Quantifying anisotropic thermal transport in two-dimensional perovskite (PEA$_2$PbI$_4$) through cross-sectional scanning thermal microscopy

Abhishek Maiti[1,2,*,#], Khushboo Agarwal[1,#], Sergio Gonzalez-Munoz[1], and Oleg. V. Kolosov[1,3,†]

[1]*Physics Department, Lancaster University, LA14YB, UK*

[2]*School of Physical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032, India*

[3]*Material Science Institute, Lancaster University, Lancaster, LA14YB, UK*

In this work, we investigated the anisotropic thermal transport in two-dimensional (2D) perovskite (phenethylammonium lead iodide) nanolayers through a novel measurement technique called cross-sectional scanning thermal microscopy (xSThM). In this method, a target perovskite layer on a substrate was oblique polished with an Ar ion beam to create a low-angle wedge with nanoscale roughness that is followed by high vacuum SThM to obtain the thermal conductance map as a function of local thickness. The experimentally obtained data were processed with an analytical model and validated by the finite elemental analysis simulation to quantify the in-plane ($k_{l,xy}$) and cross-plane thermal conductivities ($k_{l,z}$) of the 2D perovskite from a single set of measurements with nanoscale resolution. We obtained ultra-low thermal conductivity ($k_l = 0.25 \pm 0.05$ Wm^{-1}K^{-1}) for the 2D perovskite along with an anisotropy ($k_{l,xy} = 0.45 \pm 0.05$ Wm^{-1}K^{-1} and $k_{l,z} = 0.13 \pm 0.05$ Wm^{-1}K^{-1}) linked to the unique structure of the perovskite and different phonon lifetimes and group velocities for in-plane and out-of-plane directions. The results that are available for the first time, are essential for the thermal management of 2D perovskite-based optoelectronic devices, and potential thermoelectric applications of these materials.

Keywords: 2D perovskite, xSThM, Ruddlesden-Popper phase, anisotropic thermal conductivity, nanoscale heat transport.

Correspondence address: [†]o.kolosov@lancaster.ac.uk, [*]abhishek.juphysics@gmail.com

[#] These authors contributed equally

I. INTRODUCTION

In recent years, Ruddlesden-Popper (RP) hybrid halide perovskites have gained widespread attention as an emerging class of two-dimensional (2D) materials owing to their novel electronic and photo-physical properties [1-4]. This particular class of quantum well-like materials exhibiting excellent light emitting and optoelectronic properties is considered an alternative to their three-dimensional (3D) counterparts [5]. The excellent performance of the compound in solar cells, photodetectors, and light-emitting diodes has been ascribed to many exceptional properties, such as solution-processability [6], bandgap tunability [7], high extinction coefficient [8], high photoluminescence quantum yield (PLQY) [9], excitonic effects [1,10], and improved ambient stability [11]. While the photo-physics and carrier dynamics have been intensively studied [12,13], a much less explored aspect of this exciting class of materials is their thermal properties. A fundamental understanding of different thermal parameters and phonon transport is essential for the proper thermal management of 2D perovskite-based existing devices [14], potential thermoelectric applications of these materials [15,16], and development of advanced photovoltaic devices based on the hot phonon bottleneck effect [17].

In this direction, conventional methods were employed to measure the thermal conductivity of different 3D and 2D perovskites [18-24]. An ultra-low thermal conductivity (0.3-0.5 $Wm^{-1}K^{-1}$) was obtained for the 3D perovskite through 3ω-method, frequency or time domain thermo-reflectance, time-resolved vibrational-pump visible-probe spectroscopy, and so forth [21-24]. On the other hand, the 2D perovskites also exhibit a low thermal conductivity; however, due to the anisotropic layered structure, it was found to be anisotropic in nature. As a result, different sets of measurements were required to measure the in-plane (transient thermal grating, time domain thermo-reflectance) and out-of-plane (frequency domain thermo-reflectance, thermal diffusivity) contribution of the thermal conductivity tensor [19,20,25,26]. Despite these reports on ultra-low thermal conductivity (k_l) and underlying phonon transport mechanism, a complete understanding of heat dissipation in 2D perovskite layers remains ambiguous till now due to the limitations of existing thermal characterization techniques. As such, the prevailing macroscopic measurement methods are not appropriate for these compounds, especially in their thin-film form where ballistic heat transport and phonon scattering at the interfaces significantly influence the diffusive heat flow [27]. In this regard, non-destructive scanning thermal microscopy (SThM) approaches may open a novel route to determine local thermal properties of 2D perovskite thin films overcoming the limitations of classical thermal characterization techniques [28-30]. Moreover, it would be more intriguing to develop a method for the measurement of both in-plane ($k_{l,xy}$) and out-of-plane ($k_{l,z}$) components of thermal conductivity simultaneously from a single set of measurements in order to minimize the systematic error of the existing methods.

In this work, we measured k_l of an archetypal 2D perovskite named phenethylammonium lead iodide ((PEA)$_2$PbI$_4$) through a novel unique tool called cross-sectional scanning thermal microscopy (xSThM). This microscopic technique is not only capable of the qualitative thermal imaging of the perovskite with the nanoscale resolution to map the local thermal conductance, but also holds the unprecedented opportunity to provide absolute quantitative values of $k_{l,xy}$ and $k_{l,z}$ components of thermal conductivity via matched analytical model. In this method, a low-angle wedge cut in the perovskite thin film (on Si/SiO$_2$ substrate) was formed through a beam exit cross-sectional polishing (BEXP) followed by a high vacuum SThM investigation [31]. As a result, SThM in one map obtains a dependence of the thermal resistance as a function of thickness, t, replacing the need to create and measure a set of samples of different thicknesses. The quantitative values of both $k_{l,xy}$ and $k_{l,z}$ are then obtained along with interfacial thermal resistance (r_{int}) once the experimental data was compared to an appropriate analytical Muzychka-Spièce model, that was independently validated via finite elemental analysis (FEA) simulation [32-34]. To be specific, the measured values of $k_{l,xy}$ and $k_{l,z}$ in the material were 0.45±0.05 Wm^{-1}K^{-1} and 0.13±0.05 Wm^{-1}K^{-1}, respectively. Our results also reveal the existence of thermal anisotropy ($k_{l,xy}/k_{l,z}$~3.4) in the compound that originates in the differences between (in-plane) heat conduction in the continuous inorganic layer versus the out-of-plane heat transport interrupted at the organic-inorganic interfaces. This work provides a novel generic technique to measure the quantitative ultra-low value of average thermal conductivity, k_l, in 2D materials, as well as its deconvolution into anisotropic thermal conductivity components $k_{l,xy}$ and $k_{l,z}$ using a single set of measurement. Moreover, this work is beneficial for development of the thermal management strategies for 2D perovskite-based optoelectronic devices and also their possible thermoelectric applications.

