

Vol. 13 • No. 1 • January 7 • 2026

www.advmatinterfaces.de

ADVANCED MATERIALS INTERFACES

Open Access

RESEARCH ARTICLE

Impact of Grain Size on Low-Temperature Carrier Phase Coherence Length in Polycrystalline Halide Perovskite Films

Aungkan Sen, Liam J. Scanlon, Axel Melchor Gaona Carranza, Jose L. Mendoza-Cortes,* Johannes Pollanen,* Richard R. Lunt,* and William J. Gannon*

Halide perovskites are now being studied for a full range of optoelectronic devices due to their excellent electronic and optical properties. This work explores the impact of grain boundaries on low-temperature carrier transport in polycrystalline cesium tin iodide (CsSnI_3) within the quantum diffusive transport regime, comparing a range of polycrystalline samples with varying grain sizes with epitaxial counterparts. Low-temperature magnetoresistance measurements reveal the presence of weak anti-localization (spin-orbit effects) with a shorter coherence length (L_ϕ) than the epitaxial films. Surprisingly, L_ϕ is not found to be impacted by grain size, despite being nearly an order of magnitude larger for the epitaxial samples. Rather, it is found that these differences are largely dictated by the control of the crystal structure (and strain). First-principle density functional theory (DFT) calculations demonstrate lower phonon density of states (PhDOS) across frequencies in the epitaxial tetragonal phase compared to its less symmetric orthorhombic counterpart in polycrystalline films. This supports the hypothesis of lower electron-phonon scattering in the single-domain epitaxial films resulting in longer L_ϕ . These findings will likely help in understanding low temperature quantum coherent transport in semiconductors and other halide perovskites, and further develop this material class for quantum device applications.

1. Introduction

Halide perovskites have emerged as a unique class of tunable direct bandgap semiconductors^[1–3] with exceptional properties including high absorption coefficients,^[4] high carrier mobilities,^[5] long carrier lifetimes,^[6] and long carrier diffusion lengths.^[7] Such remarkable properties make them excellent candidates for efficient photovoltaics,^[8] light emitting diodes (LEDs),^[9] photodetectors^[10] and solar fuel production.^[11] Lately, there has been an increasing trend of research focusing on uncovering other intrinsic properties in halide perovskites to extend their application beyond optoelectronics. For example, Rashba splitting,^[12] spin-orbit coupling,^[13] ferroelectricity,^[14] and superconductivity^[15] have been reported for this class of materials suggesting their application in spintronic and quantum devices. Despite showing exotic quantum phenomena, these materials have not yet been

thoroughly studied to test the factors that impact quantum transport effects.

Quantum interference (QI), which usually affects the outcome of the probabilistic superposition state, lies at the foundation of understanding the behavior of quantum electronic devices (QEDs). For example, in quantum computers, qubits can be prepared in superposition states and QI can manipulate the time evolution of qubits during computation.^[16] QI also affects the quantum transport behavior in low-dimensional QEDs:^[17] when the QI of diffusive transport trajectories is constructive, a decrease in conductivity near zero magnetic field is observed and is known as weak localization (WL). If the QI is destructive, an increase in conductivity is observed which is called weak antilocalization (WAL). One of the key parameters that fundamentally governs these localization phenomena is the phase coherence length (L_ϕ),^[18] which characterizes the average distance charge carriers maintain their phase (coherence of the electronic state wavefunctions). A larger coherence length than the device size causes carriers to travel along multiple trajectories and results in macroscopic QI.^[18] Thus, L_ϕ is a fundamental figure of merit for many quantum applications. If decoherence occurs, the superposition of “0” and “1” states of qubits are lost.^[19] Thus,

A. Sen, A. M. G. Carranza, J. L. Mendoza-Cortes, R. R. Lunt
Department of Chemical Engineering and Materials Science
Michigan State University
East Lansing, Michigan 48824, USA
E-mail: jmendoza@msu.edu; rlunt@egr.msu.edu

J. Pollanen, R. R. Lunt
Department of Physics and Astronomy
Michigan State University
East Lansing, Michigan 48824, USA
E-mail: pollanen@msu.edu

L. J. Scanlon, W. J. Gannon
Department of Physics and Astronomy
University of Kentucky
Lexington, Kentucky 40506, USA
E-mail: wgannon@uky.edu

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admi.202500567>

© 2025 The Author(s). Advanced Materials Interfaces published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution](#) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/admi.202500567

understanding L_ϕ and the factors that determine its magnitude in materials is important to realize their use in quantum sensors, computers, spintronic devices, and other QEDs.

Low-temperature magnetoresistance measurements are typically used to observe the localization of charges and quantify L_ϕ .^[20] Our group previously demonstrated the first controllable epitaxial growth process for halide perovskites, which enabled quantum well formation and magnetoresistance measurements on epitaxial halide perovskite films including CsSnI_3 ,^[20,21] and CsSnBr_3 .^[20,22] Coherent transport in both epitaxial materials was observed along with WAL in epitaxial CsSnI_3 grown on KCl ^[20] and giant negative magnetoresistance with coherent 2D Mott variable range hopping (VRH) in epitaxial CsSnBr_3 on NaCl ^[22] layers. Particularly notable were the results demonstrated with epitaxial CsSnI_3 that was stabilized in a tetragonal (non-bulk) structure. In this case, an extraordinary L_ϕ of $\approx 5 \mu\text{m}$ was observed at 16 mK, which maintained a L_ϕ of $\approx 200 \text{ nm}$ up to 20 K. However, the origin of this extraordinarily long value of L_ϕ in epitaxial CsSnI_3 is still not fully understood, warranting further study to understand the impact of epitaxy, strain, crystal structure, grain size, doping, and preferred orientation on coherence phenomena in this material. This in effect will determine the structure-morphology-property relationship in the regime of quantum transport to realize effective strategies of tuning this material class for quantum device application.

Although quantum coherent transport has not been reported for 3D polycrystalline halide perovskites, several interesting quantum phenomena have been observed in other forms of halide perovskites as well as in other polycrystalline films. For example, WL in quasi-epitaxial CsPbBr_3 ,^[23] thermally activated charge carrier hopping in MAPbBr_3 single crystals,^[24] WAL in polycrystalline SnTe films,^[25] WL in polycrystalline SnO_2 films,^[26] increased phase coherence length in porous Bi_2Te_3 films,^[27] and Aharonov-Bohm interference in polycrystalline 2D graphene.^[28]

In this study, we investigated quantum coherent transport in polycrystalline and epitaxial CsSnI_3 thin films via low-temperature magnetoresistance measurement. Polycrystalline CsSnI_3 has a distinct crystal structure (orthorhombic)^[29] and morphology (grain boundaries) from its epitaxial counterpart. We utilize this material set to determine the structure-property relation in the quantum transport regime and also to specifically answer the question of the role of high-angle grain boundaries impact on the low-temperature coherence length, which is difficult to answer with traditional semiconducting material systems. We hypothesized that smaller grain size would lead to a reduction in the coherence length analogous to carrier mobility and diffusion length trends observed in many semiconductors at room temperature as well as exciton diffusion length trends in organic semiconductors.^[30–33]

Surprisingly, we find that the low-temperature phase coherence length (L_ϕ) of CsSnI_3 is independent of grain size and the large difference with the epitaxial films predominately stems from control of the crystal structure (and strain) rather than grain boundaries. To the best of our knowledge, there is no such report in the literature that delineates the structure-morphology effect on L_ϕ or quantum coherent transport in general. Hence, this study is unique not only because it is the first report on

the quantum transport in 3D polycrystalline halide perovskite films but also because it provides key insights into which material parameters (crystal structure, grain size, or strain) have the largest impact on the quantum coherent transport of halide perovskites.

2. Results and Discussion

Polycrystalline CsSnI_3 thin films with varying grain sizes were fabricated by spin coating. Detailed fabrication procedures are provided in the experimental section and illustrated in the Figure S1 (Supporting Information). Epitaxial CsSnI_3 films were grown on KCl substrates using a vapor phase epitaxy previously reported elsewhere.^[21] Polycrystalline devices were grown on the same sized ($12.6 \text{ mm} \times 12.6 \text{ mm}$) glass substrates by solution processing. Four devices with distinct grain sizes and two with distinct textures were measured at low temperatures and compared to epitaxial CsSnI_3 devices. As CsSnI_3 devices are prone to degradation in air over hours,^[21] protocols were developed for device handling to avoid/minimize direct air exposure (see Figure S2, Supporting Information). For simplicity, the representative data from distinct groupings of grain size were labeled S1, S2, S3, and S4 in the order of increasing grain size, and the epitaxial film was labeled as S5. Film thickness was kept the same for all polycrystalline samples and measured to be $\approx 118 \pm 11 \text{ nm}$ by ellipsometry whereas the epitaxial film has a typical thickness of $20 \text{ nm} \pm 1 \text{ nm}$. Four terminal devices having device geometry as shown in Figure 1a were fabricated for low-temperature magnetoresistance measurement. Thermal evaporation was used to deposit 100 nm thick gold contacts on perovskite layers through a shadow mask, where gold has been previously demonstrated as a highly ohmic contact with a contact resistance of $< 10 \text{ Ohm}$ when in contact with epitaxial CsSnI_3 .^[20] The deposition was performed at less than 3×10^{-6} torr pressure and the growth rate was kept at $0.1 \text{ \AA s}^{-1}$ for the first 2 nm and increased to $5 \text{ \AA s}^{-1}$ for the remaining growth.

