Ultralow thermal conductivity in all-inorganic halide perovskites

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Ultraslow thermal conductivity in all-inorganic halide perovskites

Woochul Lee,a,b,1 Huashan Li,c,1 Andrew B. Wong,a,d,1 Dandan Zhang,d,1 Minliang Lai,y Yi Yu,a,d,1 Qiao Kong,a Elbert Lin,a Jeffrey J. Urban,b Jeffrey C. Grossman,c and Peidong Yang,a,d,e,f,2

aDepartment of Chemistry, University of California, Berkeley, CA 94720; bMolecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; cDepartment of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; dMaterials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; eDepartment of Materials Science and Engineering, University of California, Berkeley, CA 94720; and fKavli Energy NanoScience Institute, Berkeley, CA 94720

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Controlling the flow of thermal energy is crucial to numerous applications ranging from microelectronic devices to energy storage and energy conversion devices. Here, we report ultralow lattice thermal conductivities of solution-synthesized, single-crystalline all-inorganic halide perovskite nanowires composed of CsPbI3 (0.45 ± 0.05 W m−1 K−1), CsPbBr3 (0.42 ± 0.04 W m−1 K−1), and CsSnI3 (0.38 ± 0.04 W m−1 K−1). We attribute this ultralow thermal conductivity to the cluster rattling mechanism, wherein strong optical–acoustic phonon scatterings are driven by a mixture of 0D/1D/2D collective motions. Remarkably, CsSnI3 possesses a rare combination of ultralow thermal conductivity, high electrical conductivity (282 S cm−1), and high hole mobility (394 cm2 V−1 s−1). The unique thermal transport properties in all-inorganic halide perovskites hold promise for diverse applications such as phononic and thermoelectric devices. Furthermore, the insights obtained from this work suggest an opportunity to discover low thermal conductivity materials among unexplored inorganic crystals beyond caged and layered structures.

Significance

Discovery of materials with low thermal conductivity in simple, fully dense, and single-crystalline solids has proven extremely challenging. This paper reports the discovery of ultralow thermal conductivity (~0.4 W m−1 K−1) in single-crystalline, all-inorganic halide perovskite nanowires, which is comparable to their amorphous limit value. We attribute ultralow thermal conductivity to a cluster rattling mechanism, based on strong phonon–phonon scattering via the coexistence of collective motions involving various atom groups. These results call attention to the vital thermal transport processes and thermal management strategies for applications with all-inorganic halide perovskites. Further, CsSnI3 shows a rare combination of ultralow thermal conductivity and high electrical conductivity, so it can be a promising material for unique applications as an electrically conductive thermal insulator.


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The authors declare no conflict of interest.

1W.L., H.L., and A.B.W. contributed equally to this work.
2To whom correspondence should be addressed. Email: p_yang@berkeley.edu.

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transport in AIHP. Whereas we have developed solution-phase synthetic methods for CsPbI₃ and CsPbBr₃ NWs (17, 23) (details in SI Appendix), we report the successful low-temperature solution-phase synthesis of black orthorhombic phase CsSnI₃ (B-CsSnI₃) NWs in this work (SI Appendix, Figs. S1 and S4), which has been a challenge because of the tendency to form a more stable yellow polymorph of CsSnI₃ based on [Sn₂I₆]⁻ double chains (24, 25). The B-CsSnI₃ has a direct bandgap of 1.3 eV, and unlike other materials with strong emission in the near-infrared, this material does not contain toxic lead or cadmium or require highly reactive metal-organic chemical vapor deposition precursors (24). We confirmed B-CsSnI₃ by X-ray powder diffraction and single-NW photoluminescence (SI Appendix, Fig. S2).

At room temperature, CsPbI₃ NWs adopt a double-chain structure in the orthorhombic Pnma space group (6) while CsPbBr₃ and B-CsSnI₃ NWs have a distorted perovskite phase in the orthorhombic Pbnm space group (γ) (Fig. 1 A–C). Although δ-CsPbI₃ does not possess the 3D bonding network characteristic of the perovskite structure, we investigate δ-CsPbI₃ along with γ-CsPbBr₃ and γ-CsSnI₃ as this is a perovskite-related material (see SI Appendix for more details). In addition, the distinct connectivity patterns within these materials composed of similar chemical elements provide a desirable platform for understanding the impact of the topological character of the bonding network on thermal transport properties. High-resolution transmission electron microscopy, fast Fourier transforms of the lattice images, and selected area electron diffraction data for CsPbI₃, CsPbBr₃, and CsSnI₃ NWs confirm that these NWs are single crystalline, and that the crystal growth directions are [010], [110], and [110], respectively (Fig. 1 D–F and SI Appendix, Fig. S3). The difference of crystal growth direction in CsPbI₃ NWs resulted from the different crystal structure as described above.

To measure the thermal conductivity along the length of the AIHP NWs, we used suspended microisland devices (Fig. 1 G–I) (26). We validated the experimental platform by measuring the thermal conductivity of amorphous SiO₂ NWs (SI Appendix, Fig. S5). Further, we estimated the thermal contact resistance between the AIHP NWs and Pt electrodes, and the contact resistance is found to be ~3% of the intrinsic thermal resistance of the AIHP NWs (SI Appendix, Fig. S6).

The measured temperature-dependent thermal conductivity for a representative NW of each composition is presented in Fig. 2. The characteristic lengths of the NWs, which can be represented in terms of the Casimir length (√4wh/π, where w is the width and h is the height) (27), are 134, 240, and 400 nm for CsPbI₃, CsPbBr₃, and CsSnI₃, respectively. To obtain the lattice thermal conductivity (k_lattice) from the measured total thermal conductivity (k_total) in CsSnI₃, we directly measured electrical conductivity (details are described below and in SI Appendix) and estimated electronic thermal conductivity (k_electron) from the Wiedemann–Franz law. Subsequently, k_lattice is obtained by subtracting k_electron from k_total (k_lattice = k_total − k_electron). In contrast to CsSnI₃, measured thermal conductivity in CsPbI₃ and CsPbBr₃ is k_lattice, since these NWs are electrically insulating (SI Appendix). Despite their different compositions and phases, k_lattice of AIHP NWs is found to be ultralow: 0.45 ± 0.05 W m⁻¹ K⁻¹ for CsPbI₃, 0.42 ± 0.04 W m⁻¹ K⁻¹ for CsPbBr₃, and 0.38 ± 0.04 W m⁻¹ K⁻¹ for CsSnI₃ at room temperature. Further, while amorphous-like thermal transport behaviors are observed in several crystalline materials with low thermal conductivity (28, 29), AIHP NWs exhibit crystal-like thermal conductivity in which the k_lattice initially increases and then decreases as temperature rises.

To benchmark the observed ultralow k_lattice of single-crystalline AIHP NWs, we estimated the amorphous limit of k_lattice (k_min) using the model developed by Cahill et al. (6). As can be clearly seen in Fig. 2 A–C, k_lattice approaches k_min near room temperature in all AIHP NWs. To verify our experimental results, we measured the thermal conductivity of several single NWs of each composition and confirmed consistent results (SI Appendix, Fig. S8). Given the ultralow k_lattice in single-crystalline AIHP NWs, it is worth comparing with other classes of single-crystalline materials with ultralow thermal conductivity (Fig. 2D). Remarkably, k_lattice of AIHP NWs are comparable to and even smaller than various crystals such as Zintl compounds, clathrates, and skutterudites (4). Further, the ratio of k_lattice to k_min of AIHP NWs at room temperature is only ~2 for all cases (Fig. 2D, Inset). This ratio is lower than that of other crystals exhibiting low thermal conductivity (SI Appendix, Table S1), particularly for CsPbBr₃ and CsSnI₃. We also note that AIHP NWs have far smaller thermal conductivity compared with traditional inorganic oxide perovskites whose values are 2–10 W m⁻¹ K⁻¹ (30).

![Fig. 1. AIHP NWs and suspended microisland devices to measure their thermal and electrical properties. (A–C) Crystal structures of CsPbI₃, CsPbBr₃, and CsSnI₃. Atoms are colored by Cs: green, Pb: gray, I: purple, Sn: light purple, Br: brown. (D–F) High-resolution transmission electron microscopy images and corresponding fast Fourier transform patterns of CsPbI₃, CsPbBr₃, and CsSnI₃ demonstrate the single-crystalline nature of the AIHP NWs. (G and H) SEM images of suspended microisland devices. Individual AIHP NW is suspended between two membranes. The transport measurement direction is along the growth direction of the NWs. (I) SEM image of the individual AIHP NW. (Scale bars in D–F, 5 nm; in G, 10 μm; in H, 3 μm; in I, 1 μm.)](https://www.pnas.org/doi/10.1073/pnas.1711744114)
To elucidate the fundamental mechanisms responsible for the observed ultralow thermal conductivity, we apply a combination of density-functional theory (DFT) and the Boltzmann transport equation (BTE) (details in SI Appendix (31). Considering the intrinsic uncertainty associated with perturbation theory and DFT-based simulations, the calculated \( k_{\text{lattice}} \) without fitting parameters are in reasonable agreement with the experimental values at high temperature (Fig. 2 A–C). At low temperature, an empirical model is adopted to describe defect and boundary scatterings, and the computed data qualitatively agree with the trend observed in experimental data (Fig. 2 A–C).