II. MATERIALS AND METHODS

A. Materials

Phenethylammonium iodide (PEAI, 99%), lead iodide (PbI$_2$, 99%), and anhydrous N, N-dimethyl formamide (DMF, 99.8%) were purchased from Sigma-Aldrich chemical company. All the materials were kept inside a nitrogen-filled glovebox with well-maintained oxygen and moisture levels below 0.1 ppm and used without further purification.

B. Fabrication and characterization of the thin-films

For the fabrication of (PEA)$_2$PbI$_4$ thin films, a precursor solution was prepared by dissolving PEAI (2 M) and PbI$_2$ (1 M) into DMF solvent. The mixture was stirred continuously at 70 °C to form a clear and homogeneous solution. After that, glass and SiO$_2$-coated Si substrates (Si/SiO$_2$) were cleaned following a usual protocol with ethanol, acetone, and isopropyl alcohol for 15 minutes each in a bath-sonicator (37

kHz), followed by a plasma cleaning to remove organic residues. Finally, the precursor solution was spun at 2500 rpm for 30 seconds followed by an annealing of the film at 80 °C for 15 minutes. The perovskite films were characterized through conventional techniques such as X-ray diffraction (XRD), optical absorbance, and photoluminescence (PL) spectroscopy to ensure their phase purity. Such measurements were carried out in a Rigaku Smart Lab X-ray diffractometer (Cu Kα radiation = 1.5406 Å), Shimadzu UV-vis spectrophotometer, and Horiba Jobin Yvon spectrofluorometer (excitation at 405 nm), respectively.

C. Beam exit cross-sectional polishing (BEXP)

In order to obtain an ultralow wedge-like cut in the sample (2D perovskite on Si/SiO$_2$ substrate), we used the BEXP technique carried out in an EM TIC 3X triple ion beam cutter system (Leica Microsystems). In this technique (Fig. S1a, within supplemental material [35]), the sample was placed on a tilted (5°) stage to the horizontal plane. A shade mask was used in front of the stage so that the cut could be executed on the exposed material by intersecting co-planar argon (Ar) beam coming from three guns. The entire process was executed in a high vacuum (10^{-5} Torr) through different steps such as warm-up of the guns (1 kV, 1 mA, 15 minutes), pre-polishing (5 kV, 2 mA, 15 minutes), nano-cutting or polishing (7 kV, 2.6 mA, 7 hours), and post-polishing (1 kV, 1 mA, 1 hour). This technique is called beam-exit cross-sectional polishing as the beam exits at a glancing angle to the sample surface to produce the cut with near-atomic roughness and negligible surface damage [36].

D. Scanning thermal microscopy (SThM)

The cross-sectioned 2D perovskite film was then transferred to the high vacuum chamber for SThM measurements that could image the thermal response with a high spatial resolution (~50 nm) in contrast to the far-field optical techniques [34,37]. It may be noted that a high vacuum is desirable to avoid additional heat transfer through air and the formation of water meniscuses at the tip apex [38-40]. The experiments were carried out in a Smena (NT-MDT Spectrum) scanning probe microscope with custom-built SThM electronics. In this system, the thermal probe was composed of a Si$_3$N$_4$ cantilever with a palladium (Pd) film deposited on it through thermal evaporation. The spring constant of the tip was 0.4 Nm^{-1} spring constant with <100 nm tip radius. The probe used a thermal resistive heater and could sense the variations in temperature during the scan over the material [40,41]. At a more technical detail level (Fig. S1b, within supplemental material [35]), the thermal probe was a resistor with electrical resistance R_{probe} in a Wheatstone bridge circuit with two known resistors (R_1 and R_2) and a variable resistor, R_3. The SThM probe is used as a local heater of the 2D perovskite with the consideration that the heat source is concentrated near the extreme point of the tip apex. When the probe is energized via DC and AC voltage and brought into close contact with the perovskite surface, a heat flow is generated from the tip to the sample due to a temperature gradient. This changes the temperature of the probe and hence the resistance

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of the probe which is monitored as the change of output voltage of the Wheatstone bridge [37]. The experimental data were fitted with an analytical model in MATLAB software. In addition, finite elemental analysis (FEA) simulation was carried out in COMSOL Multiphysics 5.6 software to validate the experimental results.

III. RESULTS AND DISCUSSIONS

A. Characterization of 2D perovskite

The crystal structure of $(PEA)_2PbI_4$ perovskite reveals that it is formed with alternatively stacking of organic spacer layers and the inorganic octahedral slabs (repetition of the structure as shown in Fig. 1a). It may be noted that due to the large size of the bulky spacer cation $(PEA)^+$, it could not be "tolerated" in between the cages of inorganic octahedrons ($[PbI_4]^{2-}$), resulting in a formation of insulating spacer layer depending on intermolecular forces. The large spacer chains are aligned in the out-of-plane direction having covalent bonds (C-C and C-N). In addition, weak van der Waals and electrostatic interactions could be observed between two vertically stacked organic chains and at the organic-inorganic interfaces. On the other hand, there are strong ionic bonds in the in-plane direction originating from the continuous $[PbI_4]^{2-}$ octahedral framework [20,42,43].

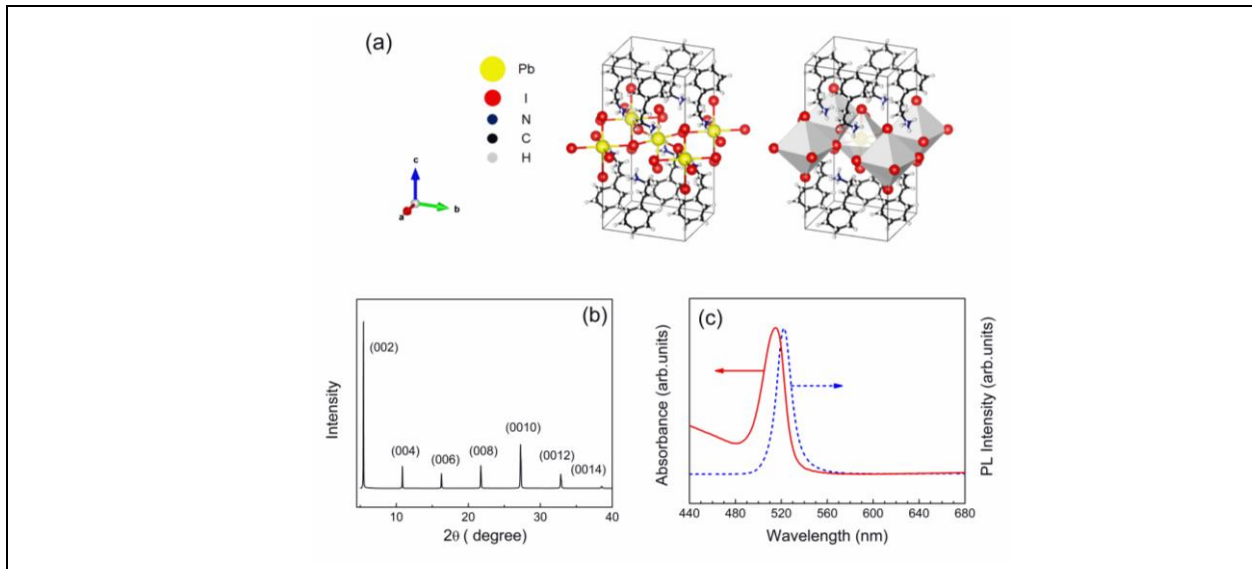**FIG. 1.** (a) Schematic representations of $(PEA)_2PbI_4$ crystal structure. The first one shows the ball-stick model of the crystal. In the second polyhedral model, the octahedra are presented. (b-c) XRD patterns, optical absorbance, and photoluminescence spectra of the $(PEA)_2PbI_4$ thin-film.