2.1. Structure and Morphology Analysis

It is well known that polycrystalline CsSnI_3 films at room temperature have an orthorhombic structure.^[29] As demonstrated in Figure 1b, octahedra in the orthorhombic structure are distorted along different crystal axes. This is in contrast to the c-axis compressed tetragonal structure without octahedral tilts in epitaxial CsSnI_3 .^[21] To confirm the structure and morphology of the prepared films, we utilize Reflection High Energy Electron Diffraction (RHEED), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM).

SEM was used to observe the morphology of the prepared CsSnI_3 films. SEM images in Figure 1c show distinct particle sizes. Average particle sizes (greater than or equal to crystallite grain sizes) were calculated using the linear intercept method utilizing ImageJ software. We found particle grain sizes of $54 \pm 17 \text{ nm}$, 86 ± 13 , 112 ± 9 , and $657 \pm 6 \text{ nm}$ for S1, S2, S3, and S4 respectively. These grain sizes are found to be consistent with the XRD analysis discussed below and indicate the particle size is essentially the same as the crystallite size within

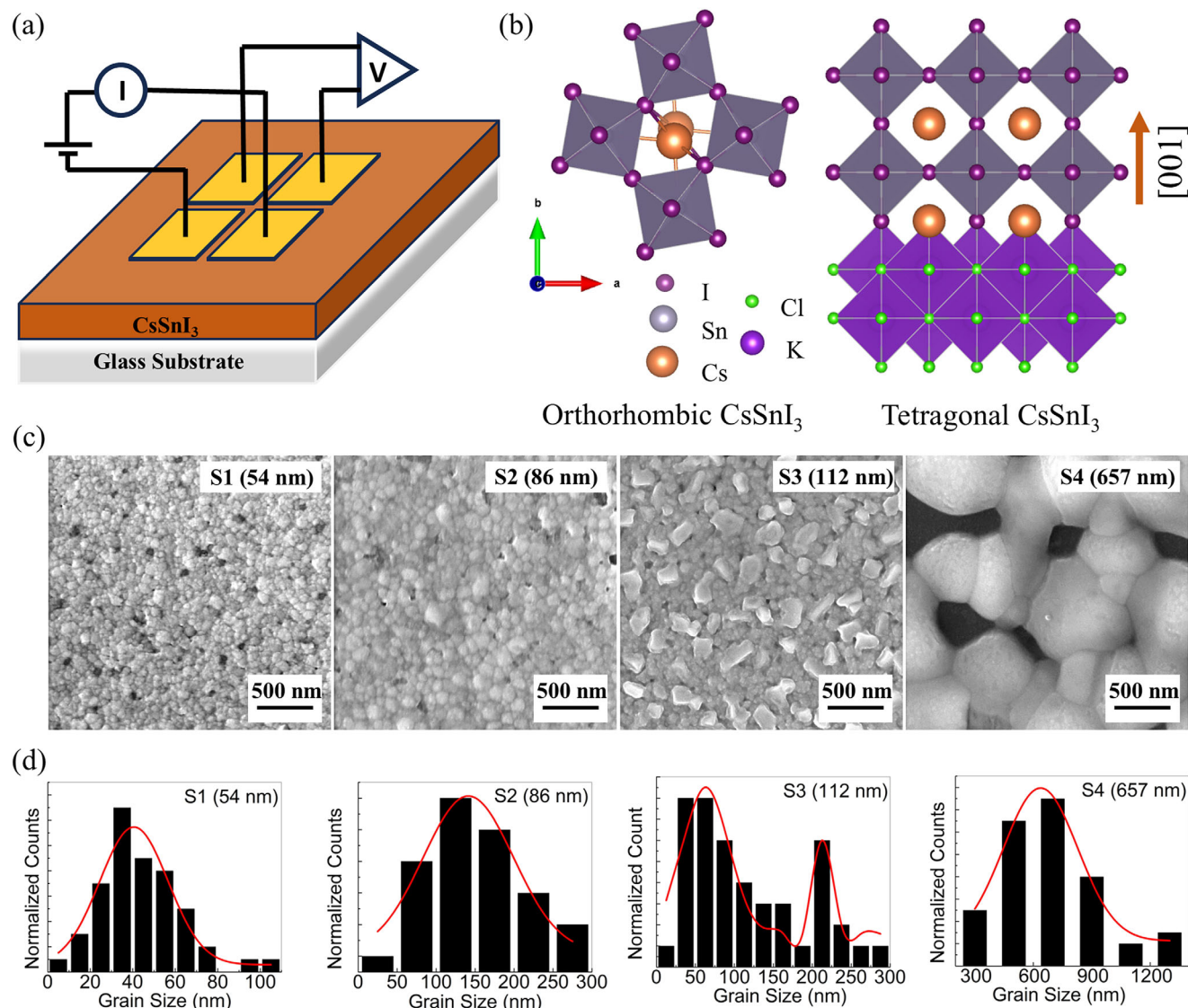


Figure 1. a) Device structure for the magnetoresistance measurement. b) A Schematic of the polycrystalline and epitaxial crystal structure of the CsSnI_3 thin films. While the polycrystalline film exhibits a distorted orthorhombic structure, the epitaxial one stabilized into a tetragonal structure on the KCl (100) substrate. c) SEM images of the deposited CsSnI_3 films. Average grain sizes of 54 ± 17 , 86 ± 13 , 112 ± 9 , and 657 ± 6 nm have been found by analyzing all the images using ImageJ for S1, S2, S3, and S4 respectively. The error bar in the grain size represents standard deviation from ten measurements using linear intercept method. In the nomenclature of each film (S1–S4), grain size is written in parenthesis. d) Grain size distribution of corresponding films. Distribution is unimodal Gaussian for all the samples except S3 which shows a bimodal distribution.

error. The corresponding grain size distribution is shown in Figure 1d. S1, S2, and S4 show a unimodal Gaussian distribution. In contrast, S3 has a different morphology as shown by a bimodal Gaussian distribution, indicating the secondary grain growth of some grains during high-temperature solvent annealing.

RHEED scans were performed at 30 kV with an ultra-low emission current of ≈ 40 –50 nA to avoid charging and beam damage. RHEED data in Figure 2a shows a clear contrast between polycrystalline and epitaxial films and an evolution with grain size. RHEED patterns captured at different azimuthal angles for epitaxial CsSnI_3 film demonstrate the presence of a single-domain epitaxial layer on single crystalline KCl substrates. For

growth on glass substrates, concentric Debye-Scherrer rings in the RHEED images further confirm the polycrystallinity nature of the films. Closer observation of the RHEED images reveals that Debye-Scherrer rings are more blurred in the RHEED patterns with the smaller grain size from S4 to S1. This occurs because smaller grain sizes increase the Full Width Half Maximum (FWHM), resulting in broader rings, and consequently making it harder to distinguish from other rings and the background noise.

X-ray diffraction (XRD) patterns of all four CsSnI_3 polycrystalline films on glass are shown in Figure 2b along with the predicted orthorhombic CsSnI_3 from the reference ICSD file (69 996). Note the background signal of the glass substrate is

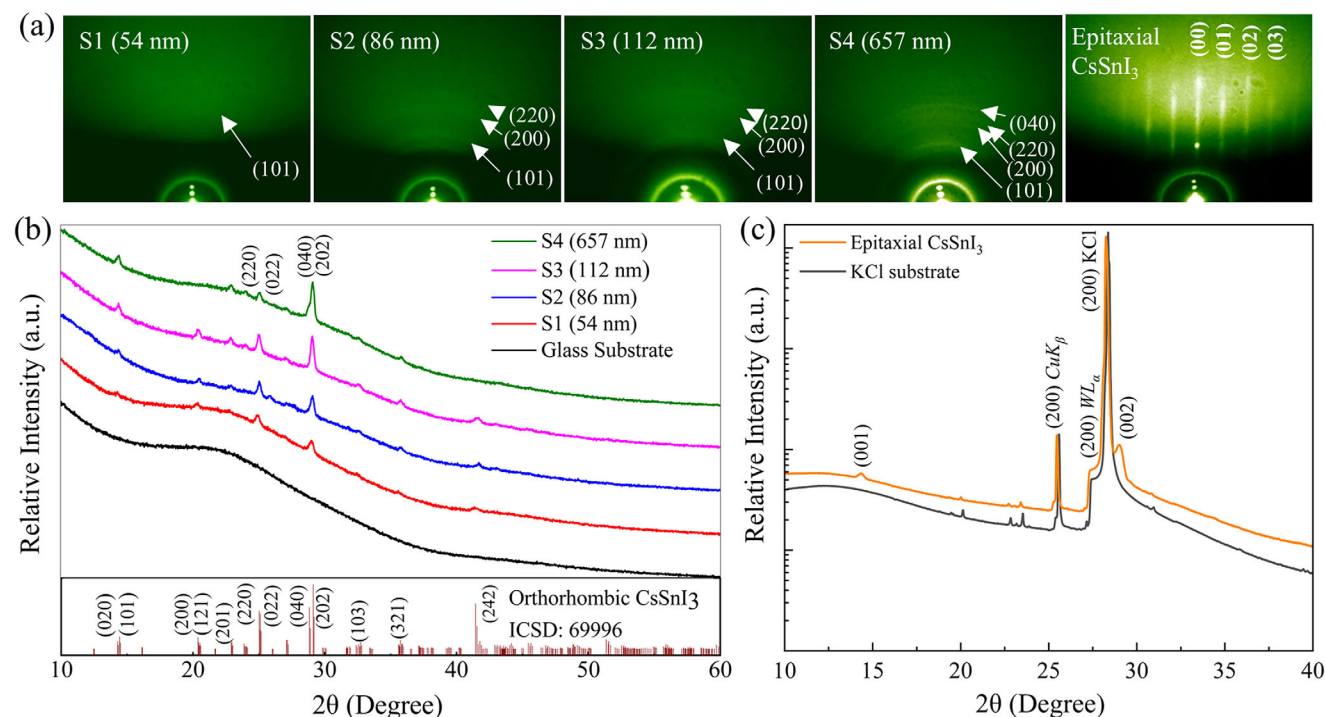


Figure 2. a) Reflection high energy electron diffraction (RHEED) ring patterns of the polycrystalline CsSnI₃ thin films (S1–S4) compared to the streaks in the epitaxial CsSnI₃ thin film (S5). b) X-ray Diffraction (XRD) analysis of the polycrystalline CsSnI₃ films prepared by different methods to vary the grain sizes. XRD patterns of all four samples match well with the orthorhombic CsSnI₃ standard pattern (ICSD: 69 996) as shown at the bottom, with no traces of secondary peaks. c) XRD patterns of an epitaxial CsSnI₃ film and a freshly cleaved KCl substrate.