Our simulations show that the extremely low \( k_{\text{lattice}} \) can be attributed to low group velocities (\( v_g \)) and more importantly to extremely short phonon mean-free paths (\( l \)). The calculated \( v_g \) in all cases is quite small (\( v_g < 2,000 \) m/s) due to constituent heavy atoms in AIHP (SI Appendix, Fig. S9 and Table S3). In general, \( l \) is suppressed by scattering with intrinsic defects and with the NW surface at low temperature, and by phonon–phonon scattering at high temperature (Fig. 3A and SI Appendix, Figs. S12 and S13). In AIHP, strong interactions between optical and acoustic modes are stimulated as a result of the large number of band crossings in the low-frequency range (Fig. 3A, Inset). Although the \( l \) distribution is much broader and the phonon scattering rates are slightly smaller in the \( \gamma \)-phase than in the \( \delta \)-phase, these factors in combination with their distinct phonon density of states (DOS) still lead to a similar \( k_{\text{lattice}} \) in both situations (SI Appendix, Fig. S10).

Extremely short maximum \( l \) associated with 95% contribution to total \( k_{\text{lattice}} \) (Fig. 3A) is caused by dramatic anharmonicity due to a cluster rattling mechanism (Fig. 3A). The rattling mechanism associated with local soft modes is widely accepted to be responsible for the low \( k_{\text{lattice}} \) in clathrates (32) and \( Zn_4Sb_3 \) (33). From the cage structure of the \( \gamma \)-phase, it is intuitive to consider the rattling mechanism as the main source of anharmonicity. However, it is nontrivial why such an effect would be especially significant in the \( \gamma \)-phase, and how this concept would extend to the \( \delta \)-phase where there are no explicit cages. To answer these questions, we correlate the rattling strength with structural inhomogeneity via an analysis of bond length distributions. In the case of \( \gamma-CSnI_3 \) (Fig. 3B), the different distances between the Cs rattler and the surrounding atoms generates soft optical modes as evidenced by the projected DOS on Cs atoms (SI Appendix, Fig. S10). In \( \delta-CSnI_3 \) (Fig. 3C), although no single atom can be isolated from the network, the inhomogeneous bond length map enables us to identify clusters composed of Pb and I atoms that are loosely bound to their neighbors. These clusters play a similar role as atomic rattlers.

![Graphs](https://via.placeholder.com/150)

**Fig. 2.** Thermal conductivity of AIHP NWs. (A–C) Measured thermal conductivity (\( k_{\text{lattice}} \) for A and B, and \( k_{\text{lattice}} \) for C), ab initio calculated lattice thermal conductivity (\( k_{\text{computed}} \)), and estimated minimum thermal conductivity (\( k_{\text{min}} \)) for each NW. Electronic thermal conductivity (\( k_{\text{electron}} \)) for CsPbI_3 NW is estimated from measured electrical conductivity and the Wiedemann–Franz law, and lattice thermal conductivity (\( k_{\text{lattice}} \)) is obtained by subtracting electron thermal conductivity (\( k_{\text{electron}} \)) from total thermal conductivity (\( k_{\text{total}} \)). (D) Comparison between inorganic perovskites and other single crystals with ultralow thermal conductivity [\( Ba_8Ga_{16}Ge_{30} \) (36), \( Yb_{11}InSb_{9} \) (37), \( Yb_{11}Sb_{10} \) (38), \( La_2Mo_2O_9 \) (39), \( Yb_{14}AlSb_{11} \) (40)]. (Inset) Ratio of lattice thermal conductivity to the minimum thermal conductivity for AIHP NWs.
but with a larger characteristic size, which is consistent with the dominant contribution from Pb and I atoms to the phonon DOS in the low-frequency range (SI Appendix, Figs. S10 and S11), and this explains the longer $l$ in the $\delta$-phase compared with that in the $\gamma$-phase as a consequence of the reduced scattering rates between phonons with short wavelengths. Within this framework, we further identified a variety of low-frequency phonon modes that contribute to the cluster rattling mechanism, which are associated with 0D/1D/2D collective motions in both $\gamma$-CsSnI$_3$ and $\delta$-CsPbI$_3$ crystals (SI Appendix, Fig. S11).

Since the rattling mechanism has been widely believed to rely on the presence of sufficient interstitial space that enables intensive vibration of rattlers, relevant investigations have been limited to a few types of materials with large cages (34) or layered structures (35). In addition, most of the rattlers reported so far contain only one atom/molecule (34) or components with incoherent motions (35), and the reduction of thermal conductivity was attributed to a single type of rattler. Via quantitative joint experimental–theoretical analysis, we present the unambiguous demonstration of the impact of cluster rattling mechanism on thermal transport properties: comparable and even lower $k_{\text{lattice}}$ of AIHPs compared with HHPs (18) ($k_{\text{HHP}} = 0.5 \text{ W m}^{-1} \text{K}^{-1}$) imply that the strength of phonon–phonon scattering induced by the cluster rattling mechanism is comparable to that originating from the individual rattlers. While the size, shape, symmetry, and vibrational modes of the organic molecule are key parameters for thermal transport properties in HHP (20), the topological pattern and bond strength distribution of the entire framework dictates thermal transport properties in AIHP.

To understand other transport properties of CsSnI$_3$, we measured the four-probe electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) of the exact same NW studied for thermal transport in Fig. 2C with the suspended microisland devices (Fig. 4A). At room temperature, $\sigma$ is 282 S/cm and $S$ is 79 $\mu$V/K. Temperature-dependent $\sigma$ exhibits metallic behavior, and the positive sign of $S$ indicates a hole-dominant ($p$-type) semiconductor, in agreement with previous studies (24). We also performed experiments on several single CsSnI$_3$ NWs, and the results are consistent (SI Appendix, Fig. S8). Remarkably, CsSnI$_3$ NWs have a relatively high electrical conductivity, yet ultralow thermal conductivity ($k_{\text{total}} = 0.57 \text{ W m}^{-1} \text{K}^{-1}$ at 300 K). We also estimated the hole mobility ($\mu$). Electronic relaxation time is extracted by fitting the calculated $\sigma$ to experimental

Fig. 3. Theoretical analysis of lattice thermal conductivity ($k_{\text{lattice}}$) based on the cluster rattling model. (A) Cumulative $k_{\text{lattice}}$ with respect to mean-free path ($l$) at room temperature computed by a combination of BTE and DFT, with dashed lines illustrating the defect concentrations fitted to the experimental data shown in Fig. 2. (Inset) Phonon dispersion curve of CsSnI$_3$ calculated by DFT, with the band crossing between optical and acoustic modes highlighted by the purple circle. (B and C) Inhomogeneous bonding structures associated with (B) atomic and (C) cluster rattling mechanisms in CsSnI$_3$ and CsPbI$_3$, respectively. The $\delta$-I bonds with length <3.90 Å are shown as sticks, while the others are denoted by dashed lines. The rattling units are highlighted by orange-shaded regions.

Fig. 4. Experimental data of thermoelectric properties in CsSnI$_3$. (A) Temperature-dependent electrical conductivity ($\sigma$, black squares) and Seebeck coefficient ($S$, blue circles) of a single CsSnI$_3$ NW, which is the exact same NW studied in Fig. 2C. The positive sign of $S$ indicates $p$-type behavior, and CsSnI$_3$ exhibits a relatively high electrical conductivity despite its ultralow thermal conductivity. (B) Figure of merit $ZT$ (black dots) and power factor (blue squares) obtained from the exact same single CsSnI$_3$ NW studied in Fig. 2C. Power factor and $ZT$ of as-synthesized CsSnI$_3$ before any attempts at optimization are 186 $\mu$W m$^{-1}$ K$^{-2}$ and 0.11 at 320 K, respectively.
data, and a high hole-mobility value of 394 cm$^2$/V·s at 300 K is obtained from $\sigma = \frac{\mu q n}{m}$ in the low concentration limit, with the carrier concentration estimated by fitting the calculated Seebeck coefficient to the experimental data (theoretical analyses of charge transport in AIHP are discussed in detail in SI Appendix, Figs. S15–S17). We also report the power factor and ZT of as-synthesized CsSnI$_3$ before any attempts at optimization, 186 $\mu$W·cm$^{-1}$·K$^{-2}$ and 0.11 at 320 K, respectively (Fig. 4B and SI Appendix, S5K). We note that electrical conductivity, Seebeck coefficient, and thermal conductivity are measured from the exact same CsSnI$_3$ NW, and these values are used to obtain the power factor and ZT. Data for two other CsSnI$_3$ NWs are presented in SI Appendix, Fig. S8 and the results are consistent.