To confirm the phase purity of the thin film, we have presented the X-ray diffraction (XRD) pattern in Fig. 1b. The diffraction pattern is indexed according to the previous report and suggests the evolution of strong (002*l*) reflection series [44]. Such an XRD pattern indicates the formation of the film with layers

oriented parallel to the substrate preferred along the <001 > direction [43]. In addition, the optical absorbance and photoluminescence (PL) spectra of the as-prepared film are presented in Fig. 1c, showing a characteristic bandgap of the material around 2.2 eV, typical narrow exciton absorption and emission lines, with a small Stokes shift [45]. Such results confirmed the phase pure formation of the material before proceeding to further measurements.

B. Cross-sectional scanning thermal microscopy (xSThM)

After ensuring the purity of the 2D perovskite phase, we proceeded towards the cross-sectioning of the film (fabricated on Si/SiO$_2$ substrate) through the BEXP method followed by SThM investigation as described previously. As the entire sample system is composed of an assembly of different materials (Si, SiO$_2$, and 2D perovskite), the obtained wedge cut provides a perfect platform that includes three different regions and interfaces and can be studied in a single measurement as a function of tip position during SThM characterization. In Fig.2a, the 3D topography of the cross-sectional surface is presented. It is difficult to identify different materials and interfaces from the topography image due to the near-perfect nano-cross-sectioning via BEXP. On the contrary, the deflection and thermal images allow good differentiation of these different layers (Figs.2b & 2c). The extracted data (Fig.2d) revealed the height profile (Z-height) of the layers (SiO$_2$ and 2D perovskite) as a function of tip position x, along the section. Due to the dissimilar properties of Si, SiO$_2$, and perovskite, a different milling rate is also expected with the Ar beams, which due to the low angle incidence, results in an observable but minor change of angle at the interfaces. Such change is useful to identify different interfaces of the entire sample system. In addition, a very thin layer of aluminum (Al) was observed at the top of the 2D perovskite layer which could be formed during the BEXP cut when the Ar beams exit from the cut sample (see supplemental material [35]). At the same time, due to the calibration of the scanner, the thickness of the layer is directly measured as a function of the lateral position as described elsewhere with sub-nm precision [31].

Now, during scanning when the tip moves over the wedge cut, contact thermal voltage (V_c) could be obtained as a function of t simultaneously along with the topography as well throughout the cut defined as $V_c(t)$; such thermal signal profile is presented in Fig. 2e. The raw thermal results showed a different voltage contrast of the Si, SiO$_2$, and 2D perovskite layers due to the different thermal properties of each material. The thermal resistances of different regions over the cut were derived as a function of t as follows [46]:

$$R_x(t) = C_{corr} \frac{V_c(t)}{V_{nc} - V_c(t)} R_P \qquad (1)$$

where, R_P represents the probe thermal resistance at high vacuum (2.38×10^5 KW^{-1}) that was obtained through a calibration [47] and C_{corr} represents a correction factor that accounts for the deviation of the

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approximation that the heat source is concentrated only at the extreme point of the tip apex due to tip geometry [47]. The value of V_{nc} for the tip out of the contact with the sample is obtained by doing an approach and retract thermal scan over the cut and averaging them. In Fig. 2f, we have presented variation of $R_x(t)$ at different regions and interfaces through the wedge cut. First of all, we observed stable thermal resistance of Si followed by a clear increase at SiO_2 due to a much higher thermal conductivity of Si (135 $Wm^{-1}K^{-1}$) than SiO_2 (1.4 $Wm^{-1}K^{-1}$) [48,49]. Similarly, the 2D perovskite showed a higher thermal resistance than the SiO_2 and finally reached a quasi-constant nature at higher thickness. In addition, we witnessed a sudden jump of $R_x(t)$ at the SiO_2-perovskite interface suggesting a high interfacial thermal resistance at the SiO_2-perovskite interface. Although, these preliminary observations are consistent with the existing literature regarding the ultra-low thermal conductivity of 2D perovskite [18-20], it is not enough for the quantitative analysis that has been undertaken below.
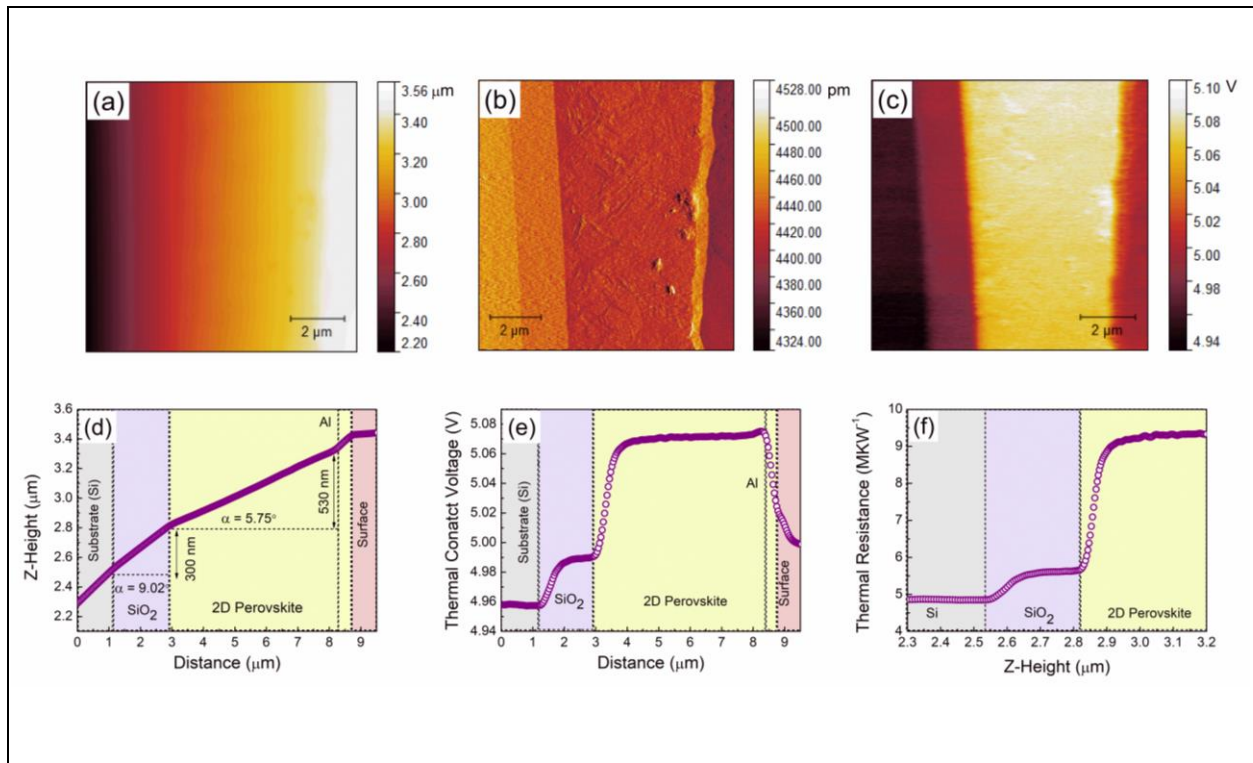

