LO) lines were drawn based on the calculated phonon dispersion by SED. Phonon modes by IXS and SED are in good agreement. Note that our calculated directions (Γ -X: (X 0.05 0) Γ -Y: (0.05 Y 0)) are not exactly along high symmetric lines ((Γ -X: (X 0 0) Γ -Y: (0 Y 0)) since the SED calculations are based on a $20 \times 20 \times 1$ supercell and an even larger supercell is too computationally expensive. The calculated Γ -Z is along the high symmetric line. (b) The unit cell of 2D BA₂PbI₄

single crystal with arrows denoting preferential heat conduction paths along both in-plane and out-of-plane directions.

Conclusion

In summary, we perform TTG and IXS measurements, along with MD simulations to investigate the thermal transport properties of 2D BA_2PbI_4 crystals at 300 K. Despite the anisotropic crystalline structure, we find its thermal conductivity is amorphous-polymer-like with the anisotropic ratio approaching the isotropic limit. Further analysis reveals that the weak anisotropy comes from the comparable phonon group velocities and moderately different phonon lifetimes in the in-plane and out-of-plane directions. The continuous inorganic PbI_4^{2-} framework with strong intraplanar Pb-I ionic/covalent bonds in the framework forms favorable heat conduction paths along the in-plane direction, while the weak vdW/electrostatic interactions among organic chains and at organic-inorganic interfaces lead to strong phonon scatterings and thus smaller phonon lifetimes along the out-of-plane direction. The preferential orientations of organic $\text{C}_4\text{H}_9\text{NH}_3^+$ chains in the out-of-plane direction and the large volume fraction of the organic layers results in comparable phonon group velocities between the out-of-plane and in-plane directions. The fundamental insights obtained in this study can advance the understanding of 2D hybrid perovskites and guide the rational design of materials with desired thermal conductivity for optoelectronic and thermoelectric applications.

ASSOCIATED CONTENT

Supporting Information

Crystal Synthesis; XRD measurements and Crystal Structure; TTG measurements; Specific heat capacity measurements; Mechanical Properties; IXS measurements; EMD simulations; SED Method; Phonon Dispersion Analysis; Phonon group velocity; additional figures.

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Author Contributions

‡Both authors (C.L. and H.M.) contributed equally to this work. C.L., H.M., and Z.T. conceived the study. T.L. and D.M. synthesized sample #2 and conducted SC-XRD on single crystals used in IXS and powder XRD on crystals used in TTG measurements. J.D. assisted with TTG measurements. M.R. and J.F. synthesized samples #1 and conducted XRD and DSC measurements on sample #1. A.S. and B. R. performed the pulse echo measurements. A.M. provided the MYP force field. Z.W. and S.B. assisted with the nanoindentation measurements. M.T. assisted with the SEM measurements. A.A. assisted with the IXS measurements. The manuscript was written through contributions of all authors. The authors declare no competing interests.

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