Our work reveals that single-crystalline AIHP NWs synthesized by facile low-temperature solution processes have ultralow $\kappa_{\text{Lattice}}$, and CsSnI$_3$ uniquely also possesses high electrical conductivity. Ultralow $\kappa_{\text{Lattice}}$ in AIHP calls attention to the vital thermal transport processes and thermal management strategies needed for the viable development of applications such as phononic devices, thermoelectric devices, optoelectronic devices, and electrically conductive thermal barrier coatings. Further, the generality of the cluster rattling mechanism will provide insights to discover other inorganic crystals with ultralow thermal conductivity.

Materials and Methods

Additional details regarding the materials and methods may be found in the SI Appendix.

Synthesis of $\gamma$-CsSnI$_3$ NWs. A saturated solution of CsI (99.999%, anhydrous, beards, Aldrich) in anhydrous methanol (99.8%, Spectrum) is prepared by allowing the solution to stir for at least 1 h. Afterward, clean Si or SiO$_2$ substrates (1 cm$^2$) are heated to 100 °C and are allowed to equilibrate for 10 min. The saturated CsI solution (70 μL) is pipetted dropwise onto the substrates without spilling, and the solution is allowed to completely dry for 30 min. Afterward, the CsI-coated substrates are placed in a 20-mL vial with the carrier concentration estimated by fitting the calculated Seebeck coefficient to the experimental data (theoretical analyses of charge transport in AIHP are discussed in detail in SI Appendix, Figs. S15–S17). We also report the power factor and ZT of as-synthesized CsSnI$_3$ NWs before any attempts at optimization, 186 $\mu$W·cm$^{-1}$·K$^{-2}$ and 0.11 at 320 K, respectively (Fig. 4B and SI Appendix, S5K). We note that electrical conductivity, Seebeck coefficient, and thermal conductivity are measured from the exact same CsSnI$_3$ NW, and these values are used to obtain the power factor and ZT. Data for two other CsSnI$_3$ NWs are presented in SI Appendix, Fig. S8 and the results are consistent.

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Supporting Information for

Ultralow thermal conductivity in all-inorganic halide perovskites

1. Synthesis of the all-inorganic halide perovskite nanowires

1.1. Synthesis of the CsSnI$_3$ Nanowires:

CsSnI$_3$ nanowires were synthesized as shown in Fig. S1, Fig. S2A,B. For this work, the yield of nanowires was optimized, and individual CsSnI$_3$ nanowires were utilized for further characterization. CsSnI$_3$ nanowires were synthesized on clean substrates that were loaded with a layer of CsI and allowed to react in a solution of SnI$_2$ in anhydrous 2-propanol. All reagents were used as received without further purification. A scheme for the general reaction is shown in Fig. S1. As reflected in Fig. S1 and Fig. S2A,B, in addition to the CsSnI$_3$ nanowires, other structures may also grow in solution. To grow CsSnI$_3$ nanowires, Si or SiO$_2$ (1 cm$^2$) substrates are cleaned by sequential sonication in acetone, 2-propanol, and deionized water, which is followed by drying under a stream of nitrogen. Subsequent steps are performed in an argon-filled glove box with an oxygen level of < 0.1 ppm and a H$_2$O level of < 2.0 ppm. A saturated solution of CsI (99.999%, anhydrous beads, Aldrich) in anhydrous methanol (99.8%, Spectrum) is prepared by allowing the solution to stir for at least 1 hour. Afterwards, the clean substrates are heated on a clean hotplate to 100°C and are allowed to equilibrate for 10 minutes. The saturated CsI solution of 70 µL is pipetted dropwise onto the hot substrates, which wets the surface completely, without spilling. For substrates of different size, the volume of the CsI/MeOH must scale appropriately to wet the surface of the substrate without spilling. The substrates are allowed to completely dry for up to 30 minutes on the hotplate. Anhydrous dimethyl sulfoxide (DMSO, >99.9%, Aldrich) also can be used as a substitute for anhydrous methanol for this step. Afterwards, the CsI-coated substrates are placed in a clean 20 mL vial (Kimble, #FS74504-20) with the CsI-coated side facing up. The vial containing the CsI-coated chip is heated to 60°C before the reaction begins.

Separately, a saturated stock solution of SnI$_2$ (99.999%, ultra-dry, Alfa Aesar) in anhydrous 2-propanol (99.5%, Aldrich) is prepared (6.6 mmol/L) by stirring overnight, and the solution is diluted with anhydrous 2-propanol to 4 mmol/L to 0.3 mmol/L. To begin the reaction, 1 mL of SnI$_2$/2-propanol solution is pipetted onto the warm CsI-coated substrates, and the vial is capped and allowed to react for 90 to 120 minutes. To minimize oxygen and moisture contamination of the glove box, any paper inserts on the vial caps are removed prior to the reaction. The substrates darken with the nucleation and growth of CsSnI$_3$ in the SnI$_2$/2-propanol solution.

To stop the reaction, the chip is lifted out of the solution, and the chip is tipped towards the corner. Any excess solution is wiped away with a kimwipe to absorb the growth solution while minimizing the deposition of salts on the chip after evaporation of the growth solution. Optionally, the sample can be quickly washed in anhydrous 2-propanol and dried in the same manner. After synthesis, the sample is stored and transported in a sealed centrifuge tube to minimize air/humidity exposure.
**Figure S1.** Schematic of CsSnI$_3$ solution phase synthesis in anhydrous 2-propanol.

**Figure S2.** Characterization of solution-synthesized CsSnI$_3$ nanowires. (A) Optical microscopy image of as-synthesized CsSnI$_3$ nanowires grown on a Si substrate. (B) SEM image of as-synthesized CsSnI$_3$ nanowires. (C) Powder X-ray diffraction of CsSnI$_3$ sample. The red drop down lines show the fitting to the standard pattern for the room temperature black orthorhombic phase of CsSnI$_3$ with ICSD number: 69996. (D) Single nanowire photoluminescence from a CsSnI$_3$ nanowire showing strong photoluminescence around 1.3 eV, which is indicative of the black phase of CsSnI$_3$.

1.2. Synthesis of the CsPbBr$_3$ Nanowires:

Synthesis of CsPbBr$_3$ nanowires in methanol follows our previously published report (1). This synthesis produces a mixture of nanostructures from which nanowires were isolated. Unless
otherwise stated, all of the chemicals were purchased from Sigma-Aldrich and used as received. To prepare the substrate, a 1×1 cm² cut glass was washed sequentially with acetone, deionized water, and 2-propanol. Clean glass substrates were O₂ plasma treated for 10 min, and then they were spin coated with PEDOT:PSS (Solarmer) at 3000 rpm for 30 s. Afterwards, the coated substrates were annealed at 150°C for 15 min before being transported into a glove box.

PbI₂ (99.999%, Aldrich) was dissolved in 1 mL of anhydrous dimethylformide (DMF, Aldrich), stirred at 70°C overnight before further use. The PbI₂ solution was spun onto the PEDOT:PSS-coated glass substrates at 1000 rpm for 120s, and they were annealed at 100°C for 15 min. The PbI₂ film was carefully dipped into a glass vial containing 2 mL of 8 mg/mL CsBr (99.999%, Aldrich) in methanol (anhydrous, 99.8%, Spectrum), with the PbI₂ side facing up. The reaction was carried out at 50°C for 12 hrs with the glass vial capped tightly, and then the substrate was taken out to wash in anhydrous 2-propanol for 30 s. The sample was then dried by heating at 50°C for 5 min. This whole process was carried out in a glovebox filled with N₂.

1.3. Synthesis of the CsPbI₃ Nanowires:

Synthesis of CsPbI₃ nanowires in colloidal solution follows our previously published report (2). Cs-oleate solutions were prepared via a reported approach developed by Protesescu et al (3). Briefly, 0.2 g Cs₂CO₃ (99.9%, Aldrich) and 0.6 mL oleic acid (OA, 90%, Aldrich) were loaded into a 3-neck flask along with 7.5 mL octadecene (ODE, 90%, Aldrich). This mixture was degassed and dried under vacuum at 120°C for 20 min, and it was heated under Ar to 150°C until all Cs₂CO₃ reacted with OA. All of the temperatures mentioned in this section refer to the temperature of the oil bath or the salt bath.