FIG. 2. (a) Topography (b) deflection (c) thermal signal image (d) section analysis (e) thermal voltage and (f) variation of thermal resistance at different regions of the BEXP cut sample as mentioned in the plots.

C. Analytical model for SThM response to study the anisotropic material

For the quantitative estimation of thermal conductivity in 2D perovskite, we used an analytical model that describes heat spreading within the layer on a substrate, as mentioned elsewhere [32,33]. It may be recalled that the 2D perovskite film was fabricated on a Si substrate having a SiO_2 layer. Hence, the entire system could be represented as a combination of two different heterojunctions (Si/SiO_2 and SiO_2/2D

perovskite) and demonstrated as a layer (top material) with thermal conductivity k_l on a uniform substrate (bottom material) having a thermal conductivity k_s. As mentioned earlier, the wedge cut allow us to carry out SThM measurement as a function of t in a single measurement as effective thickness of the layer under the probe is changed depending on the position of the tip (Fig. S2, within supplemental material [35]).

To quantify the thermal properties through this analytical model, we have expressed the total thermal resistance of the "tip-sample system" (Fig. 2f) as a combination of two components connected in series as $R_x(t) = R_s(t) + R_c$ where R_s represents the total spreading thermal resistance of the sample and R_c denotes the contact thermal resistance between the tip and sample [34]. As the experiments were carried out in vacuum, the contribution of water meniscus conductance has been eliminated [39], and we could consider that R_c is constant and solely governed by the solid-solid contact thermal resistance depending on the contact radius (a) and the thermo-physical properties of the scanned material [30]. Although R_c is independent of the tip position during scanning, it has a non-zero contribution that should be eliminated as the analytical model describes only the heat spreading within the layer on a substrate [32,33]. In addition, for both heterostructures, at the interfaces the tip-sample contact could be occurring simultaneously touching both materials, resulting in a sudden jump of thermal resistance at the transition point(s), leading to artifacts during fitting. In order to eliminate this, only the data at distance away from the transition point by the contact radius were used, with t_l denoting the thickness of each consecutive points starting from the point $t_l = t_0$. In order to exclude the unknown value of the tip-sample contact resistance, R_c, the difference between the thermal resistances at thickness t_l and t_0 was used as follows

$$R_l(t_l) = R_x(t_l) - R_x(0) = R_s(t_l) + R_c - R_s(0) - R_c = R_s(t_l) - R_s(0) \tag{2}$$

where, $R_x(0)$ represents the initial spreading resistance at $t_0 \to 0$ nm of thickness and $R_l(t_l)$ denotes the difference in the spreading resistance at each consecutive thickness point above t_0 and the thermal resistance at the point t_0. Then the final experimental data for both the nanostructure could be interpreted as R_l as a function of t_l which is compatible for fitting to the isotropic heat spreading model for $R_l(t_l)$ described by Muzychka and Spièce [32-34]:

$$R_l(t_l) = \frac{1}{\pi k_l a} \int_0^\infty \left[\frac{1 + K e^{-(\frac{2xt_{eff}}{a})}}{1 - K e^{-(\frac{2xt_{eff}}{a})}} \right] J_1(x) \sin(x) \frac{dx}{x^2} \tag{3}$$

where, k_l represents the top layer isotropic thermal conductivity and J_1 corresponds to the first-order Bessel function. In addition, K and t_{eff} are defined as

$$K = \frac{1 - k_l/k_s}{1 + k_l/k_s} \quad \text{and} \quad t_{eff} = t_l + r_{int} k_l \tag{4}$$

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and k_s represents the substrate's thermal conductivity, r_{int} denotes the layer-substrate interfacial thermal resistance, and t_l is the thickness of each layer. While this model is appropriate when the top layers exhibit inherent isotropic thermal transport, for an anisotropic transport of the top layer it is possible to modify these formulae by transforming t_l and k_l as following [32,33]:

$$t_{l,anis} = \frac{t_l}{\sqrt{\frac{k_{l,z}}{k_{l,xy}}}} \quad \text{and} \quad k_{l,anis} = \sqrt{k_{l,xy}k_{l,z}} \tag{5}$$

D. Quantitative analysis of thermal conductivity: Fitting results and FEA simulation

In order to obtain average thermal conductivity, $k_{l,anis}$, of the 2D perovskite layer using the abovementioned model, we applied a two-step fitting due to the need to find several independent parameters (Equations 3-5) such as a, C_{corr}, $k_{l,xy}$, $k_{l,z}$ and r_{int}. In the first step, the analytical fitting was carried out in Si/SiO$_2$ heterostructure considering it as a reference with known values of k_s (k_{Si}) and k_l (k_{SiO2}) to obtain a and C_{corr} as fitting parameters. In the next step, these values were served as known inputs when the model was applied to the SiO$_2$/2D perovskite heterostructure to obtain k_l ($k_{l,anis}, k_{l,xy}, k_{l,z}$) of 2D perovskite and r_{int} between SiO$_2$ and 2D perovskite. In addition, we have validated our fitting results with FEA simulation which is also helpful to qualitatively understand the thermal properties of the system in terms of temperature distribution and heat flow directions.