present in all the samples. XRD pattern of the epitaxial CsSnI₃ film shown in Figure 2c along with a KCl substrate resembles the tetragonal pattern as reported previously.^[21] Insulating glass and KCl substrates are beneficial here to eliminate parasitic conductance from the substrate which might lead to erroneous results in magnetoresistance analysis. All four polycrystalline XRD patterns resemble the standard orthorhombic CsSnI₃ pattern - to further confirm the structure, XRD data were refined (Le Bail method) as shown in Figures S4 and S5 (Supporting Information). From the refinement, it was found that polycrystalline CsSnI₃ has the orthorhombic *Pnma* symmetry (space group 62, point group mmm). One key distinction for S4 compared to other samples is that it is more textured and shows (Figure S4, Supporting Information) preferential alignment along the (202) plane as depicted by its much higher intensity relative to other peaks. For S1–S3, all the peak intensity ratios roughly match with the expected peak heights of orthorhombic structure indicating a 3D polycrystalline powder thin film with little texture or preferred alignment. Another important observation is the increasing intensity of all the major peaks from S1 to S4. This increasing peak intensity and the narrowing of the peak widths clearly indicate the increase in crystallite size. To quantify the crystallite size, Williamson Hall (W-H) plots were prepared (Figure S4c, Supporting Information) from the corresponding XRD data. We fitted each peak of the spectrum to calculate the FWHM and deconvolute both the orthorhombic peak overlap and the instrumentation broadening from the calculated FWHM. We used these plots to determine both the crystallite size (less than or equal to the grain size from SEM) and non-uniform strain. We found crystal-

lite sizes of 32 ± 12 , 60 ± 26 , 83 ± 21 , and $>110 \pm 29$ nm for S1, S2, S3, and S4 respectively, and all strains were zero within error.

2.2. Temperature-Dependent Zero-Field Resistance Change

We measured the temperature-dependent electrical properties of polycrystalline and epitaxial CsSnI₃ devices using a standard Quantum Designs Physical Property Measurement System (PPMS). To prepare the four-terminal measurement-ready devices, four $0.5 \text{ cm} \times 0.5 \text{ cm}$ gold pads spaced by $50 \mu\text{m}$ were deposited on top of each perovskite film. Figure 3a shows the resistance change of a polycrystalline CsSnI₃ device with grain size 112 nm when it was cooled from 300 K to 1.95 K. Resistance increased from 1.4 to 3.5 k Ω with cooling. This increasing trend of resistance is in contrast to the epitaxial CsSnI₃ behavior for which resistance decreases from 130 to 37 Ω with decreasing temperature from 300 to 1.95 K (Figure 3b). The increasing resistance trend in polycrystalline CsSnI₃ with the decrease of temperature is similar to the characteristics of intrinsic or lightly doped semiconductors. Similar trends are observed in other lead and tin based halide perovskites^[34] as well as in epitaxial CsSnBr₃.^[22] Usually, these halide perovskites behave as intrinsic or lightly doped semiconductors and thus thermally activated carrier transport dominate the transport behavior. Four-terminal resistance measurements were found to be useful in eliminating the contribution from the contact resistance.

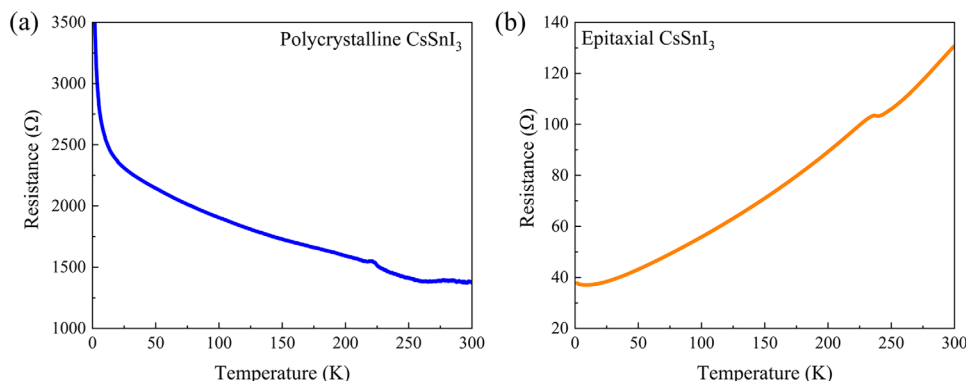


Figure 3. Temperature-dependent zero field ($B=0$) resistance change of a) polycrystalline (112 nm) and b) epitaxial CsSnI_3 thin films.

Next, the low-temperature resistance data were evaluated for power-law temperature dependence (see Figures S6 and S7, Supporting Information) by the following equation:

$$\ln R(T) \propto \frac{1}{T^X} \quad (1)$$

where R is the resistance, T is the temperature and X is the exponent of the power law. None of the samples show good power law dependency as indicated in Figures S6 and S7 (Supporting Information). Polycrystalline data is found to be slightly better fitted with the equation for 2D Mott variable range hopping (VRH) transport characteristics as characterized by $\ln R \propto T^{-\frac{1}{3}}$. Epitaxial CsSnI_3 fit roughly by the nearest neighbor hopping (NNH) equation as characterized by $\ln R \propto T^{-1}$. In both cases, the fits are still not compelling and other mechanisms cannot be ruled out. 2D Mott VRH usually indicates the phonon-assisted quantum mechanical tunneling possibility in the device at low temperatures.^[22] In this transport mechanism, charge carriers tend to localize in the vicinity of lattice defects. Thus, hopping from one localized site to the other takes place with the dominant one between the distant sites rather than the nearest localized sites as in NNH. Although VRH transport often leads to WL, the presence of WAL and VRH transport has also been observed in a few compounds.^[35–37] Still, the simultaneous presence of 2D Mott VRH and WAL (as discussed next) is counterintuitive suggesting no strong dependency on any of the power law characteristics for CsSnI_3 .

2.3. Magnetic Field-Dependent Quantum Coherent Transport

Magnetoresistance experiments were conducted at low temperatures (down to 1.8 K) and varying magnetic fields up to ± 8.5 T. The application of a magnetic field perpendicular to the film surface at a low temperature modifies the transport behavior as shown in Figure 4. The CsSnI_3 data presented in Figure 4 can be explained by weak anti-localization (WAL) from which the quantum phase coherence length (L_ϕ) of charge carriers in these devices can be extracted. A clear decrease of resistance as magnetic field is decreased near zero field is seen in all the curves of Figure 4 indicating the WAL behavior in both polycrystalline and epitaxial CsSnI_3 devices. Figure 4 also depicts that this WAL feature fades with the increase in temperature until it is no longer

observed past roughly 8 K for polycrystalline CsSnI_3 and 20 K for epitaxial CsSnI_3 .^[20] This decrease in WAL with increasing temperature likely stems from increased thermal scattering. Several scattering mechanisms are possible, i.e., electron-electron scattering, electron-phonon scattering, impurity, and grain boundary scattering.^[38] Any of these scattering events can potentially result in carrier decoherence and thus a reduction in phase coherence length.

To extract the phase coherence lengths (L_ϕ), we analyzed the magnetoresistance data at near-zero magnetic fields (Figure 5) using the simplified Hikami-Larkin-Nagaoka (HLN) theory^[39] as:

$$\sigma(B) - \sigma(0) = \frac{\alpha}{\pi} \left[\psi \left(\frac{1}{2} + \frac{\hbar}{4eBL_\phi^2} \right) - \ln \left(\frac{\hbar}{4eBL_\phi^2} \right) \right] \quad (2)$$

where e is the electron charge, $\hbar$ is the reduced Planck's constant, $\psi(x)$ is the digamma function, and α indicates the type of localization (WAL $\alpha < 0$ and WL $\alpha > 0$). We note that in our analysis the magnitude of α has no significance as our magnetoresistance measurement does not provide a measure of absolute conductivity of the samples. The magnitude of α is utilized only to scale the fit of the magnetoresistance data. However, the sign of α has significance as it indicates intrinsic physical information about spin-orbit coupling in the material. Here, α is negative for all cases indicating WAL behavior in the polycrystalline and epitaxial CsSnI_3 . The WAL behavior also indicates the presence of spin-orbit coupling in the polycrystalline CsSnI_3 . The magnitude of the spin-orbit coupling depends either on the mass of the constituent elements or on the lack of inversion symmetry.^[40,41] From the Le Bail refinement (Figure S5, Supporting Information), we find that polycrystalline CsSnI_3 has the orthorhombic $Pnma$ symmetry (space group 62, point group mmm). As this specific space group is centrosymmetric, we can expect the presence of inversion symmetry in all the polycrystalline CsSnI_3 films. Thus, the origin of WAL (and spin-orbit coupling) in polycrystalline CsSnI_3 likely stems from the presence of heavy elements.