7 mL ODE and 0.18 mmol PbI₂ (99%, Aldrich) were loaded into a 3-neck flask and degassed under vacuum for 20 min at 120°C. 0.5 mL oleylamine (OAm, 70%, Aldrich) and 0.5 mL OA were injected at 120°C under Ar. After the temperature was raised to 150°C, the solution was heated for 20 min until the complete dissolution of the PbI₂ salt was observed. Afterwards, the flask was transferred to a salt bath with temperature set to 250°C, and 0.7 mL of as-prepared Cs-oleate solution was injected. After 5 - 10 mins, the reaction mixture was cooled by pouring the solution into a glass bottle cooled by an ice-water bath. The nanowires were isolated by centrifugation at 6000 rpm for 5 mins and washed once with hexane (99.9%, Fisher Scientific). The obtained precipitated nanowires were re-dispersed in hexane for further use.

2. Characterization of the all inorganic halide perovskite nanowires:

2.1. X-ray diffraction

XRD of CsSnI₃ was acquired using a Bruker AXS D8 Advance diffractometer, which used Co Kα radiation with a wavelength of 1.79026 Å. To prepare the sample for XRD, a drop of PMMA (C4, MicroChem) was deposited and baked onto a CsSnI₃ sample grown on clean glass to improve the stability of the sample for XRD measurements in ambient air.

2.2. Scanning Electron Microscopy

SEM images of as-synthesized CsPbI₃, CsPbBr₃, CsSnI₃ nanowires and nanostructures were taken using a JEOL JSM-6340F field emission scanning electron microscope. A Zeiss 1540 EsB instrument was used to take SEM images of single-nanowire devices and to perform electron beam induced deposition (EBID) of Pt-C.
2.3. Transmission Electron Microscopy

HRTEM and SAED of CsSnI$_3$, CsPbBr$_3$, and CsPbI$_3$ were collected on a FEI Titan microscope operated at 300 kV at the National Center for Electron Microscopy. The accelerating voltage of 300 kV was chosen to maximize contrast of the image through the relatively thick nanowires. As these samples were particularly beam sensitive, the electron dose was carefully controlled and was minimized to below 6000 to 200 e/Å$^2$ s, depending on the nanowire. In all cases, the beam exposure of the nanowire was minimized before the HRTEM image was acquired.

2.4. Photoluminescence

Photoluminescence of CsSnI$_3$ single nanowires was measured using a focused 325 nm excitation from a HeCd laser with emission collected on a Nikon A1 microscope coupled to a multimode fiber. The spectra were acquired using a liquid-nitrogen-cooled InGaAs CCD (PI Acton).

2.5. Preparation of all-inorganic perovskite nanowires on devices

All-inorganic perovskite nanowires are manipulated onto suspended devices using a micromanipulator. Then, Pt-C is deposited to improve thermal and electrical contact between the nanowire and the Pt electrodes on the suspended devices. CsSnI$_3$ is air-sensitive, and upon air-exposure black phase CsSnI$_3$ slowly changes to yellow phase CsSnI$_3$, consistent with previous reports (4). Therefore, it requires special attention to prepare CsSnI$_3$ nanowires on suspended devices. To maintain the black-phase of CsSnI$_3$, we manipulate NWs to the suspended devices inside a chamber that is continuously purged with dry nitrogen gas. In addition, we keep the suspended devices inside a portable container filled with dry nitrogen to minimize air exposure when we transferred the devices between the EBID tool and the experimental setup.

3. Discussion of the synthesis and characterization of the CsSnI$_3$ nanowires

Synthesis of lead-free halide perovskites is a potentially important area for the development of halide perovskites for applications such as in optoelectronic and energy conversion devices. This work describes the first synthesis of CsSnI$_3$ nanowires on solid substrates as shown in Fig. S1 and Fig. S2A,B.

Overall, it has proven non-trivial to synthesize the black phase of CsSnI$_3$ in solution with the product typically being the yellow CsSnI$_3$ polymorph, which consists of double chains of $[\text{Sn}_2\text{I}_6^{2-}]$. Recently, it has been demonstrated that it is possible to synthesize CsSnI$_3$ nanocubes in the presence of a trioctylphosphine reducing agent in colloidal solution. (5) In our synthesis of CsSnI$_3$ nanowires, it is interesting to note that in a well-maintained glove box atmosphere with high purity reagents, a reducing agent is not necessary to obtain the black orthorhombic phase of CsSnI$_3$. Following previous reports on thin films, we note that reagent purity is important for obtaining the black orthorhombic phase of CsSnI$_3$. (6)

A SEM image of the CsSnI$_3$ nanowires shows that the nanowires are faceted with a typical rectangular cross section (Fig. S2B). The bulk film and the single nanowires can be indexed to the black orthorhombic phase of CsSnI$_3$ (ICSD Number: 69996) by powder X-ray diffraction and selected area electron diffraction, respectively (Fig. S2C, S3F). The CsSnI$_3$ nanowires are found to be single crystalline as are the CsPbI$_3$ and CsPbBr$_3$ nanowires as shown in Figure S3.
In addition, a representative photoluminescence spectrum from a single CsSnI$_3$ nanowire is shown in Fig. S2D. Single nanowires of CsSnI$_3$ only display IR light emission centered around 950 nm without any visible light emission, this also confirms that the individual nanowires are in the black orthorhombic phase of CsSnI$_3$ (4) as opposed to the yellow double chain phase of CsSnI$_3$, which will exhibit photoluminescence in the visible range.

For this reaction, a film of CsI and a solution of SnI$_2$ in 2-propanol serve as the precursors for the reaction to grow nanostructures on the substrate that is submerged in the anhydrous 2-propanol solution. Previous reports for the synthesis of CH$_3$NH$_3$PbX$_3$ (X=Cl, Br, I) mixed nanowires, nanosheets, and nanocubes demonstrate the reaction of a lead acetate or lead iodide film on a substrate with a solution of CH$_3$NH$_3$X in 2-propanol. (7, 8) For these reactions, the Pb precursor is deposited on the substrate, and the Pb$^{2+}$ cation occupies the B site in the ABX$_3$ perovskite structure. Interestingly, for the growth of CsSnI$_3$, the precursor for the A site cation, which is CsI, should be loaded onto the substrate first to produce well-faceted black phase CsSnI$_3$ nanowires. Another difference is that although the reaction to grow CH$_3$NH$_3$PbX$_3$ nanowires can be performed in air, the reaction to synthesize CsSnI$_3$ requires air-free conditions, which requires a N$_2$ or Ar glove box. The reactions to grow CH$_3$NH$_3$PbX$_3$ nanowires are believed to occur via both a liquid-solid interfacial reaction and a dissolution-recrystallization mechanism, which yields the growth of faceted nanostructures via the existence of a low and controllable supersaturation of precursors from the continued dissolution of the underlying film. We believe that CsSnI$_3$ may crystalize via a similar mechanism. As shown in Fig. S4, when the concentration of SnI$_2$ is too high, the products are a mixture of many large and small cuboids with very few high aspect ratio products. Furthermore, when the concentration is too low, the majority of the products are relatively large with relatively low aspect ratio. This trend suggests that at high concentrations there is too much rapid nucleation and growth of CsSnI$_3$ particles, and at low concentrations, fewer CsSnI$_3$ particles nucleate, but these particles will eventually grow to a relatively large size with poor control over the aspect ratio. Overall, intermediate concentrations of SnI$_2$ in 2-propanol are best for the synthesis of CsSnI$_3$ nanowires.
Figure S3. TEM and corresponding SAED of perovskite nanowires. (A-C) TEM image of a CsPbI₃, CsPbBr₃, and CsSnI₃ nanowire, respectively. (D-F) Corresponding SAED image of the above nanowires. In all cases, the nanowires are single-crystalline. After performing SAED on multiple nanowires, the typical growth directions observed are [010], [110], and [110] for CsPbI₃, CsPbBr₃, and CsSnI₃, respectively.
Figure S4. Effect of SnI$_2$ concentration on morphology of CsSnI$_3$. (A) 6.6 mmol/L SnI$_2$. (B) 3.3 mmol/L SnI$_2$. (C) 1.7 mmol/L SnI$_2$. (D) 1.1 mmol/L SnI$_2$. (E) 0.83 mmol/L SnI$_2$. (F) 0.66 mmol/L SnI$_2$. For all substrates, the reaction time was 120 minutes. All scale bars are 5 µm.