Isotropic model fitting for Si/SiO₂ heterojunction: According to previous studies, SiO$_2$ on Si substrates exhibit an isotropic thermal transport [34,48]. Hence, introducing $k_s = 130$ Wm^{-1}K^{-1} and $k_l = 1.4$ Wm^{-1}K^{-1} as known parameters during the first fitting [48-50], we could extract a and C_{corr} along with r_{int} as fitting parameters by applying the isotropic model (Equations 3, 4). However, before proceeding to the actual refinement of the experimental data, it would be intriguing to understand how each of these fitting parameters governs the overall thermal spreading resistance analytically and theoretically (Fig S3, within supplemental material [35]). Using this approach, a desired goodness of fit was achieved (Fig. 3a and Table I). We extracted $a = 55.4 \pm 0.2$ nm from the fitting which is a good agreement with the specification of the probe with the tip radius < 100 nm. Similarly, we obtained a reasonable value of $C_{corr} = 5.15$; in ideal case this should be unity suggesting that the heat source is concentrated only at the extreme point of the tip apex [47]. Moreover, the interfacial thermal resistance between Si and SiO$_2$ (r_{Si-SiO_2}) was found to be ~10^{-11} Km^{2}W^{-1}. While this value is much smaller than the previously reported value of 10^{-9} Km^{2}W^{-1} [34], our analysis (see the forward curves in Fig S3, supplemental material [35]) inferred that the influence of interfacial thermal resistance on the thermal transport in such a system is negligible in the range of 10^{-9} to 10^{-11} Km^{2}W^{-1}; in this range, these curves overlap with each other over the entire thickness region. Given a wide range of values that satisfy our fitting, these data do not contradict the literature values. This means

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that, first, our measurements mainly provide the upper range of the thermal resistance, and, significantly, that sample-substrate interfacial thermal resistance does not affect the absolute values of the layer thermal conductivity and its anisotropy- the key parameters of interest for this study.
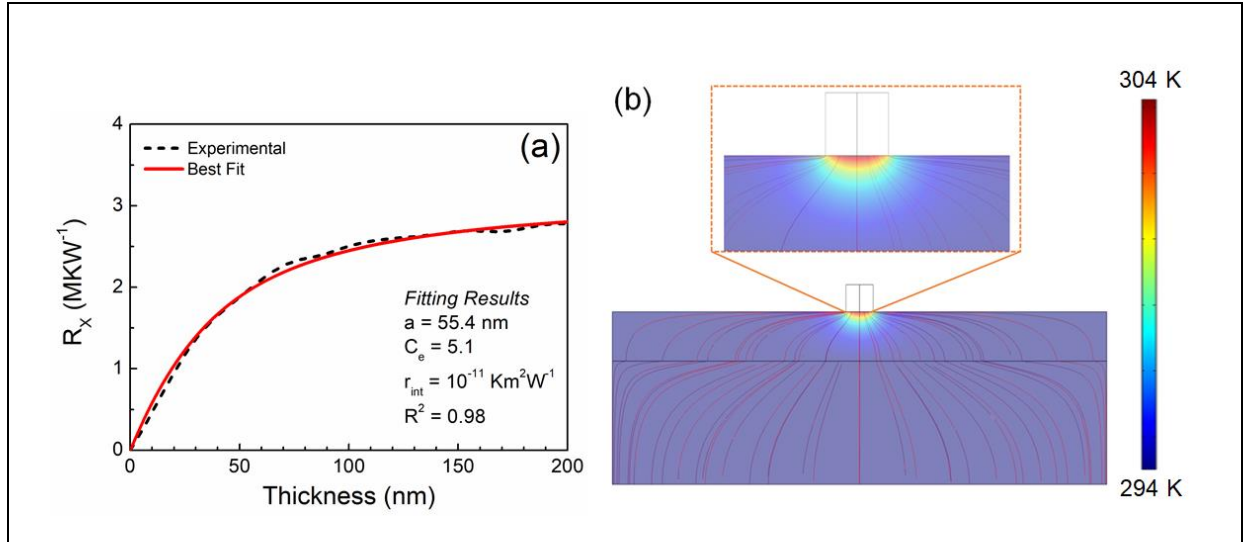

FIG. 3. (a) The fitting plot for Si/SiO₂ heterojunction (analytical model). (b) FEA simulated the results of thermal gradient and heat flow at a high thickness (the inset shows a zoomed-in view).

These obtained fitting parameters were also introduced in a realistic model in the COMSOL interface to obtain the idea of thermal transport in this system. A planar mode was used for an optimized simulation experience analogous to a real device system, and given the extreme similarity with the wedge model (Fig. S4, within supplemental material [35]), we can argue that the results extracted from the plane model are highly reliable and descriptive. In this direction, we mainly proceeded to understand the temperature distribution (color gradient) and heat flow direction (streamlines) in the YZ direction. As such, we depicted the thermal behavior at two different tip positions indicating two different thicknesses (thick and thin layers). At a higher thickness, a higher temperature gradient and an isotropic heat flow were observed (Fig. 3b). On the other hand, at a lower thickness (Fig. S5, within supplemental material [35]), the temperature gradient was found to be very localized under the tip and did not influence its surroundings creating only a minor temperature difference. Under this situation, mainly r_{Si-SiO_2} restricts the heat transport towards Si resulting in a small thermal gradient.

Anisotropic model fitting for SiO₂/2D perovskite heterojunction: After obtaining some of the common parameters from the previous analysis, we could finally use the Muzychka-Spièce model of heat spreading (Equation 5) for the second heterojunction considering SiO₂ as a substrate and the 2D perovskite as a top layer to determine its average thermal conductivity ($k_{l,anis}$ or k_{avg}). Due to the anisotropic layered structure, such 2D perovskites are expected to exhibit anisotropic thermal transport [20]; hence the