Fitted magnetoresistance data by HLN theory (Figure 5) yield phase coherence lengths (L_ϕ) which are compared in Figure 6. The temperature dependence of L_ϕ for all five devices is quite evident in Figure 6a decrease in L_ϕ with increasing temperature

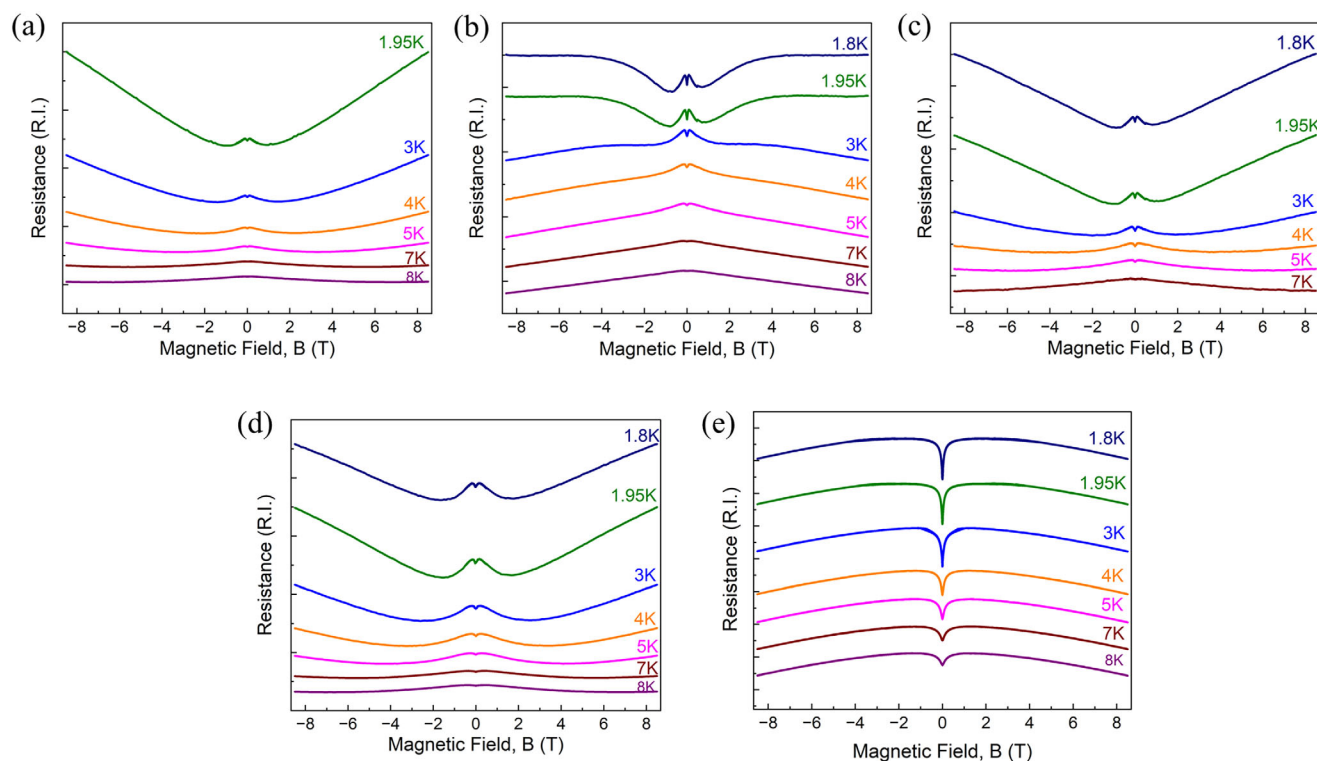


Figure 4. Low-temperature magnetoresistance data of polycrystalline and epitaxial CsSnI_3 devices a) S1 (54 nm), b) S2 (86 nm), c) S3 (112 nm), d) S4 (657 nm) and e) S5 (epitaxial). The applied magnetic field is normal to the device. Increasing the device temperature leads to the broadening of the WAL peak, indicating the weakening of the spin-orbit effect and possible reduction of the phase coherence length.

is found to be consistent for all the devices. Another noticeable insight from Figure 6 is that at each measured temperature, the phase coherence length (L_ϕ) remains relatively constant across polycrystalline samples with different grain sizes, with values in the low hundreds compared to thousands in epitaxial samples. To be more explicit, all polycrystalline sample values are within $\pm 25\%$ of each other at the same temperature with no trend between L_ϕ and grain size. This indicates that grain size has minimal influence on L_ϕ at a given temperature. For most of the polycrystalline devices, the calculated L_ϕ is found to exceed the grain size of the corresponding sample. Even in the smallest-grained sample (S1) where the average grain size is 54 nm, we found an L_ϕ of 286 ± 2.6 nm at 1.8 K; the lowest L_ϕ was 87 ± 1.1 nm at 7 K, all larger than the grain size of this sample. This clearly (and surprisingly) indicates that L_ϕ for polycrystalline CsSnI_3 is not limited by the grain size. The slightly higher L_ϕ of S4 at 1.8 K (441 ± 15 nm) and 1.9 K (315 ± 6.8 nm) might stem from its texture as it shows preferential orientation along (202), however, this would be a small effect. In comparison, epitaxial CsSnI_3 exhibits L_ϕ of 1400 ± 5.4 nm at 1.8 K and goes down to 339 ± 2.4 nm at 8 K. As more distinctly observed in Figure 6, L_ϕ for the epitaxial film is much higher than all the polycrystalline films at all temperatures from 1.8 to 8 K. Additionally, L_ϕ (WAL feature) for the epitaxial sample was reported to be present up to 20 K,^[20] whereas the WAL feature gradually ends ($L_\phi \sim 0$) at roughly 8 K for most polycrystalline samples.

The lack of dependence of the grain size on the carrier phase coherence length of halide perovskites is in stark contrast to the

impacts of grain size on mobility or even exciton diffusion length trends reported in the literature. For example, Lunt et al., experimentally showed that the exciton diffusion length increases nearly fourfold, from 6.5 ± 1.0 to 21.5 ± 2.5 nm, when average grain size increases from 0 ± 5 nm (amorphous limit) to 400 nm for PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) films caused by the decrease in lifetime due to the nonradiative loss at grain boundaries.^[33] Karl et al. reported dramatic trends in mobility with grain size in a range of soft semiconductors.^[31] Although no clear relationship has been established in the literature for phase coherence length and grain size, an interesting insight is reported by Hsieh et al. who experimentally showed the presence of WL at the grain boundaries of graphene by magnetoconductance measurement and extracted L_ϕ by HLN fitting.^[42] They found a L_ϕ of ≈ 300 nm at grain boundary region at 0.3 K temperature having carrier densities of $6 \times 10^{12} \text{ cm}^{-2}$. Coincidentally, the coherence length scale is similar to what we observed here. This observation hints that carrier dephasing is probably not prominent at grain boundaries of either high or low angles at low temperatures. But this leads to the question of what occurs as a function of grain boundary gap distance and how far grains can be disjointed before dephasing strongly occurs. Hsieh additionally noted that the scattering rate was shown to decrease and saturate below 7 K, particularly at grain boundaries, because of frozen magnetic ordering which lessens spin-flip interactions. Electron-electron and electron-phonon scatterings also diminish at such low temperatures. The overall impact is the incomplete dephasing and presence of phase coherence phenomena at grain