4. Discussion of the crystal structure of CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$ pertaining to this work

The halide perovskite class of materials consists of a 3D ABX$_3$ structure that is similar to BaTiO$_3$ with a variety of cations such as (CH$_3$NH$_3^+$, CH(NH$_2$)$_2^+$, Cs$^+$, etc.) and (Pb$^{2+}$, Sn$^{2+}$, etc.) occupying the A and B sites, respectively. In this work, we are focused on the all-inorganic perovskite compositions of CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$. The orange orthorhombic phase of CsPbBr$_3$ and black orthorhombic phase of CsSnI$_3$ possess a 3D network of PbBr$_6$ and SnI$_6$ octahedra, respectively. In addition, the high temperature phase of CsPbI$_3$ also possesses a 3D network of PbI$_6$ octahedra. In the case of as-synthesized room temperature orthorhombic CsPbI$_3$, the Pb-I network is arranged as double chains with quasi-1D connectivity. As discussed in the main text, we consider the room temperature CsPbI$_3$ double chain phase to be a perovskite-related phase given its similar composition and its transition to the high temperature CsPbI$_3$ perovskite upon heating. Consequently, we consider the thermal transport properties of CsPbI$_3$ along with CsPbBr$_3$ and CsSnI$_3$ in our study of the thermal properties of the all-inorganic perovskites.

To facilitate the direct comparison of the orthorhombic phase of CsPbBr$_3$ to the black orthorhombic CsSnI$_3$ phase, the direction of the unit cell and description of the space group should be matched between these two different phases. To accomplish this, we transformed the unit cell of CsPbBr$_3$ and CsSnI$_3$ into Pbnm in order to facilitate direct comparison. This description of the space group is used for the theoretical and structural descriptions involving the directions within these crystals. The lattice constants of the materials are tabulated in Table S2. The typical growth directions of CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$ nanowires are found to be [010], [110], and [110] respectively as shown by SAED in Figure S3.
5. Validation of the experimental setup: control experiment with amorphous SiO$_2$ NW (a-SiO$_2$ NW) and comparison between measured thermal conductance and noise equivalent conductance (NEG)

In order to validate our thermal conductivity experimental results, we performed a control experiment on amorphous SiO$_2$ NWs that are known to have low thermal conductivity (9). We first converted Si NWs grown by the vapor-liquid-solid (VLS) method to amorphous SiO$_2$ (a-SiO$_2$) NWs by dry oxidation at 1000 °C for ~4 hours. As shown in Fig. S5A, conversion to a-SiO$_2$ is confirmed by HRTEM. We manipulated single a-SiO$_2$ NWs onto suspended thermal devices followed by Pt-C electron beam induced deposition (EBID) to improve thermal contacts between a-SiO$_2$ and membranes. The measured thermal conductivity of a-SiO$_2$ NWs with diameters 104 and 312 nm is in very good agreement with the thermal conductivity of bulk a-SiO$_2$ (Fig. S5B). Thermal conductivity reduction due to a decreased characteristic length scale, such as a decreased diameter in this case, is not expected since the nanowires are amorphous. Therefore, it clearly demonstrates that our experimental setups are valid and accurate.

One could argue that thermal conductivity measurements of a-SiO$_2$ NW alone are not fully supportive of the validity of the experimental setup because the thermal conductivity of inorganic perovskite NWs is smaller than that of a-SiO$_2$ NW. To provide additional validation, we estimated the noise equivalent conductance (NEG) of suspended devices and compared it with measured thermal conductance of AIHP NWs and a-SiO$_2$ NWs. We followed the procedure described in our earlier work (10) and estimated the minimum thermal conductance one can measure, which is set by the NEG. As seen in Fig. S5C, the measured thermal conductance of an a-SiO$_2$ NW and a CsPbI$_3$ NW is at least five times larger than NEG. To make a conservative comparison, we specifically chose the AIHP NW that has the lowest thermal conductance, which is CsPbI$_3$ with a 134 nm diameter. Other inorganic perovskite NWs studied here have larger thermal conductance, thus it clearly demonstrates that the experimental results are in measurable range and accurate.

![Figure S5](Figure S5. Validation of thermal conductivity experiment: control experiment with amorphous SiO$_2$ (a-SiO$_2$) nanowires and comparison between measured thermal conductance and estimated noise equivalent conductance (NEG) (A) a-SiO$_2$ NW is confirmed by HRTEM. (B) Thermal conductivity of a-SiO$_2$ NWs with diameters 104 and 312 nm agrees very well with bulk a-SiO$_2$, proving that our experimental setups are firmly valid. (C) Measured thermal conductance of an a-SiO$_2$ NW and a CsPbI$_3$ NW is sufficiently larger than estimated NEG.)
6. Characterizations of thermal contact resistance

When measuring thermal conductivity using suspended devices, one must consider thermal contact resistances between NWs and membranes. Experimentally measured thermal resistance (R) is the summation of the intrinsic thermal resistance of the nanowires ($R_{nw}$) and the thermal contact resistance of the two interfaces between nanowire and Pt electrode ($R_c$) as $R = R_{nw} + R_c$. In order to quantify the thermal contact resistance, we have measured the length-dependent thermal resistance of CsSnI$_3$ nanowires. Since the cross-sectional geometry is rectangular as seen in Fig. II, we followed the method (11), where thermal contact resistance ($R_c$) multiplied by the cross-sectional area (A) is plotted against the length of nanowire (Fig. S6). Based on the dimensions of the nanowires and the y-intercept, we can extract the thermal contact resistance. Estimated thermal contact resistance ranges from $0.5 \times 10^6$ to $3 \times 10^6$ K/W. These values are similar to previous measurements on other nanowires such as ZnO ($R_c \sim 1 \times 10^6$ K/W) and carbon nanofibers ($R_c \sim 5 \times 10^6$ K/W) (12, 13). In addition, the estimated thermal contact resistance is only up to ~3% of the intrinsic thermal resistance of the perovskite NWs. To obtain accurate thermal conductivity, we subtracted the estimated thermal contact resistances from the measured total resistances.

![Figure S6. Characterization of the thermal contact resistances of the two interfaces between CsSnI$_3$ nanowire and Pt electrode. Measured total thermal resistances multiplied by the cross-sectional area of nanowires are plotted against the lengths of the nanowires. From the y-intercept of $0.21 \times 10^{-6}$ K·m$^2$·W$^{-1}$, we estimate the thermal contact resistance to range from $0.5 \times 10^6$ to $3 \times 10^6$ K/W, and the contribution of thermal contact resistance is only up to ~3% of the intrinsic thermal resistance of the AIHP NWs.](image-url)
7. Measurement of electrical conductivity ($\sigma$) and Seebeck coefficient ($S$)

We describe in this section how we measured the electrical conductivity and Seebeck coefficient of black phase CsSnI$_3$ using suspended devices. We measured four-probe resistance ($R$) to eliminate electrical contact resistances and obtained the electrical conductivity at various temperatures, which is $\sigma = L / (R \cdot A)$ where $L$ is the length and $A$ is the cross-sectional area of the NW (Fig. S7A). We used a current source (Keithley 6221) to supply the current through the outer electrodes and measured the voltage across inner electrodes using a nanovoltmeter (Keithley 2182). In order to obtain the Seebeck coefficient, the temperature differential ($\Delta T$) across individual NWs is created by applying Joule-heating into one of two membranes. Open-circuit voltages ($\Delta V$) are subsequently measured with the nanovoltmeter (Keithley 2182) at several $\Delta T$ points (Fig. S7B). Since Seebeck coefficient is given by $S = -\Delta V / \Delta T$, the Seebeck coefficient can be readily calculated. We note that the Seebeck coefficient reported in this work is relative to the Seebeck coefficient of 50 nm Pt.

We also measured the electrical resistances of CsPbI$_3$ and CsPbBr$_3$ NWs. The measured current with the two-probe method at 1V is less than 1 pA, which results in resistance values larger than 1 T$\Omega$. Resistivity is estimated to be larger than 0.1 G$\Omega$·cm. Our experimental results are consistent with previous studies in which the resistivity of CsPbBr$_3$ is reported to be 1 ~ 343 G$\Omega$·cm (14).

![Figure S7. Experimental details of four-probe electrical measurement and Seebeck coefficient measurement. Measured I-V (A) and V-\Delta T (B) of a black phase CsSnI$_3$ single nanowire at various temperatures.](image)

8. Experimental data of other single nanowires

In the main text, we showed data for the thermal conductivity of representative CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$ nanowires. In this section, we present thermal conductivity of other single nanowires to show that other single perovskite nanowires exhibit consistent thermal conductivity values (Fig. S8A,B). Based on calculated mean free paths (Fig. S13), the perovskite nanowires in this study are not expected to display diameter dependent thermal conductivity. This is also confirmed in our experimental results over the diameter range of the nanowires studied in this study.
work. We also show electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) data for three individual CsSnI$_3$ nanowires (Fig. S8C). Finally, we obtain the power factor ($S^2\sigma$) and calculated figure of merit ZT ($S^2\sigma T/k_{\text{total}}$) of each CsSnI$_3$ nanowire (Fig. S8D). We note that ZT and power factor are obtained from the transport properties on the exact same individual CsSnI$_3$ nanowire in each case. For the best CsSnI$_3$ nanowire, the calculated ZT is 0.11 at 320 K. As the thermal conductivity of CsSnI$_3$ is ultralow, it is very likely that the ZT can be further optimized by controlling carrier concentration and by alloying with other compositions.