anisotropic model was considered instead of the isotropic one (Equation 3). Although we considered Si/SiO$_2$ and SiO$_2$/2D perovskite as two different heterojunctions during this analytical method, no significant change was expected for a and C_e as all three materials (Si/SiO$_2$/2D perovskite) were thermally imaged sequentially as a single system under same SThM probe and similar geometrical configuration. Hence, the previously determined values of a =55.4 nm and C_{corr} = 5.15 along with k_s =1.4 Wm^{-1}K^{-1} were used as known inputs during the fitting to obtain $k_{l,anis}$ (k_{avg}) = $\sqrt{k_{l,xy}k_{l,z}}$), Δ_{anis}= $\frac{k_{l,xy}}{k_{l,z}}$, and interfacial thermal resistance between SiO$_2$ and 2D perovskite ($r_{int_{SiO2-Perovskite}}$), respectively as fitting parameters and to deconvolute them into $k_{l,xy}$ and $k_{l,z}$ finally. However, similar to the Si/SiO$_2$ heterojunction, we first generated a series of simulated curves for different $k_{l,anis}$ (k_{avg}) and Δ_{anis} to get a preliminary idea about these parameters before the original fitting (Figs. 4a-b & Figs. 4d-e). To start with, by comparing the experimental data and the forward curves, the value of $k_{l,anis}$ (k_{avg}) of the top 2D perovskite layer can be reasonably well estimated to be close to 0.25 Wm^{-1}K^{-1} (Fig. 4a). On the other hand, visual curve comparison appears to be less very sensitive to the anisotropy ratio; for example, it looks different curves (Δ_{anis}= 3, 5, 10) lie close to each other (Fig. 4b). However, a close inspection reflects that these theoretical curves are closer at a high thickness and become quasi-constant to overlap with each other. Hence, it is predominantly the transition region (Fig. 2f) vis-à-vis the initial slope (Fig. 4b), that reflects the anisotropic behavior of the heat transport. Based on the similarity of the initial slope we could conclude that the experimental curve lies between 3 and 5 (inset Fig. 4b), to be specifically closer to a value of 3, with some amount of error. In this direction, we refined these results through an iterative method to obtain much smaller error for both average heat conductivity $k_{l,anis}$ (k_{avg}) = 0.25$\pm$0.05 Wm^{-1}K^{-1} and, essentially, anisotropy ratio Δ_{anis} = 3.4$\pm$0.3 (Fig. 4c). The errors in this case are directly provided by several measurements followed by statistical analysis. These values, in turn, result in the in-plane and/or out-of-plane values of the thermal conductivity of $k_{l,xy}$ = 0.45$\pm$0.05 Wm^{-1}K^{-1} and $k_{l,z}$ = 0.13$\pm$0.05 Wm^{-1}K^{-1}. In summary, this iterative fitting method allows for achieving good agreement with the theoretical model as well as the adequate goodness of fit (> 95%) and a minimum root mean squared error.
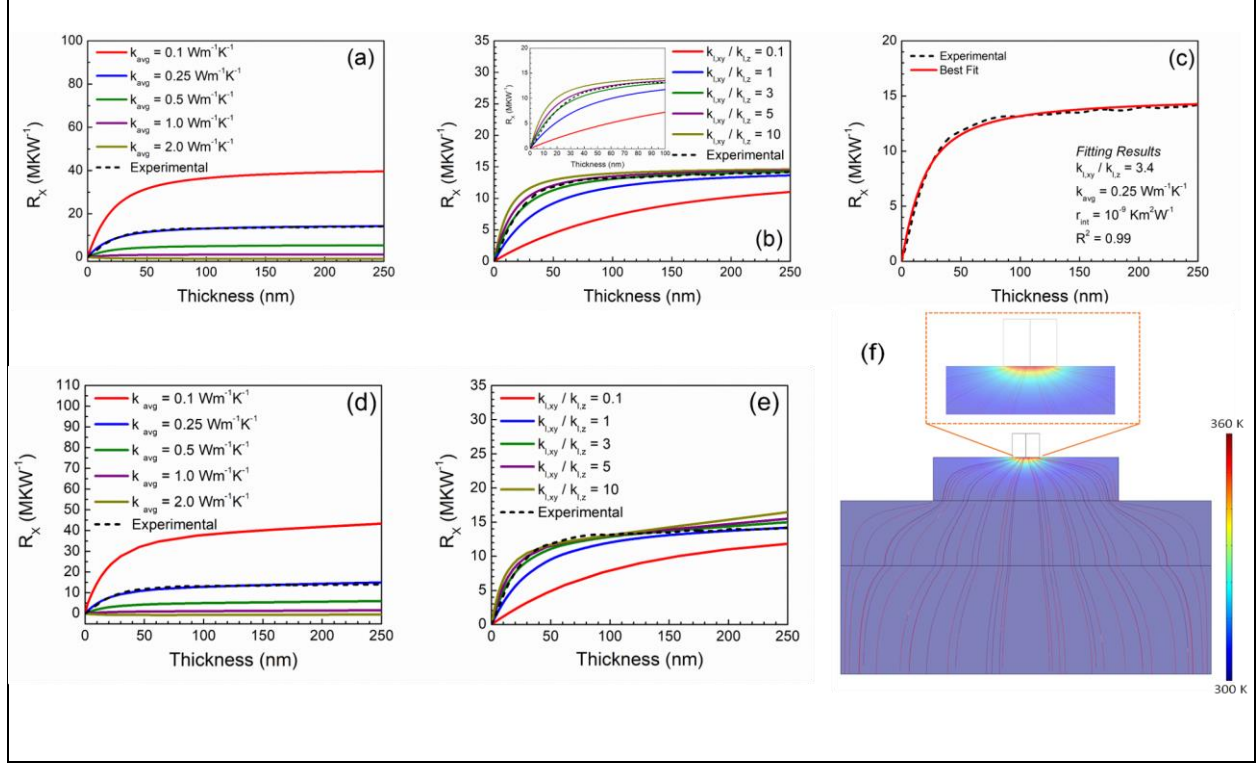
FIG. 4. (a-b) Simulated thermal resistance dependence for different $k_{l,anis}$ (k_{avg}) and Δ_{anis} ($\frac{k_{l,xy}}{k_{l,z}}$,) and (c) the fitting plots for Si/SiO$_2$ heterojunction (analytical model). (d-e) FEA simulated forward plots for different $k_{l,anis}$ (k_{avg}) and Δ_{anis}. ($\frac{k_{l,xy}}{k_{l,z}}$). (f) FEA simulated results of thermal gradient and heat flow (inset shows a zoomed-in view).

It may be stated that the independent determination of several thermal parameters in a single experiment became possible, as the measurements were performed for the varied thickness of the sample, which was equivalent to the multiple experiments on the same system (Fig. S2, within supplemental material [35]). Finally, for the justification, we also introduced these fitting parameters in our FEA model structure similar to the reference sample. We observed a negligible thermal gradient at a low thickness in contrast to that for higher thickness where the interface does not influence the heat spreading (Fig. 4f and Fig. S5, within supplemental material [35]). Moreover, at higher thicknesses, the direction of heat flow is also found to be anisotropic having a slightly larger contribution toward the in-plane direction.

We compared the quantitative results with some of the reported perovskites obtained through other conventional techniques (Table S1, within supplemental material [35]) which includes Refs [19-26,29,51,52]. We found that the obtained value of k_l having an ultra-low nature matches well with other 2D perovskites which is even lower than their 3D counterpart MAPbI$_3$ possessing a continuous inorganic framework of strong ionic/covalent bonds [19,20,28,29,53]. It is also found that the in-plane thermal

conductivity of the 2D perovskite (PEA$_2$PbI$_4$) is larger than its 1D counterpart (PEAPbI$_3$) [19]. On the other hand, Δ_{anis}=3.39 was also found to be larger than a recent report of a similar 2D perovskite (BA$_2$PbI$_4$) having a value of 1.5 [20]. It should be noted that most of the existing techniques to measure anisotropic thermal conductivity involve a different set of macroscopic experiments [19,20,25,26,54]. In this regard, our novel method of measuring anisotropic thermal conductivity using the xSThM method with a single set of measurements and nanoscale resolution paves the way as an alternative and efficient route.