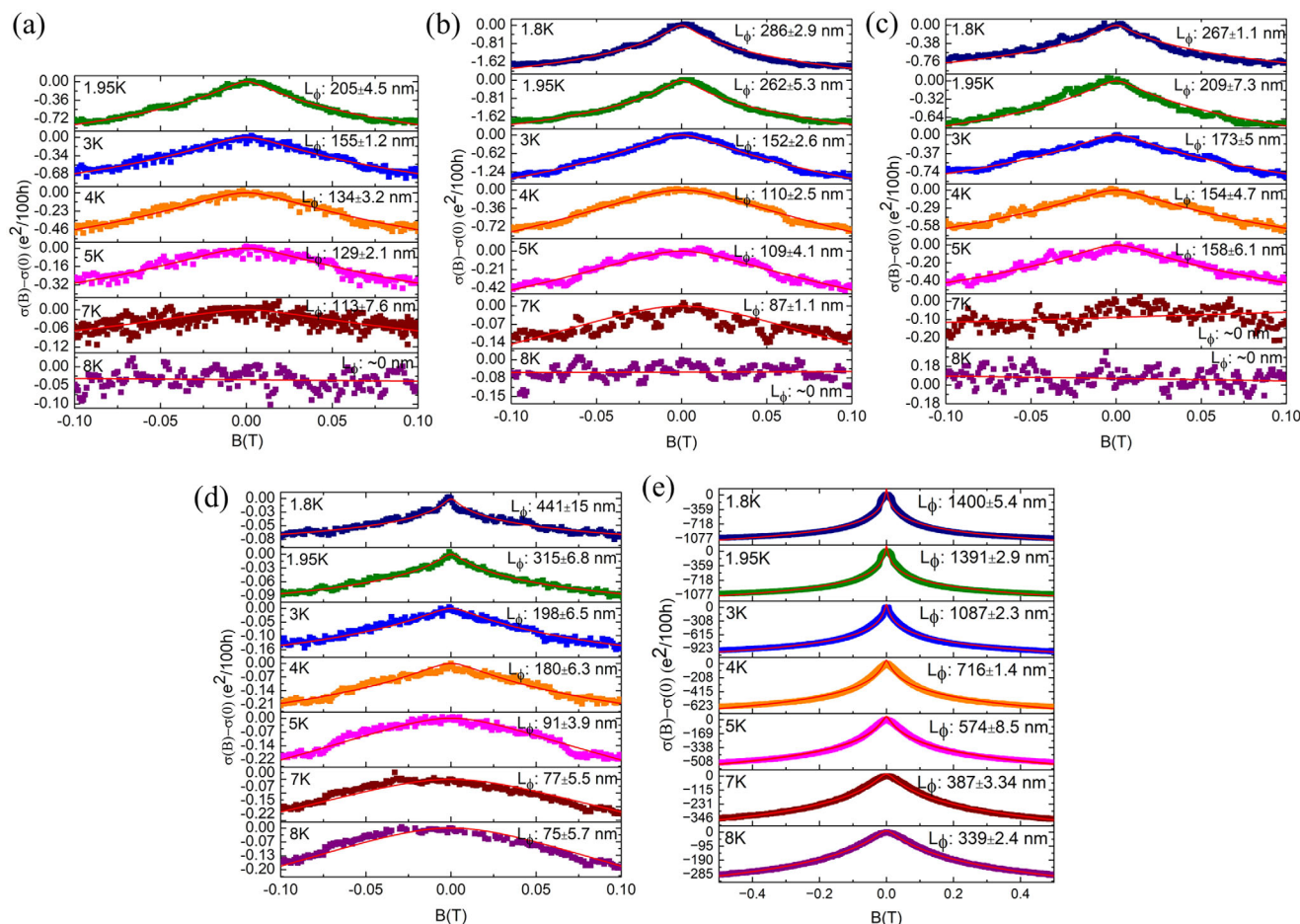


Figure 5. Magnetoconductance of polycrystalline and epitaxial CsSnI_3 thin films, a) S1 (54 nm), b) S2 (86 nm), c) S3 (112 nm), d) S4 (657 nm) and e) S5 (epitaxial) as a function of magnetic field normal to the plane of the device at near zero magnetic fields and at various temperatures. The vertical axis is the magnetoconductivity, $\sigma(B)$, minus the value of the conductivity at zero magnetic field, $\sigma(0)$. The solid line is a fit to the simplified HLN function (Equation 2) from which we can extract the charge carrier coherence length, L_ϕ . As the temperature is increased the WAL peak broadens and weakens as L_ϕ decreases due to increased inelastic scattering of charge carriers. The error bars represent fitting uncertainties obtained from nonlinear curve fitting of magnetoresistance measurement data.

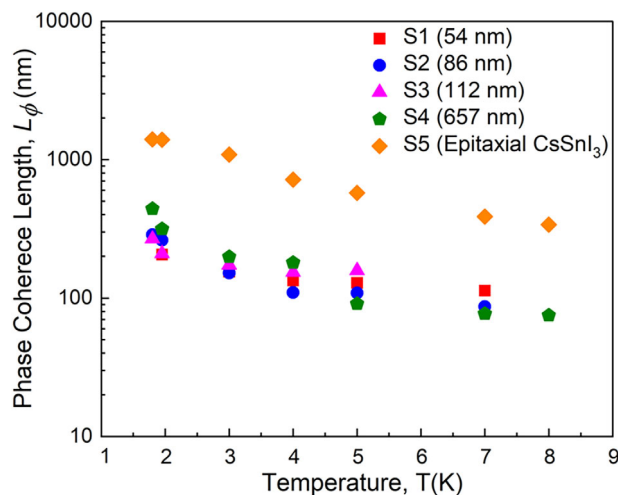


Figure 6. Temperature and grain size dependence of the charge carrier phase coherence length, L_ϕ , in the polycrystalline CsSnI_3 thin film compared to its epitaxial counterpart.

boundary regions below a certain low temperature, similar to our findings. Consistently, the lack of a significant variation in L_ϕ across grain sizes can also probably be explained by the saturation of the scattering rate below 7 K and considering identical defect densities (scattering points) in all samples. Once the scattering rate saturates, any decoherence mechanisms that are proportional to it should also reach saturation. Consequently, further reductions in scattering sites, such as grain boundaries, may no longer lead to significant improvements in coherence length at these low temperatures in the same type of samples. Above 7 K, the overall scattering rate increases exponentially thus eliminating the coherence phenomena.

Another scattering mechanism particular to halide perovskites could be iodide ion migration. The ionic nature of halide perovskites facilitates halide ion migration or segregation across their lattices.^[43] Halide ion migration is more prominent in polycrystalline films due to their preferential migration toward grain boundaries. For example, N. Phung et al. showed that ionic defects including iodide ions are trapped at grain boundaries via photoluminescence microscopy experiments as well as atomistic

simulations on MAPbI₃ single crystals and thin films.^[44] H. Lee et al. studied the time evolution of ion migration to and from grain boundaries of mixed halide perovskites using Kelvin probe force microscopy and indicated that halide segregation at grain boundaries is dominated largely by iodide ions causing faster ion migration in halide perovskites having higher iodine content.^[45] Here, we cannot rule out the possibility of iodide ion migration at grain boundaries during film formation and its subsequent influence on carrier transport. However, despite having different grain boundary areas across the samples (S1–S4), we have not observed any notable changes in the low temperature phase coherence in any of the different samples. One plausible explanation of this phenomenon could be the ion migration freezing at such low temperature (<10 K). G. Liu et al. studied the ion migration in cesium tin halide perovskites and found that ion motion freezes below 260 K.^[46] In another study, G. Nenashev also pointed out that below 250 K ionic conduction freezes and electronic transport predominates.^[47] In short, it is unlikely that at the low temperatures reported here ion migration plays a role on the carrier transport beyond the ion distribution that is frozen during processing. Since it is expected that the ion distribution will dominate around grain boundaries, the lack of grain size dependence also suggests minimal impact of any frozen ion migration.

Similarly, trap states could act as localized scattering center by accumulating at grain boundaries and cause dephasing. However, deviation from this classical transport behavior have been observed in thin film form or 2D systems particularly at low temperature. G. Horowitz reported that carrier tunneling through the grain boundary barrier becomes predominant at low temperature in organic semiconductor films, although carrier transport in those inter-grain regions is controlled by traps in ambient condition.^[48] F. Tafuri et al. studied coherent transport at the grain boundary junctions of YBa₂Cu₃O_{7-d} and showed that L_ϕ (0.13 μm) exceeds the size of microbridges at the grain boundary junction (50 nm) implying the presence of quantum interference across the junction at sufficiently low temperature.^[49] Both studies suggest that quantum coherent transport can occur across grain boundaries irrespective of grain orientation or trap sites at sufficiently low temperature and corroborate our findings.

We also ruled out the notable effect of chemical state and grain boundary orientation in this case. Since XRD analysis revealed no secondary phases, indicating high phase purity, the likelihood of substantial compositional deviation or contamination is negligible. In addition, the XRD patterns of all polycrystalline films show no preferential grain orientation except at the largest grains size. We compared the relative intensities of all peaks (normalized to the most intense (202) peak) with the standard XRD peak intensities (CIF) of CsSnI₃ as listed in Table S2 (Supporting Information). It is evident that the polycrystalline films exhibit isotropic polycrystalline (powder) diffraction. This implies the absence of preferred orientation and that the grains are distributed in all possible crystallographic directions.

While we might expect lower coherence length in the polycrystalline samples, the lack of grain size dependence suggests that the difference in the magnitude must be attributed to another factor. Given that the compositions and elements are identical between the polycrystalline and epitaxial samples, the only obvious remaining factors are the different crystal structures and strain; the polycrystalline films are an orthorhombic struc-

ture without uniform or non-uniform strain, and the epitaxial films are a uniformly strained tetragonal structure. Different crystal structures can contribute to different phonon density of states (PhDOS) and the number of variable phonon modes at each frequency can directly influence the electron scattering due to the electron-phonon interaction. Low PhDOS means weak electron-phonon scattering and thus could lead to longer L_ϕ . Orthorhombic CsSnI₃ might then be expected to have more distinct phonon mode splitting causing more complex phonon dispersions due to its lower symmetry than the higher symmetry tetragonal phase. Nematov et al. showed by first principle calculations that the high-temperature tetragonal CsSnI₃ phase has a lower PhDOS than its orthorhombic modifications due to higher symmetry in the former.^[50] Although the high-temperature tetragonal phase differs from our epitaxial tetragonal phase in terms of lattice parameters and space group (The high temperature β -phase possess the space group $P4/mbm$ while the epitaxial tetragonal phase presented here have the space group $P4/mmm$), both possess the same order (number of symmetry operations) and the same point group ($4/mmm$). As this epitaxial tetragonal phase of CsSnI₃ is not reported elsewhere, the PhDOS calculation is also missing in the literature. Therefore, to better understand the scattering mechanism in polycrystalline and epitaxial films, we calculated PhDOS for orthorhombic, epi-tetragonal, and (theoretical) cubic phases of CsSnI₃ using DFT. The details of the calculation are given in the experimental section. As shown in Figure 7, the phonon band structure is significantly different for different crystal structure of CsSnI₃. In particular, there are more phonon dispersion modes and the partial density of states is higher for the orthorhombic phase than its high symmetric counterparts- epi-tetragonal and cubic phases. This further supports the conclusion that the more symmetric tetragonal phase of the epitaxial film contributes to less phonon scattering than the polycrystalline orthorhombic phase, resulting in the substantially longer L_ϕ as well as a more pronounced WAL phenomenon.