**Figure S8.** Experimental transport properties of single nanowires of CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$. (A) Consistent thermal conductivity results are confirmed from several single nanowires of CsPbI$_3$ and CsPbBr$_3$. (B) Total thermal conductivity ($k_{\text{total}}$), lattice thermal conductivity ($k_{\text{lattice}}$), and electronic thermal conductivity ($k_{\text{el}}$) of various single CsSnI$_3$ nanowires. Electronic thermal conductivity is estimated by the measured four-probe electrical conductivity and the Wiedemann-Franz law with Lorenz number $2.44 \times 10^{-8}$ W Ω K$^{-2}$. Lattice thermal conductivity is obtained by subtracting electronic thermal conductivity from total thermal conductivity. Thermal conductivity results of CsSnI$_3$ are consistent among individual nanowires. (C) Four-probe electrical conductivity ($\sigma$) (black, filled) and Seebeck coefficient ($S$) (blue, empty) of single CsSnI$_3$ nanowires. (D) Figure-of-merit (ZT) (black, filled) and power factor ($S^2\sigma$) (blue, empty) for single CsSnI$_3$ nanowires.
9. Theoretical Analysis of Phonon and Charge Transport

9.1. Computational Methodology

The phonon contribution to thermal conductivity \( k_{\text{lattice}} \) of the bulk CsSnI\(_3\), CsPbI\(_3\) and CsPbBr\(_3\) crystals were calculated by solving the Boltzmann transport equation (BTE) iteratively, as implemented in the ShengBTE package (v1.0.2) \(^{(15)}\), with the second and third order interatomic force constants (IFCs) obtained by ab-initio simulations within the framework of density functional theory (DFT) using the Vienna Ab Initio Simulation Package (VASP, v5.3) \(^{(16)}\).

In the linear region, \( k_{\text{lattice}} \) is defined by the relationship

\[
J^\alpha = - \sum_\beta k_{\text{lattice}}^{\alpha\beta} (\nabla T)^\beta \cdot \vec{j}
\]

\[
\vec{j} = \sum_\beta \int f_\lambda \hbar \omega_\lambda \vec{v}_\lambda \frac{d\vec{q}}{(2\pi)^3}
\]

where \( \vec{j} \) is the heat current, \( J^\alpha \) is the heat current along the \( \alpha \) direction, \( T \) is the temperature, \( \lambda \) is a comprised index of phonon branch \( p \) and wave vector \( \vec{q} \), and \( \vec{v}_\lambda \) and \( \omega_\lambda \) are the group velocity and frequency of phonon mode \( \lambda \). The phonon distribution function \( f_\lambda \) can be expanded to first order in \( \nabla T \) \(^{(15)}\),

\[
f_\lambda = f_0(\omega_\lambda) - \vec{F}_\lambda \cdot \nabla T \frac{df_0}{dT}
\]

Then the linearized BTE is written as

\[
\vec{F}_\lambda = \tau_0^\lambda (\vec{v}_\lambda + \vec{\Delta}_\lambda)
\]

Here \( \tau_0^\lambda \) is the relaxation time of mode \( \lambda \) as obtained within the relaxation time approximation (RTA). \( \vec{F}_\lambda \) is the vector phonon mean free path, and \( \vec{\Delta}_\lambda \) is the correction term from the RTA. In a perfect infinite crystal, the only scattering source is the three-phonon processes, which leads to

\[
\frac{1}{\tau_\lambda^0} = \frac{1}{N} \left( \sum_{\alpha'\alpha''}^+ \Gamma_{\alpha'\alpha''}^{\lambda'\lambda''} + \sum_{\alpha'\alpha''}^- \Gamma_{\alpha'\alpha''}^{\lambda'\lambda''} \right)
\]

\[
\vec{\Delta}_\lambda = \frac{1}{N} \sum_{\alpha'\alpha''}^+ \Gamma_{\alpha'\alpha''}^{\lambda'\lambda''} \left( \xi_{\alpha'\alpha''} \vec{F}_{\alpha''} - \xi_{\alpha'\alpha''} \vec{F}_{\alpha'} \right) + \frac{1}{N} \sum_{\alpha'\alpha''}^- \Gamma_{\alpha'\alpha''}^{\lambda'\lambda''} \left( \xi_{\alpha'\alpha''} \vec{F}_{\alpha''} + \xi_{\alpha'\alpha''} \vec{F}_{\alpha'} \right)
\]

where \( \xi_{\alpha'\alpha''} = \omega_{\alpha'} / \omega_{\alpha''} \). The \( \Gamma_{\alpha'\alpha''}^{\lambda'\lambda''} \) and \( \Gamma_{\alpha'\alpha''}^{-\lambda'\lambda''} \) are the three-phonon scattering rate associated with the absorption and emission processes, and \( N \) is the number of sampling points within the Brillouin zone. The + and – notations are associated with the phonon absorption and emission processes respectively. Then the scalar mean free path \( \Lambda_\lambda \) for each mode can be expressed as

\[
\Lambda_\lambda = \frac{\vec{F}_\lambda \cdot \vec{v}_\lambda}{|\vec{v}_\lambda|}
\]
At room temperature, the approximation of nanowires by bulk crystals is justified by the fact that $\Lambda_\lambda$ is much smaller than the defect spacing, while the defect spacing is much smaller than the diameters of the nanowires. However, at low temperature, both defect and boundary scatterings play important roles as their characteristic lengths become comparable to $\Lambda_\lambda$. Precisely accounting for the impact of vacancy defects and nanowire boundary requires the introduction of complicated terms in the expressions of $F_\lambda$, $\tau_\lambda^0$, and $A_\lambda$, which is beyond the scope of this study. Instead, we applied two methods to qualitatively illustrate their effects.

In the first approach, which provides the data for Fig. 2 in the main text, we assumed that the phonons with moderate wavelengths are completely suppressed by vacancy scattering, while phonons with long wavelengths are eliminated by boundary effects. The defect concentration ($n_v$) is treated as a fitting parameter to match the curve of the $T$-dependent $k_{\text{lattice}}$ measured experimentally. The length ($l_\nu$) corresponding to $n_v$ was then used as the cutoff for accumulating the contributions from phonons with increasing $\lambda$,

$$k_{\text{lattice}} = \sum_{\lambda < l_\nu} k_{\text{lattice}, \lambda}, \quad (l_\nu = n_v^{-1/3})$$

In the second approach, we tried to adjust the relaxation time by empirical formulas assuming that the intrinsic defects are homogeneously distributed vacancies,

$$\frac{1}{\tau_{\lambda}^{\nu r}} = \frac{1}{\tau_{\lambda}^{\nu}} + \frac{1}{\tau_{\lambda}^{\nu v}} + \frac{1}{\tau_{\lambda}^{\nu b}}$$

where the vacancy scattering is described by (17)

$$\frac{1}{\tau_{\lambda}^{\nu v}} = n_v \left(\frac{\Delta M}{M}\right)^2 \frac{\pi \omega^2 g(\omega)}{2G}$$

with $\Delta M / M = 3$. Here, $\omega$ and $g(\omega)$ are the phonon frequency and density of states (DOS), and $G$ is the number of atoms in the crystal. The relaxation time associated with the boundary effect is written as (18)

$$\frac{1}{\tau_{\lambda}^{\nu b}} = \frac{|\vec{v}_{\lambda}|}{D} (1 - p)$$

where $D$ is the diameter of nanowire, and $p$ is a parameter in the range of [0,1] depending on the specific surface.

While these empirical formulas have been shown to work quite well within the RTA framework for considering low frequency phonons, combining them with the method used in this study induces serious numerical problems because the intensive fluctuation of phonon velocity, DOS, and scattering rate requires the descriptions of defect and boundary scatterings to be treated with sufficient accuracy as that of anharmonic effects. Despite such a limitation, the second approach enables us to qualitatively examine the assumptions adopted in the first approach.

For the DFT calculations, plane-wave and projector-augmented-wave (PAW) type pseudopotentials (19) with kinetic-energy cutoffs of up to 400 eV were applied, with the PBESol (20) exchange-correlation functional as implemented in the VASP package (v5.3) (16). An energy convergence criterion of $10^{-8}$ eV was used, and the structures were relaxed until all forces are smaller than 0.001 eV/Å. 4x4x4 and 4x8x2 Gamma k-point grids were used for crystals in $\gamma$ and
δ phases, respectively. The second-order IFC, phonon dispersion relation, and phonon eigenvector were obtained by the finite displacement method (FDM) employing the Phonopy package (v1.10.0) (21). 2×2×2 and 2×4×1 supercells were used for γ and δ phases, with a 2×2×2 k-point mesh. Non-analytical term correction was applied to account for polarization effects, with the effective Born charge obtained by the density functional perturbation theory (DFPT). The Debye temperature ($T_D$) was associated with the highest frequency of phonon modes. The third-order IFC, $\Lambda_\lambda$, and $k_{\text{lattice}}$ were calculated by the ShengBTE package (15). Only the three-phonon interactions between atoms spaced less 0.7 nm were included. 6×6×6 and 6×8×3 q-point grids were used for γ and δ phases, respectively.