TABLE I. Fitting parameters as obtained from the analytical model (Muzychka-Spièce formulation) when experimental data is fitted to Equations 3-5.

Fitting Parameters	Si/SiO$_2$		SiO$_2$/Perovskite	
	Substrate	Top layer	Substrate	Top layer
	Si	SiO$_2$	SiO$_2$	(PEA)$_2$PbI$_4$
Contact radius, a (nm)	55.0			
Interfacial thermal resistance, r_{int} (10^{-11} Km^{2}W^{-1})	1.99		100	
Correction factor, C_e	5.15	5.15	5.15	5.15
Average thermal conductivity of substrate, k_s (Wm^{-1}K^{-1})	130.0	-	1.4	-
Average thermal conductivity of top layer, k_l (Wm^{-1}K^{-1})	-	1.4	1.4	0.25
In-plane thermal conductivity of top layer, $k_{l,xy}$ (Wm^{-1}K^{-1})	-	1.4	-	0.45
Out-of-plane plane thermal conductivity of top layer, $k_{l,z}$ (Wm^{-1}K^{-1})	-	1.4	-	0.13

Evaluation of the systematic error: As this technique is comparatively unique, to evaluate the size of the systematic error, these results were corroborated with similar measurements and analysis on a standard sample with known low thermal conductivity in the range of the 2D perovskite we studied (Fig. 5). We picked an isotropic polymer thin-film SU-8 for such study which is reported to possess a thermal conductivity of 0.2 Wm^{-1}K^{-1} [55,56]. We repeated similar xSThM measurements and analytical fitting to quantify the thermal conductivity and anisotropy of the material so that the effect of any systematic error could be understood. In Fig. 5a, the mapping of thermal voltages of the Si/SiO$_2$/SU-8 control sample has been presented along the wedge cut prepared from a similar BEXP method. We observed low thermal voltages at the Si region followed by a clear increase at the SiO$_2$ layer inferring a decrease in thermal spreading due to a much higher thermal conductivity of Si than SiO$_2$. Similarly, in the SU-8 polymer layer, a further increase in the thermal voltage was observed compared to the SiO$_2$ indicating even smaller thermal conductivity. To quantify the average k_{avg}($k_{l,anis}$) $k_{l,xy}$, $k_{l,z}$ of the SU-8 layer using our model, we similarly applied the two-step fitting. In the first step, the analytical fitting (Fig. 5b) returned the value of a and C_{corr} as fitting parameters. These served as inputs at the second step of fitting of SU-8 on SiO$_2$ (Fig.

13

5c) heterostructure to obtain k_l ($k_{l,anis}$, $k_{l,xy}$, $k_{l,z}$). The results showed that k_{avg}($k_{l,anis}$) of the top SU-8 layer lies close to 0.24 ± 0.01 Wm^{-1}K^{-1} with adequate goodness of fit; on the other hand, Δ_{anis} was found to be 0.92 ($k_{l,xy} = 0.23 \pm 0.01$ Wm^{-1}K^{-1} and $k_{l,z} = 0.25 \pm 0.01$ Wm^{-1}K^{-1}) signifying the near isotropic nature of the thermal conductivity. Hence, we could claim the size of the systematic error through this unique xSThM approach in measuring the thermal conductivity is about 20% and below 10% for the anisotropy factor, confirming that quantification of anisotropic thermal transport in 2D perovskite is highly reliable.
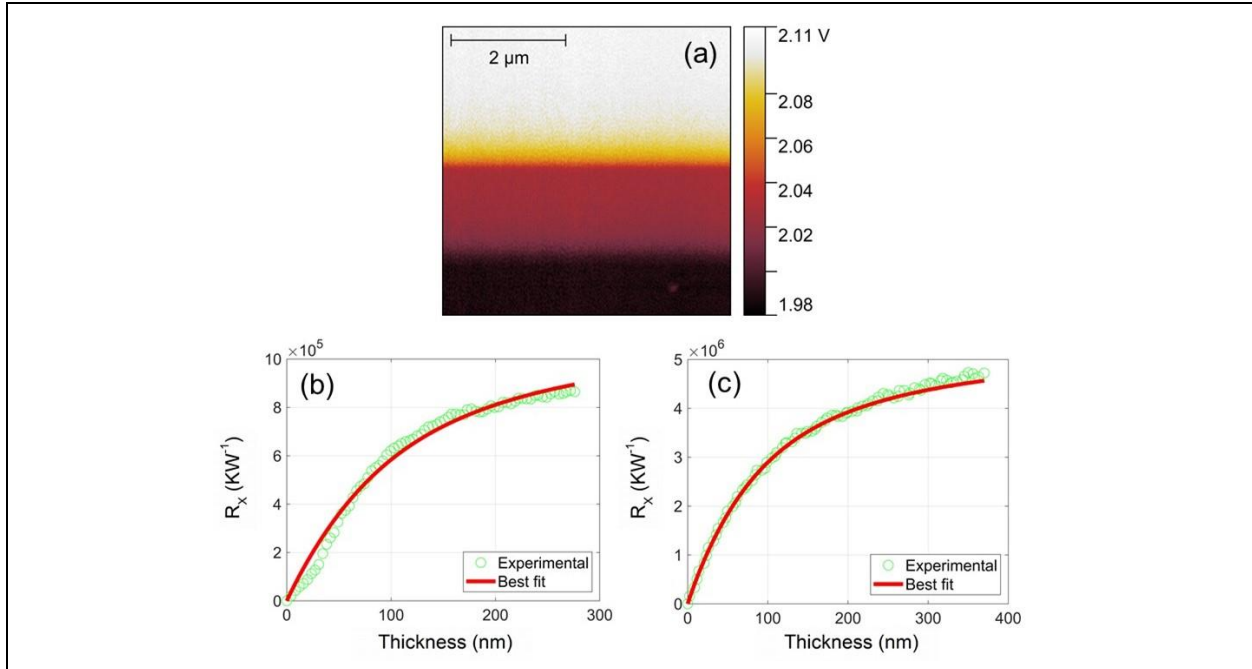

FIG. 5. (a) Thermal signal image of Si/SiO$_2$/SU-8 heterojunction as obtained from xSThM. (b-c) The fitting plots for Si/SiO$_2$ and SiO$_2$/SU-8 heterojunctions, respectively through the analytical model.