While this conclusion is valid for CsSnI₃, we also speculate that this could also hold true for other halide perovskite compositions as well. However, literature on the phase coherence lengths (L_ϕ) of other halide perovskites is rare, having only been reported in two other systems. Zhang et al. found that L_ϕ is greater than 100 nm at 0.5 K for epitaxial CsSnBr₃ system.^[22] Wang et al. reported an L_ϕ of 49 nm at 3.5 K for quasi-epitaxial CsPbBr₃.^[23] One key challenge is highlighted in Figures S8 and S9 (Supporting Information), where we prepared polycrystalline thin film devices of five other halide perovskites (MAPbI₃, α -, γ -, δ -CsPbI₃ and CsSnBr₃) and checked their two-terminal DC resistance. The physical property measurement system (PPMS) for magnetoresistance measurement in our systems is usually limited by a DC resistance of 5 M Ω . Unfortunately, most of the halide perovskite films including lead-based compositions have two terminal DC resistances of above 5 M Ω (Figure S9, Supporting Information) and thus not suitable for coherent transport study without lowering the resistance by direct doping, delta-doping, etc. In fact, CsSnI₃ is one of the very few halide perovskite compounds suitable for this type of study due to the low DC resistance (1500 Ω) in its polycrystalline form as well as having different structure and much lower resistance in its epitaxial form. Nonetheless, the conclusions from this work likely hold for lead based systems and we

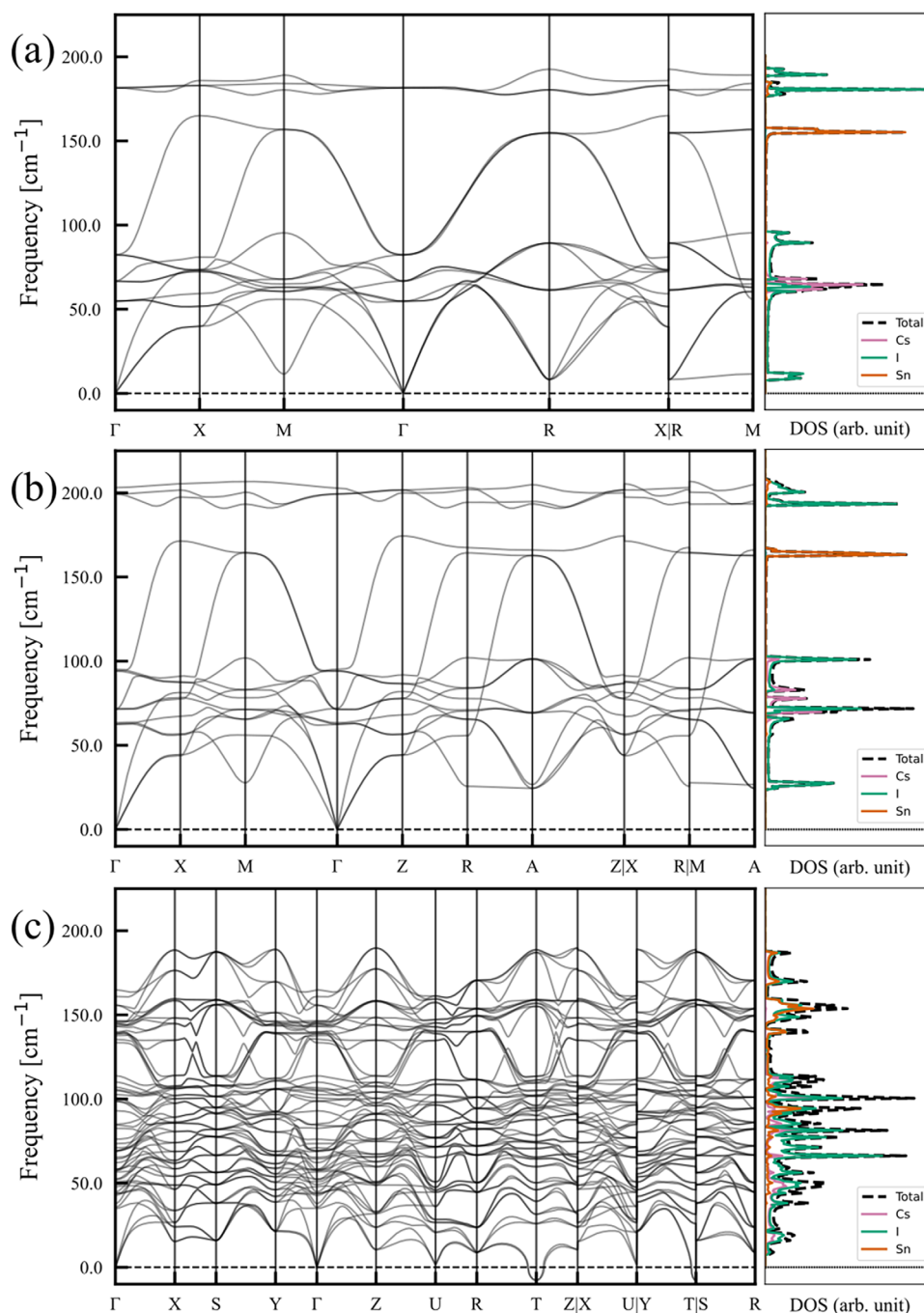


Figure 7. Phonon band structure and density of states for a) cubic b) epi-tetragonal, and c) orthorhombic CsSnI_3 .

would expect that higher symmetry systems will similarly lead to higher phase coherence lengths.

3. Conclusion

In summary, we aim to answer the question of whether grain size affects the low-temperature carrier phase coherence length in halide perovskites. To do this, we characterized several halide perovskite compounds, altered grain sizes, and fabricated epi-

taxial devices of the same material having a different crystal structure and strain profile for comparison. By performing low-temperature magnetoresistance measurements on polycrystalline CsSnI_3 thin film devices of varying grain sizes, we were able to provide insight that is difficult to elucidate in traditional systems such as Si and graphene. In particular, we show that 1) spin-orbit coupling in CsSnI_3 is dominated largely by the selection of heavy elements in the perovskite composition, 2) low-temperature phase coherence is surprisingly preserved through

grain boundaries, and 3) the magnitude of the phase coherence length is largely dictated by the crystal structure and/or strain profiles. Very few studies have ever attempted to look at the impact of grains on such phase coherence, making this data set particularly unique. This ultimately helps us better understand the key parameters impacting quantum transport phenomena in a range of thin-film semiconductors, including halide perovskites, and could help guide future developments.

4. Experimental Section

Materials: Cesium Iodide (CsI, 99.9%), Dimethyl Sulfoxide (DMSO, 99.8%), *N, N*-dimethyl formamide (DMF, 99.8%), Acetonitrile (ACN, 99%), Methoxy Acetonitrile (MACN, 99%), Anhydrous Chlorobenzene (99.8%), Acetone (99%) and Isopropyl Alcohol (IPA, 99%) were purchased from Millipore Sigma. Tin (II) Iodide (SnI_2 , 99.9%) was purchased from Strem. All reagents were used as received without further purification.

Polycrystalline CsSnI_3 Film Deposition: All the polycrystalline CsSnI_3 thin films were deposited on precleaned glass substrates by spin coating inside an N_2 -filled glovebox following procedures reported elsewhere with some variations.^[51,52] For simplicity, we named the samples S1, S2, S3, and S4 in the order of increasing grain size. Sample S1 was prepared by spin coating 70 μL precursor solution on a precleaned glass substrate at a rate of 4000 rpm for 45 s and thermal annealed on a hot plate at 70 °C for 10 min. The precursor solution was prepared by dissolving 0.8 mmol CsI and 0.8 mmol SnI_2 in 1.5 mL of mixed solvent (5:3:1 DMF:ACN:MACN). The solution was stirred overnight until a clear solution was obtained and filtered using 0.45 μm PTFE filters before use for spin coating. Glass substrates were cleaned by sonication in detergent water, DI water, IPA, and acetone for 15 min each. Substrates were heated on a hotplate at 100 °C for 5 min to remove the remaining solvents followed by plasma cleaning for 15 min and used immediately. Samples S2 and S3 were prepared following the same spin coating procedures as S1. As coated films were then solvent vapor annealed for 20 min. Solvent vapor annealing temperature was 100 °C for S2 and 150 °C for S3. Sample S4 was prepared by spin coating 70 μL of a different precursor solution on a precleaned glass substrate at a rate of 4000 rpm for 45 s and 200 μL of CB was used at the last 15th second of spinning as antisolvent. As coated films were first annealed at 70 °C for 5 min and then solvent vapor annealed at 100 °C for 20 min. The precursor solution for S4 was prepared by mixing 0.8 mmol CsI and 0.8 mmol SnI_2 in 1.2 mL 4:1 DMF:DMSO mixed solvent.

For solvent vapor annealing, 20 μL DMF was dropped at the edge of a glass lid which was used to cover the samples. We also optimized the solvent volume and temperature for CsSnI_3 solvent vapor annealing. A volume of 20 μL DMF and a temperature of 100 °C were found to be optimum for CsSnI_3 . More solvent volume or temperature yielded degraded porous and grey (sometimes degraded) CsSnI_3 films; similar results were found for MAPbI_3 as discussed by Zhong et al.^[53] Thus, an intentional increase of solvent vapor annealing temperature was useful here in obtaining different morphology (bimodal grain distribution) for S3.

Epitaxial CsSnI_3 Film Deposition: Epitaxial CsSnI_3 was grown on freshly cleaved (100) surfaces of KCl single crystal substrates using thermal co-evaporation in a customized RHEED integrated physical vapor deposition system (Angstrom Engineering). The growth details discussed in previous report^[21] have been followed here to get single-crystalline smooth epitaxial layers.