The electronic structures of bulk CsSnI$_3$, CsPbI$_3$ and CsPbBr$_3$ crystals were computed by standard DFT including spin-orbit coupling (SOC) with 8×8×6 and 8×16×3 Gamma centered k-point grids for γ and δ phases, and a 300 eV kinetic-energy cutoff. Since CsSnI$_3$ exhibits p-type character in experiments, and the valence band structure near the band edge is barely affected by the SOC, we recalculated its band structure without SOC but using a very dense k-point grid of 20×20×16. The transport coefficients were then calculated by semi-classical Boltzmann theory with the RTA using the BoltzTraP package (v1.2.5) (22). The hole concentration ($n_h$) was determined by fitting the computed $T$-dependent Seebeck coefficient ($S$) to the experimental values. Similarly, the $T$-dependent relaxation time ($\tau_h$) was obtained by fitting the calculated electrical conductivity ($\sigma_h$) to the experimental data. The electrical thermal conductivity ($\kappa_e$) and power factor ($S^2\sigma$) were then computed with these $\tau_h$ and $\sigma_h$. Finally, the influence of Sn vacancy on the electronic structure was studied using a 2×2×2 supercell containing one defect.

9.2. Phonon Dispersion Relation

The lattice constants obtained by our simulation are consistent with the values measured on bulk crystals (Table S2), with the deviations caused by the inaccuracy of the PBEsol exchange-correlation functional for describing interactions between weakly bonded atoms. To confirm that these small differences only affect the phonon properties slightly, we calculated the phonon dispersion curve of a similar material, the PbI$_2$ layered crystal, and the results are in good agreement with previous experiments (23).

The similarity between the phonon dispersion curve of γ-CsSnI$_3$ and that of γ-CsPbBr$_3$ as well as their differences from that of δ-CsPbI$_3$ suggest that the dispersion relation depends on the crystal phase while it is relatively insensitive to the components (Fig. S9). The discontinuities near the Γ point are due to the variation of the dynamical matrix in the presence of a macroscopic electric field induced by polarization of collective ionic motions. All phonon modes are in the low frequency range, with the Debye temperatures of 168.9, 224.8, and 189.8 K for CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$, respectively. The plots of phonon partial density of states (PDOS) reveal that for the δ phase the acoustic modes are related to the vibrations within the Pb-I bonding network, while for γ phase the Cs atoms also contribute to the acoustic modes (Fig. S10).

In general, lattice thermal conductivity is determined by three factors: heat capacity ($C_v$), group velocity ($v_\lambda$), and phonon mean free path ($\Lambda_\lambda$). The $C_v$ of our three types of crystals are similar to each other, and they all increase sharply in the low temperature range and then approach the value of $3k_B$ per atom at around 100 K (Fig. S10). The group velocities of acoustic modes are very small and slightly anisotropic in all cases (Table S3). The crossings between acoustic and
optical modes are observed in all directions (Fig. S9), which reveals strong scattering effects that reduce $\Lambda_{3}$ substantially.

**Figure S9.** Calculated phonon dispersion relation of bulk (A) CsPbI$_3$, (B) CsPbBr$_3$, and (C) CsSnI$_3$ crystals.
Figure S10. Calculated phonon PDOS and heat capacity of bulk (A,B) CsPbI₃, (C,D) CsPbBr₃, and (E,F) CsSnI₃ crystals.
9.3. Cluster Rattling Modes

The inhomogeneity of connectivity or/and bond length imposed by crystal symmetry may generate clusters that are loosely bound to their neighbors, and thus stimulate the “cluster rattling” mechanism that reduces $k_{\text{lattice}}$ significantly. In order to verify this hypothesis, we probed the eigenvectors of optical modes in CsPbI$_3$ and CsSnI$_3$ (Fig. S11). For CsPbI$_3$, the broad bond length distribution enables the identification of two main rattling clusters (Fig. S11A). The two phonon modes with lowest frequencies (Fig. S11C,D) correspond to the collective motions of Pb-I 1D clusters (as illustrated by the ellipse in Fig. S11A), while the third mode (Fig. S11E) is associated with the rattling of Cs-I 2D rippled planes (as illustrated by the rectangle in Fig. S11A). For CsSnI$_3$, each Cs atom can be considered as a 0D “cluster”, resulting from the weak bonding between the Cs atom and its surrounding cage. In addition, the 44% larger lattice constant along the c direction compared to that along the a or b directions leads to relatively strong coupling inside the a-b plane and weak coupling along the c direction. Consequentially, each layer perpendicular to the c axis forms a 2D rattling cluster. In particular, the mode with lowest frequency (Fig. S11F) comprises two collective motions: rattling of the individual Cs atoms and that of the Sn-I planes (Fig. S11B). The modes with the second and third lowest frequencies (Fig. S11G,H) are dominated by the vibrations of Cs atoms and that of Cs-I plane, respectively (Fig. S11B).
Figure S11. Structures of rattling clusters (highlighted by orange circles and rectangles) in (A) CsPbI$_3$ and (B) CsSnI$_3$ crystals. Cs: green, I: purple, Pb: gray, Sn: light purple. Eigenvectors of optical modes for (C-E) CsPbI$_3$ and (F-H) CsSnI$_3$. The lengths of the arrows are in arbitrary units.

9.4. Temperature Dependent Lattice Thermal Conductivity

The measured $k_{lattice}$ of all types of all-inorganic halide perovskite nanowires exhibit similar crystal-like temperature dependence where $k_{lattice}$ first increases then decreases with increasing temperature. This trend reflects the distinct scattering mechanisms at different temperature ranges: in the low temperature range, both boundary and defect scattering play important roles; in the medium temperature range, defect and phonon-phonon scattering become dominant because of the
increased phonon population and decreased $\Lambda_\lambda$; in the high temperature range, $k_{lattice}$ is solely suppressed by phonon-phonon scattering as $\Lambda_\lambda$ is much smaller than the characteristic lengths of both defect and boundary. When the first approach (with $\Lambda_\lambda$ cutoff) was applied to consider the impacts of defect and boundary, the calculated $k_{lattice}$ could match the shape of the experimental data by tuning the defect densities (Fig. S12A-D). As expected, the calculated $k_{lattice}$ is sensitive to the defect densities in the low temperature range, while its deviation from pristine crystal becomes negligible in the high temperature range. When the second approach (with empirical formulas) was employed, the general trend of $k_{lattice}$ reduction caused by both defect and boundary scatterings is consistent with that obtained by the first approach, although many unrealistic spikes appear due to the inaccuracy of the method (Fig. S12E-F). Moreover, the boundary effect is insensitive to the diameter of nanowire in the range of 50-300 nm (Fig. S12F), which agrees with experimental observations.

In all cases, the calculated $k_{lattice}$ exhibits significant anisotropy as a consequence of the specific crystal symmetry (Fig. S13). This effect is particularly strong in CsPbI$_3$ due to the continuous Pb-I bonding network along the [010] direction compared to the discontinuous connectivity in other directions. With increasing temperature, the phonon-phonon scattering is intensified, leading to a sharp decrease of $\Lambda_\lambda$ (Fig. S13). At room temperature, the maximum $\Lambda_\lambda$ of CsSnI$_3$ and CsPbBr$_3$ are extremely short compared to widely used crystalized and disordered materials, while the relatively longer $\Lambda_\lambda$ of CsPbI$_3$ can be explained by the larger sizes of the rattling clusters. Such short $\Lambda_\lambda$ values originate from the strong phonon-phonon interactions over the entire frequency range and the entire Brillouin zone, rather than being limited by the energy resonance condition met only around the band crossing points, which can be clearly seen from the phonon scattering rates distribution (Fig. S14).
Figure S12. Temperature dependent thermal conductivity of (A) CsPbI₃, (B) CsPbBr₃, and (C-F) CsSnI₃. The lines present the $k_{\text{lattice}}$ with various (A-E) defect concentrations (in unit of cm⁻³) and (F) nanowire diameters (in unit of nm), calculated by (A-D) the first and (E-F) the second approach along the direction measured in experiments. The experimental data of total thermal conductivity is shown by the dots, with its contribution from phonon illustrated by crosses.
Figure S13. Computed cumulative $k_{lattice}$ with respect to phonon mean free path in various directions of (A-C) CsPbI$_3$, (D-F) CsPbBr$_3$, and (G-I) CsSnI$_3$ crystals, at temperatures of (A, D, G) 10 K, (B, E, H) 50 K, and (C, F, I) 300 K. The dotted, dashed-dotted and dashed lines illustrate the defect densities shown in the Fig. S12A-C. The cumulative $k_{lattice}$ includes the contributions from the phonons with $\Lambda_\lambda$ up to the maximum MFP.
Figure S14. Phonon scattering rates for (A,B) CsPbI$_3$, (C,D) CsPbBr$_3$, and (E,F) CsSnI$_3$ crystals at 50 K (in green) and 300 K (in blue). All bands are included in the panels (A, C, E), while only the acoustic bands are contained in the panels (B, D, F).