E. Origin of anisotropic thermal transport in 2D perovskite

Our study reveals the occurrence of thermal anisotropy in this compound. Such anisotropy in thermal transport can be explained by considering the structural landscape of a general 2D RP perovskite and associated phonon transport (Fig 6a). In such materials, the metal halide octahedra form infinite sheets in the in-plane direction and the organic spacer molecules are located between two successive sheets in the out-of-plane direction. As mentioned earlier, the large spacer cation (for example PEA chains) is aligned in the out-of-plane direction having covalent bonds (C-C and C-N). In addition, weak van der Waals and electrostatic interactions can be found between two vertically stacked organic chains and at the organic-inorganic interfaces. On the other hand, there are strong ionic bonds in the in-plane direction originating

from the continuous $[PbI_4]^{2-}$ octahedral framework [20,42,43,57]. It may be noted that the component of the thermal conductivity tensor can be expressed as:

$$k_{l,\alpha\beta} = \sum_q C_{v_q} \vartheta_{q,\alpha} \vartheta_{q,\beta} \tau_q \qquad (6)$$

where q indexes the phonon wavevector, C_{v_q} is the mode-wise heat capacity, $\vartheta_{q,\alpha}$ and $\vartheta_{q,\beta}$ are the mode-wise group velocity projected onto the α and β direction, respectively, and τ_q is the mode-wise lifetime. As such C_v does not have any directional dependence in contrast to ϑ and τ in governing the anisotropic thermal transport in the compound. Along the in-plane direction, the presence of a continuous $[PbI_4]^{2-}$ octahedral framework allows uninterrupted pathways for heat transport [58]. In short, phonons would possess relatively large lifetimes and group velocities ($\vartheta_{q,xy}$) within these inorganic layers resulting in a higher thermal conductivity ($k_{l,xy} = 0.45$ Wm^{-1}K^{-1}). In contrast, the presence of organic-inorganic interfaces and the weak interactions of two vertically stacked organic chains would result in the scattering of phonons along the out-of-plane direction [57,59]. Hence, thermal transport would be interrupted due to the shorter lifetime and group velocities ($\vartheta_{q,z}$) of phonons leading to comparably lower thermal conductivity along cross plane ($k_{l,z} = 0.13$ Wm^{-1}K^{-1}). In a nutshell, the anisotropy originates mainly due to the antagonism between continuous heat conduction in the inorganic layer along the plane versus the interrupted ones in the out-of-plane. Our experimental result matches well with the reports of Li et al. as obtained from molecular dynamics (MD) simulations of similar 2D perovskite (Fig 6b). However, the value of Δ_{anis} (~ 3.4) is found to be small compared to most of the other layered compounds (Fig 6c) [60-65]; it may be noted that due to the small volume fraction of the inorganic layers the anisotropy becomes weak.
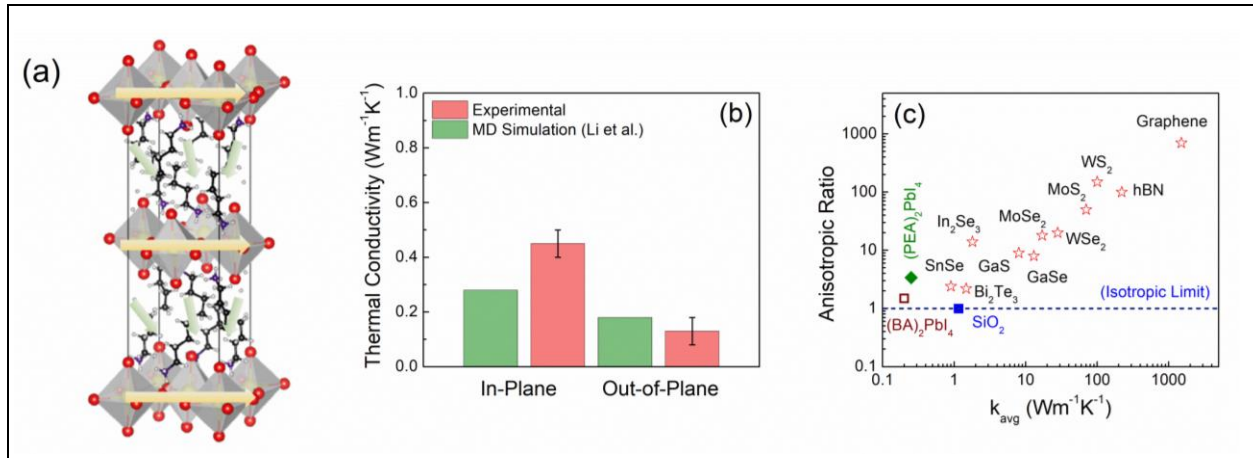

FIG. 6. (a) Heat (phonon) conduction pathways in a general 2D-RP perovskite along in-plane and out-of-plane directions. (b) Comparison of in-plane and out-of-plane thermal conductivity of (PEA)$_2$PbI$_4$ with respective to MD simulation of similar 2D perovskite [20]. (c) Anisotropic ratio vs average thermal conductivity of 2D-RP perovskite compared to other layered compounds in which the other data points were adapted [20].

IV. CONCLUSIONS

In this work, we measured thermal transport parameters ($k_{l,anis}$, Δ_{anis} vis-à-vis $k_{l,xy}$, $k_{l,z}$) of an archetypal 2D perovskite system namely (PEA)$_2$PbI$_4$, through xSThM. The low-angle nanoscale quality wedge cut of the perovskite thin film on the SiO$_2$/Si substrate was obtained through the Ar-ion BEXP method that allowed effectively in one SThM measurement to obtain thermal conductance data for the various thicknesses of all nanoscale layers. The experimentally obtained data were then used to first calibrate the SThM measurements and ultimately with an analytical model validated by FEA simulation to directly calculate the absolute values of in-plane and cross-plane anisotropic thermal conductivity $k_{l,xy}$ and $k_{l,z}$ of the 2D perovskite finally. We obtained an ultra-low value of average thermal conductivity of this material of $(k_{avg}) = 0.25 \pm 0.05$ Wm^{-1}K^{-1} for the 2D perovskite with an anisotropy factor ($k_{l,xy}/k_{l,z}$ ~ 3.4) that we attribute to the unique structure of the perovskite leading to different phonon lifetimes and phonon group velocities along cross-plane and in-plane directions. This work provides a novel technique to quantify the anisotropic thermal transport in 2D perovskites and provides new physical insights that would be useful for the thermal management of 2D perovskite-based optoelectronic devices and their potential applications in thermoelectric.

AVAILABILITY OF DATA

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR'S CONTRIBUTION

AM and OVK conceived the plan. AM fabricated the films and performed the XRD, optical absorbance, and PL characterization. AM performed the BEXP cut under the supervision of OVK. AM and KA performed the xSThM at vacuum under the supervision of OVK. KA performed the analytical calculations in which some of the codes were developed by SGM. OVK and SGM performed the FEA simulation. The validation measurement on the SU-8 sample was carried out by SGM. AM, KA, and OVK analyzed the results. AM wrote the original manuscript and OVK revised it. All the authors contributed to the manuscript.

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