Device Fabrication: Four terminal devices having device geometry as shown in Figure 1a were fabricated for low-temperature magnetoresistance measurement. Gold contacts of 100 nm thickness were deposited on the prepared film by thermal evaporation in a chamber evacuated at less than 3×10^{-6} torr pressure. To achieve a smooth and uniform gold layer, the initial growth rate was kept at 0.1 $\text{\AA s}^{-1}$ for the first 2 nm and increased to 5 $\text{\AA s}^{-1}$ for the remaining growth. In all four-terminal measurement-ready devices, there are four 0.5 cm $\times$ 0.5 cm gold pads spaced by 50 μm on top of each perovskite film grown on glass substrates.

Characterization: Reflection high energy electron diffraction (RHEED) scans were performed inside a growth chamber (Angstrom Evovac system) with a pressure less than 5×10^{-6} torr. A voltage of 30 kV and an emission current of 40–50 nA were used to reduce the damage and charging on the perovskite film. X-ray diffraction (XRD) patterns were obtained using a Rigaku Smartlab X-ray Diffractometer in Bragg-Brentano (BB) geometry with CuK_α radiation (0.154 nm) and a step size of 0.01°. The morphologies of the CsSnI_3 thin films were characterized using a scanning electron microscope (SEM; EVO LS25, Carl Zeiss, Germany). Perovskite films were sputter coated with platinum to avoid charge building during imaging with secondary electrons. Films were characterized for thickness measurement using an ellipsometer (VASE, J. A. Wollam).

Low-Temperature Magnetoresistance Measurement: Freshly fabricated devices were wired up using 50 μm gold wire and In-Sn solder in an N_2 -filled environment. Such wired devices were then soldered in a puck to make them ready for magnetoresistance measurement and stored in an argon glovebox. A Quantum Designs Physical Property Measurement System (PPMS) was used for magnetoresistance measurement. The PPMS sample chamber was purged and sealed so that the samples were in a dry helium environment when they were in the PPMS. The samples spent less than 1 min in the atmosphere during the transfer from the argon glovebox storage to the PPMS sample chamber. Zero-field temperature dependence was measured from room temperature to 1.8 K. The temperature ramp rate was 0.35 K min^{-1} . Each data point is the average of 25 measurements taken across a time span of ≈ 7 s. For measurements in magnetic fields (H), the field range was ramped from 0 kOe to 85 kOe to -85 kOe to 0 kOe. When H was between -5 kOe and 5 kOe, H was incremented by 10 Oe and would take ≈ 5 s to increment and stabilize. When the magnitude of H was larger than 5 kOe, H was incremented by 1 kOe and would take 25 s to increment and stabilize. All excitation currents were set so that measurements were current-limited for all field and temperature ranges.

Phonon Density of States Calculation: Quantum-mechanical calculations were performed within the density functional theory (DFT) as implemented in CRYSTAL23,^[54] which employs Gaussian-type basis functions. The global hybrid PBE0 functional, incorporating 25% exact exchange, was used along with Grimme's D3 dispersion correction combined with Becke-Johnson damping to account for long-range interactions.^[55] Convergence was accelerated via the direct inversion of the iterative subspace method.^[56] Cesium, tin, and iodine orbitals were described using Cs_POB_TZVP_rev2, Sn_POB_DZVP_2018, and I_POB_DZVP_2018 basis sets, respectively.^[57] For geometry optimizations, the dimensionless integral tolerances for the Coulomb and exchange series (ITOL1, ITOL2, ITOL3, ITOL4, ITOL5; see CRYSTAL manual for details) are set to 9, 9, 9, 11, 38, respectively.

The cubic phase ($Pm\bar{3}m$, space group 221) lattice constant was obtained through full geometry optimization (atoms + unit cell), with energy convergence of 2.72×10^{-11} eV. After that, a c-axis distortion yielded a tetragonal phase ($P4/mmm$, space group 123). The final tetragonal structure was obtained with final energy convergence below 2.72×10^{-5} eV. The orthorhombic phase optimizations ($Pnma$, space group 62) were started from the experimental data reported in this work, first an anisotropic volume (CELLONLY), and then an atomic position (ATOMONLY) optimization reduced the Hellmann-Feynman forces for phonon calculations, with energy convergence of 2.72×10^{-11} eV. Brillouin zone sampling used a Monkhorst-Pack grid: $12 \times 12 \times 12$ for cubic/tetragonal phases and $9 \times 6 \times 9$ for orthorhombic. For the cubic phase the optimized lattice parameter was 5.775 Å, for the tetragonal phase were $a = 5.685$ Å, $b = 5.665$ Å and for the orthorhombic phase were $a = 8.152$ Å, $b = 11.740$ Å, and $c = 8.192$ Å.

Phonon dispersion and vibrational density of states were calculated via the finite-displacement method in CRYSTAL23 within the harmonic approximation.^[58] Due to sensitivity of vibrational frequencies to structure, stricter optimization criteria were used for the cubic and orthorhombic phases: 1.54×10^{-3} eV $\text{\AA}^{-1}$ (RMS forces), 2.31×10^{-3} eV $\text{\AA}^{-1}$ (max forces), 6.35×10^{-5} Å (RMS displacement), and 9.53×10^{-5} Å (max displacement). Forces were evaluated on $2 \times 2 \times 2$ supercells with reduced k-point meshes: $6 \times 6 \times 6$ (cubic/tetragonal) and $6 \times 4 \times 6$ (orthorhombic). Phonon dispersions and vibrational density of states shown in Figure 7 are

calculated including Grimme's D3 dispersion correction combined with Becke-Johnson damping to account for long-range interactions. This level of theory (PBE0+D3) displays unphysical positive frequencies in the M and R high symmetry points in the cubic phase.^[59–62] Therefore, we proceeded to display the PBE0+D3 calculations to compare the vibrational density of states of all phases. On the other hand, a comparison of the phonon dispersions obtained by PBE0+D3, PBE0 and PBE of the cubic phase, shown in Figure S10 (Supporting Information), are consistent with previous studies on metal-halide perovskites comparing the Generalized Gradient Approximation (GGA) with hybrid functionals.^[63] Furthermore, the epi-tetragonal phase with experimental parameters as well as the optimized orthorhombic phase obtained at PBE0 level of theory are shown in Figures S11 and S12 (Supporting Information). The imaginary modes in the epi-tetragonal phase rises from the strain applied in the c-axis and could be stabilized by the KCl substrate. Atomic structures were visualized using VESTA.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work at Michigan State University was supported by the National Science Foundation (NSF SSMC 1807573). This work was supported in part through computational resources and services provided by the Institute for Cyber-Enabled Research at Michigan State University.

Conflict of Interest

The authors declare no conflict of interests

Data Availability Statement

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

Keywords

epitaxy, grain size, halide perovskites, magnetoresistance, phase coherence length

Received: June 20, 2025

Revised: August 18, 2025

Published online: September 26, 2025

- [1] S. A. Kulkarni, T. Baikie, P. P. Boix, N. Yantara, N. Mathews, S. Mhaisalkar, *J. Mater. Chem. A* **2014**, *2*, 9221.
- [2] Y. Zhao, P. Miao, J. Elia, H. Hu, X. Wang, T. Heumueller, Y. Hou, G. J. Matt, A. Osvet, Y.-T. Chen, M. Tarragó, D. de Ligny, T. Przybilla, P. Denninger, J. Will, J. Zhang, X. Tang, N. Li, C. He, A. Pan, A. J. Meixner, E. Spiecker, D. Zhang, C. J. Brabec, *Nat. Commun.* **2020**, *11*, 6328.
- [3] K. J. Savill, A. M. Ulatowski, L. M. Herz, *ACS Energy Lett.* **2021**, *6*, 2413.
- [4] N.-G. Park, *Mater. Today* **2015**, *18*, 65.
- [5] C. Motta, F. El-Mellouhi, S. Sanvito, *Sci. Rep.* **2015**, *5*, 12746.
- [6] Y. Chen, H. T. Yi, X. Wu, R. Haroldson, Y. N. Gartstein, Y. I. Rodionov, K. S. Tikhonov, A. Zakhidov, X.-Y. Zhu, V. Podzorov, *Nat. Commun.* **2016**, *7*, 12253.