9.5. Electrical Transport Properties

The superior electrical conductivity in CsSnI$_3$ NW compared to insulating CsPbI$_3$ and CsPbBr$_3$ NWs can be understood by their different electronic structures and doping densities. According to our simulations, all our pristine crystals are semiconductors, with the δ phase presenting a flat band structure, while the γ phase exhibits substantial dispersion (Fig. S15). An advantage of CsSnI$_3$ revealed by our calculations is that the dominant intrinsic defect type (Sn vacancies) can lower the Fermi level efficiently, but it affects the band structure only slightly and preserves wavefunction delocalization even at very high carrier concentration. This scenario is consistent with the measured p-type transport behavior, as well as the small deviation from the Wiedemann–Franz law that implies a high DOS around the Fermi level (Fig. S16).

The electrical transport properties of the nanowires depend not only on the electronic structure of the corresponding pristine crystals, but also on the type and concentration of intrinsic defects.
The flat band structure of CsPbI$_3$ in $\delta$ phase obtained by our simulation may explain the negligible electrical conductivity measured experimentally. By contrast, large slopes are observed in our calculated band structures for both pristine CsSnI$_3$ and CsPbBr$_3$ in the $\gamma$ phase, indicating that the inefficient charge transport in CsPbBr$_3$ is likely to arise from low carrier concentration (Fig. S15A-C). In the following discussions, we will focus on understanding the electrical transport properties on CsSnI$_3$, with the assumption that Sn vacancies ($V_{sn}$) are the dominant defects as suggested by previous studies (4). The small differences in dispersion curves near the valence band edge computed with and without SOC (Fig. S15C) justify the neglect of this effect during the calculation of electrical transport coefficients and the consideration of $V_{sn}$ in a large supercell. Our results indicate that even with a very high defect density, $V_{sn}$ will change the band structure only slightly (Fig. S15D).

Constant relaxation time is assumed for charge transport in this work. Then, carrier concentration is the only parameter required for predicting $S$ that cannot be obtained by DFT. By treating the hole density as a single fitting parameter, our calculated $S$ matches experimental data in the entire temperature range (Fig. S16A). Prediction of electrical conductivity needs the computation of $\tau_h$, which is beyond the capability of our current approach. Instead, we extracted the $T$-dependent $\tau_h$ by fitting the values of $\sigma_h/\tau_h$ obtained by our simulations to the $\sigma_h$ measured experimentally (Fig. S16B), which enables us to understand the charge scattering mechanisms. Specifically, $\tau_h$ exhibits strong dependence on temperature, indicating that electron-phonon interactions rather than impurity effects are likely to be the dominant scattering mechanism. In the high temperature range, $\tau_h$ decreases with increasing $T$ due to the increasing ion position fluctuation (Fig. S16E), which is confirmed by the linear relation between $1/\tau_h$ and $T$ (Fig. S16F). In the relatively low temperature range, $\tau_h$ depends on both electron-phonon coupling strength and phonon population. The $k_{\text{electron}}$ and power factor ($S^2\sigma$) were then calculated using the above $n_h$ and $\tau_h$ (Fig. S16C,D). Finally, we explored the influence of doping density on electrical transport properties (Fig. S17). The results suggest that all quantities are very sensitive to the variation of $n_h$, and thus a precise control of doping level is necessary for optimizing thermoelectric performance.

It is worth noting that for CsSnI$_3$, the defect density ($n_v$) estimated by comparing the $k_{\text{lattice}}$ obtained computationally and experimentally is about 1×10$^{18}$ cm$^{-3}$, while the carrier concentration ($n_h$) estimated by fitting the calculated $S$ to experimental data is about 6×10$^{18}$ cm$^{-3}$. Assuming that Sn vacancies are the only source of free carriers, then ideally, the relation

$$n_h = 4 \times n_v$$

should be satisfied. In our case, the deviation from this condition is small, which supports the model used for this study.
Figure S15. Calculated band structures of pristine (A) CsPbI₃, (B) CsPbBr₃, and (C) CsSnI₃ crystals. The blue and green lines in panel (C) are results obtained with and without the inclusion of SOC. Panel (D) presents the band structure of a 2×2×2 CsSnI₃ supercell containing one V_{sn} defect (in green), compared to that of the pristine CsSnI₃ crystals (in blue). The Fermi level of the supercell with the defect is denoted by the red dashed line.
Figure S16. Temperature dependent electrical transport properties of CsSnI₃ crystals. (A) Seebeck coefficients calculated with various carrier concentrations (in unit of cm⁻³), along with the experimental data presented by the cross symbols. (B) Electrical conductivities measured by experiment, with the curve illustrating the fitting to these values. (C) Electronic thermal conductivity calculated by our approach (in solid line) and that obtained by the Wiedemann-Franz law (in dashed line). (D) Computed power factor. (E) Hole relaxation time and (F) its inverse with the Debye temperature denoted by gray dashed lines. The green dashed line shows the linear fitting between 1/τₜ and T at high temperature.
Figure S17. Calculated carrier concentration dependent electrical transport coefficients of CsSnI$_3$ crystals at T=300 K.
Table S1. The comparison of ratio ($k_{\text{lattice}}/k_{\text{min}}$) with crystals exhibiting low thermal conductivity at room temperature

<table>
<thead>
<tr>
<th></th>
<th>$k_{\text{lattice}}$ (Wm$^{-1}$K$^{-1}$)</th>
<th>$k_{\text{lattice}}/k_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbI$_3$</td>
<td>0.45 this work</td>
<td>2.3</td>
</tr>
<tr>
<td>CsPbBr$_3$</td>
<td>0.42 this work</td>
<td>1.9</td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>0.38 this work</td>
<td>1.8</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>1.6 (24)</td>
<td>6.0</td>
</tr>
<tr>
<td>CeFe$<em>4$Sb$</em>{12}$</td>
<td>1.9 (25)</td>
<td>3.5</td>
</tr>
<tr>
<td>Ba$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td>1.1 (26)</td>
<td>2.0</td>
</tr>
<tr>
<td>Yb$<em>{14}$AlSb$</em>{11}$</td>
<td>0.6 (27)</td>
<td>2.0</td>
</tr>
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Table S2. Comparison between lattice constants obtained by simulations and experiments.

<table>
<thead>
<tr>
<th></th>
<th>CsPbI$_3$</th>
<th>CsPbBr$_3$</th>
<th>CsSnI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>a (Å)</td>
<td>10.434</td>
<td>8.416</td>
</tr>
<tr>
<td></td>
<td>b (Å)</td>
<td>4.768</td>
<td>7.990</td>
</tr>
<tr>
<td></td>
<td>c (Å)</td>
<td>17.698</td>
<td>11.674</td>
</tr>
<tr>
<td>Expt.</td>
<td>a (Å)</td>
<td>10.458 (28)</td>
<td>8.244 (14)</td>
</tr>
<tr>
<td></td>
<td>b (Å)</td>
<td>4.802 (28)</td>
<td>8.198 (14)</td>
</tr>
<tr>
<td></td>
<td>c (Å)</td>
<td>17.776 (28)</td>
<td>11.735 (14)</td>
</tr>
</tbody>
</table>

Table S3. Calculated group velocities of acoustic phonons in bulk CsPbI$_3$, CsPbBr$_3$, and CsSnI$_3$ crystals in unit of $10^3$ m/s.

<table>
<thead>
<tr>
<th>Direction</th>
<th>CsPbI$_3$</th>
<th>CsPbBr$_3$</th>
<th>CsSnI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>1.85, 1.37, 1.03</td>
<td>2.45, 1.60, 1.09</td>
<td>2.34, 1.59, 1.35</td>
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<tr>
<td>[010]</td>
<td>2.08, 1.32, 1.12</td>
<td>2.04, 1.69, 0.91</td>
<td>2.14, 1.54, 1.18</td>
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<tr>
<td>[001]</td>
<td>1.86, 1.13, 1.01</td>
<td>2.77, 1.20, 1.00</td>
<td>2.55, 1.15, 1.08</td>
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<tr>
<td>[110]</td>
<td>2.09, 1.11, 1.04</td>
<td>2.06, 1.61, 0.97</td>
<td>1.83, 1.79, 1.18</td>
</tr>
</tbody>
</table>
References