- [7] S. Shrestha, X. Li, H. Tsai, C.-H. Hou, H.-H. Huang, D. Ghosh, J.-J. Shyue, L. Wang, S. Tretiak, X. Ma, W. Nie, *Chem* **2022**, *8*, 1107.
- [8] X. Jiang, Z. Zang, Y. Zhou, H. Li, Q. Wei, Z. Ning, *Mater. Res.* **2021**, *2*, 210.
- [9] X.-K. Liu, W. Xu, S. Bai, Y. Jin, J. Wang, R. H. Friend, F. Gao, *Nat. Mater.* **2021**, *20*, 10.
- [10] Y. Dong, Y. Zou, J. Song, X. Song, H. Zeng, *J. Mater. Chem. C* **2017**, *5*, 11369.
- [11] L. Romani, L. Malavasi, *ACS Omega* **2020**, *5*, 25511.
- [12] Y. Zhai, S. Baniya, C. Zhang, J. Li, P. Haney, C.-X. Sheng, E. Ehrenfreund, Z. V. Vardeny, *Sci. Adv.* **2017**, *3*, 1700704.
- [13] A. R. B. M. Yusoff, A. Mahata, M. Vasilopoulou, H. Ullah, B. Hu, W. Jose da Silva, F. Kurt Schneider, P. Gao, A. V. levlev, Y. Liu, O. S. Ovchinnikova, F. De Angelis, M. Khaja Nazeeruddin, *Mater. Today* **2021**, *46*, 18.
- [14] S. Shahrokhi, W. Gao, Y. Wang, P. R. Anandan, M. Z. Rahaman, S. Singh, D. Wang, C. Cazorla, G. Yuan, J.-M. Liu, T. Wu, *Small Methods* **2020**, *4*, 2000149.
- [15] M. Retuerto, T. Emge, J. Hadermann, P. W. Stephens, M. R. Li, Z. P. Yin, M. Croft, A. Ignatov, S. J. Zhang, Z. Yuan, C. Jin, J. W. Simonson, M. C. Aronson, A. Pan, D. N. Basov, G. Kotliar, M. Greenblatt, *Chem. Mater.* **2013**, *25*, 4071.
- [16] L. Gui-Lu, *Commun. Theor. Phys.* **2006**, *45*, 825.
- [17] T. Sain, K. Singh Ch, E. P. Amaladass, S. Abhirami, S. Ilango, T. Mathews, A. Mani, *Mater. Lett.* **2021**, *300*, 130164.
- [18] T. Harada, P. Bredol, H. Inoue, S. Ito, J. Mannhart, A. Tsukazaki, *Phys. Rev. B* **2021**, *103*, 045123.
- [19] T. Bassan, *Medium* **2018**, (accessed: December 2024), <https://tanishabassan.medium.com/decoherence-quantum-computers-greatest-obstacle-67c74ae962b6>.
- [20] K. Nasyedkin, I. King, L. Zhang, P. Chen, L. Wang, R. J. Staples, R. R. Lunt, J. Pollanen, *iScience* **2021**, *24*, 102912.
- [21] L. Wang, P. Chen, P. S. Kuttipillai, I. King, R. Staples, K. Sun, R. R. Lunt, *ACS Appl. Mater. Interfaces* **2019**, *11*, 32076.
- [22] L. Zhang, I. King, K. Nasyedkin, P. Chen, B. Skinner, R. R. Lunt, J. Pollanen, *ACS Appl. Electron. Mater.* **2021**, *3*, 2948.
- [23] Y. Wang, Z. Wan, Q. Qian, Y. Liu, Z. Kang, Z. Fan, P. Wang, Y. Wang, C. Li, C. Jia, Z. Lin, J. Guo, I. Shakir, M. Goorsky, X. Duan, Y. Zhang, Y. Huang, X. Duan, *Nat. Nanotechnol.* **2020**, *15*, 768.
- [24] M. Keshavarz, S. Wiedmann, H. Yuan, E. Debroye, M. Roeffaers, J. Hofkens, *ACS Energy Lett.* **2018**, *3*, 39.
- [25] X. Li, Y. Yang, X. Wang, P. Zhu, F. Qu, Z. Wang, F. Yang, *Crystals* **2022**, *12*, 773.
- [26] V. Ksenevich, V. Dorosinets, D. Adamchuk, J. Macutkevicius, J. Banys, *Materials* **2020**, *13*, 5415.
- [27] A. Nguyen, G. Akhgar, D. L. Cortie, A. Bake, Z. Pastuovic, W. Zhao, C. Liu, Y.-H. Chen, K. Suzuki, M. S. Fuhrer, D. Culcer, A. R. Hamilton, M. T. Edmonds, J. Karel, *Phys. Rev. Mater.* **2022**, *7*, 064202.
- [28] V. H. Nguyen, J.-C. Charlier, *Nanoscale Adv.* **2020**, *2*, 256.
- [29] I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2012**, *134*, 8579.
- [30] N. Karl, *Synth. Met.* **2003**, *133*, 649.
- [31] N. Karl, K.-H. Kraft, J. Marktanner, M. Münch, F. Schatz, R. Stehle, H.-M. Uhde, *J. Vac. Sci. Technol. A* **1999**, *17*, 2318.
- [32] R. R. Lunt, N. C. Giebink, A. A. Belak, J. B. Benziger, S. R. Forrest, *J. Appl. Phys.* **2009**, *105*, 053711.
- [33] R. R. Lunt, J. B. Benziger, S. R. Forrest, *Adv. Mater.* **2010**, *22*, 1233.
- [34] A. K. Chilvery, A. K. Batra, B. Yang, K. Xiao, P. Guggilla, M. D. Aggarwal, R. Surabhi, R. B. Lal, J. R. Currie, B. G. Penn, *J. Photon. Energy* **2015**, *5*, 057402.
- [35] M. Jenderka, J. Barzola-Quiquia, Z. Zhang, H. Frenzel, M. Grundmann, M. Lorenz, *Phys. Rev. B* **2013**, *88*, 045111.

- [36] B. Bhattacharyya, A. Sharma, B. Sinha, K. Shah, S. Jejurikar, T. D. Senguttuvan, S. Husale, *Sci. Rep.* **2017**, 7, 7825.
- [37] S. N. Holmes, J. Gough, C. Chen, D. A. Ritchie, M. Pepper, *J. Phys. D: Appl. Phys.* **2022**, 55, 46LT01.
- [38] J. J. Lin, J. P. Bird, *J. Phys.: Condens. Matter* **2002**, 14, R501.
- [39] S. Hikami, A. I. Larkin, Y. Nagaoka, *Prog. Theor. Phys.* **1980**, 63, 707.
- [40] G. Dresselhaus, *Phys. Rev.* **1955**, 100, 580.
- [41] H. Nakamura, D. Huang, J. Merz, E. Khalaf, P. Ostrovsky, A. Yaresko, D. Samal, H. Takagi, *Nat. Commun.* **2020**, 11, 1161.
- [42] K. Hsieh, V. Kochat, T. Biswas, C. S. Tiwary, A. Mishra, G. Ramalingam, A. Jayaraman, K. Chattopadhyay, S. Raghavan, M. Jain, A. Ghosh, *Phys. Rev. Lett.* **2021**, 126, 206803.
- [43] Z. Chen, G. Brocks, S. Tao, P. A. Bobbert, *Nat. Commun.* **2021**, 12, 2687.
- [44] N. Phung, A. Al-Ashouri, S. Meloni, A. Mattoni, S. Albrecht, E. L. Unger, A. Merdasa, A. Abate, *Adv. Energy Mater.* **2020**, 10, 1903735.
- [45] H. Lee, P. Boonmongkolras, S. Jun, D. Kim, Y. Park, J. Koh, Y.-H. Cho, B. Shin, J. Y. Park, *ACS Appl. Energy Mater.* **2023**, 6, 1565.
- [46] G. Liu, Y. Wu, Y. Liu, B. Cai, Y. Dong, S. Zhang, H. Zeng, *Appl. Phys. Lett.* **2021**, 119, 031902.
- [47] G. V. Nenashev, A. N. Aleshin, I. P. Shcherbakov, V. N. Petrov, *Solid State Commun.* **2022**, 348, 114768.
- [48] G. Horowitz, *Synth. Met.* **2003**, 138, 101.
- [49] F. Tafuri, A. Tagliacozzo, D. Born, D. Stornaiuolo, E. Gambale, D. Dalena, P. Lucignano, B. Jouault, F. Lombardi, A. Barone, B. L. Altshuler, *Microelectron. J.* **2008**, 39, 1066.
- [50] D. Nematov, A. Burhonzoda, K. Kholmurodov, *Innov. Discov.* **2024**, 1, 17.
- [51] N. Wang, Y. Zhou, M.-G. Ju, H. F. Garces, T. Ding, S. Pang, X. C. Zeng, N. P. Padture, X. W. Sun, *Adv. Energy Mater.* **2016**, 6, 1601130.
- [52] T. Ye, K. Wang, Y. Hou, D. Yang, N. Smith, B. Magill, J. Yoon, R. H. Mudiyansele, G. A. Khodaparast, K. Wang, S. Priya, *J. Am. Chem. Soc.* **2021**, 143, 4319.
- [53] Y. Zhong, D. Seeberger, E. M. Herzig, A. Köhler, F. Panzer, C. Li, S. Huettner, *ACS Appl. Mater. Interfaces* **2021**, 13, 45365.
- [54] A. Erba, J. K. Desmarais, S. Casassa, B. Civalleri, L. Donà, I. J. Bush, B. Searle, L. Maschio, L. Edith-Daga, A. Cossard, C. Ribaldone, E. Ascrizzi, N. L. Marana, *J. Chem. Theory Comput.* **2023**, 19, 6891.
- [55] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, 32, 1456.
- [56] P. Pulay, *J. Comput. Chem.* **1982**, 3, 556.
- [57] L. M. Seidler, J. Laun, T. Bredow, *J. Comput. Chem.* **2023**, 44, 1418.
- [58] F. Pascale, C. M. Zicovich-Wilson, F. López Gejo, B. Civalleri, R. Orlando, R. Dovesi, *J. Comput. Chem.* **2004**, 25, 888.
- [59] L. Huang, W. R. L. Lambrecht, *Phys. Rev. B* **2014**, 90, 195201.
- [60] E. L. da Silva, J. M. Skelton, S. C. Parker, A. Walsh, *Phys. Rev. B* **2015**, 91, 144107.
- [61] C. E. Patrick, K. W. Jacobsen, K. S. Thygesen, *Phys. Rev. B* **2015**, 92, 201205.
- [62] L. Monacelli, N. Marzari, *Chem. Mater.* **2023**, 35, 1702.
- [63] W. Kaiser, M. Carignano, A. A. Alothman, E. Mosconi, A. Kachmar, W. A. Goddard, F. De Angelis, *J. Phys. Chem. Lett.* **2021**, 12, 11886.