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Differing vibrational properties of halide and chalcogenide perovskite semiconductors and impact on optoelectronic performance

Kevin Ye,^{1,*} Matan Menahem,^{2,*} Tommaso Salzillo,³ Florian Knoop,⁴ Boyang Zhao,⁵ Shanyuan Niu,⁵ Olle Hellman,^{4,6} Jayakanth Ravichandran,^{5,7,8} R. Jaramillo,^{1,†} and Omer Yaffe^{2,‡}

¹*Department of Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

²*Department of Chemical and Biological Physics,
Weizmann Institute of Science, Rehovot 76100, Israel*

³*Department of Industrial Chemistry “Toso Montanari”, INSTM-UdR Bologna, Bologna 40129, Italy*

⁴*Department of Physics, Chemistry and Biology (IFM),
Linköping University, SE-581 83, Linköping, Sweden.*

⁵*Mork Family Department of Chemical Engineering and Materials Science,
University of Southern California, Los Angeles, CA 90089, USA*

⁶*Department of Molecular Chemistry and Material Science,
Weizmann Institute of Science, Rehovot 76100, Israel*

⁷*Ming Hsieh Department of Electrical and Computer Engineering,
University of Southern California, Los Angeles, CA 90089, USA*

⁸*Core Center of Excellence in NanoImaging (CNI),
University of Southern California, Los Angeles, CA 90089, USA*

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We report a comparative study of temperature-dependent photoluminescence and structural dynamics of two perovskite semiconductors, the chalcogenide BaZrS₃ and the halide CsPbBr₃. These materials have similar crystal structures and direct band gaps, but we find that they have quite distinct optoelectronic and vibrational properties. Both materials exhibit thermally activated non-radiative recombination, but the nonradiative recombination rate in BaZrS₃ is four orders of magnitude faster than in CsPbBr₃, for the crystals studied here. Raman spectroscopy reveals that the effects of phonon anharmonicity are far more pronounced in CsPbBr₃ than in BaZrS₃. Further, although both materials feature a large dielectric response due to low-energy polar optical phonons, the phonons in CsPbBr₃ are substantially lower in energy than in BaZrS₃. Our results suggest that electron-phonon coupling in BaZrS₃ is more effective at nonradiative recombination than in CsPbBr₃ and that BaZrS₃ may also have a substantially higher concentration of nonradiative recombination centers than CsPbBr₃. The low defect concentration in CsPbBr₃ may be related to the ease of lattice reconfiguration, typified by anharmonic bonding. It remains to be seen to what extent these differences are inherent to the chalcogenide and halide perovskites and to what extent they can be affected by materials processing.

Keywords: Photoluminescence, Raman spectroscopy, perovskites, chalcogenides, halides

I. INTRODUCTION

Halide perovskites exhibit outstanding optoelectronic properties and are under intensive development for photovoltaic (PV) applications [1–3]. These materials can be synthesized at near-room temperature and feature sharp band-edge optical absorption and long excited-state charge carrier lifetimes [4–8]. However, halide perovskites suffer from thermal and chemical instability, as well as lead toxicity, and research continues into alternative materials for thin-film photovoltaics. Chalcogenide perovskites are an intriguing alternative. This class of materials possesses a similar crystal structure and range of direct band gaps as their halide counterparts [9–11]. Additionally, chalcogenide perovskites have

a very large dielectric constant, suggesting similar lattice dynamics and screening of charged defects [12, 13]. However, despite these similarities, chalcogenide and halide perovskites are quite different in other respects. Chalcogenide perovskites are made from Earth-abundant elements and present minimal toxicity concerns. Their synthesis is challenging, typically requiring very high temperatures and air-free processing. Once formed, chalcogenide perovskites are very stable [9, 14–17]. The optoelectronic properties of chalcogenide perovskites have been little reported. Existing published results suggest that photoluminescence (PL) is not strong, and defect control remains a challenge, but long PL transient decay times have been measured [9, 16–21]. No chalcogenide perovskite thin-film solar cells have been reported, likely due to the challenging conditions required for film synthesis.

Many researchers, including ourselves, have argued that the outstanding optoelectronic properties of halide perovskites are intertwined with their strongly anharmonic structural dynamics [22–31]. This poses questions

* These authors contributed equally to this work

† rjaramil@mit.edu

‡ omer.yaffe@weizmann.ac.il

of how the optoelectronic properties and lattice dynamics of chalcogenide and halide perovskites compare and what we can learn about photovoltaic performance from this comparison.

Here, we employ temperature-dependent PL and Raman scattering spectroscopy, alongside first-principles self-consistent phonons simulations, to compare single-crystal samples of two prototypical perovskite semiconductors: the chalcogenide BaZrS_3 and the halide CsPbBr_3 . These compounds share the same distorted-perovskite, corner-sharing, orthorhombic crystal structure (space group $Pnma$, no. 62) within the temperature range studied here [32, 33]. BaZrS_3 is the most widely studied chalcogenide perovskite and has been experimentally made and measured in various form factors [9, 12–21, 32, 34–38]. CsPbBr_3 is among the most widely-studied inorganic halide perovskite [39–43]. It has a band gap comparable to BaZrS_3 and it can be prepared as high-quality single crystals [44–49].

Between 80 and 300 K, the PL emission intensity of both materials decreases due to thermally activated nonradiative recombination, with electron-phonon interactions broadening the PL linewidth in both cases. However, CsPbBr_3 emission intensity surpasses that of BaZrS_3 by over four orders of magnitude, suggesting a significantly higher concentration of very-low-barrier nonradiative recombination centers in BaZrS_3 .

We use Raman spectroscopy and first-principles simulations to show that the phonon frequency spectrum in BaZrS_3 extends to nearly double that in CsPbBr_3 . Raman analysis demonstrates that CsPbBr_3 exhibits pronounced anharmonic characteristics, even at low temperatures. In contrast, BaZrS_3 exhibits predominantly harmonic vibrational behavior akin to traditional tetrahedrally bonded semiconductors. Our findings are consistent with the hypotheses that the lower-frequency and strongly anharmonic structural dynamics in CsPbBr_3 may reduce carrier capture cross-sections due to Franck-Condon effects [50]. They may also decrease defect concentration through annealing, even at room temperature [51]. Definitive tests of these hypotheses await detailed calculations of rate coefficients, supported by first-principles quantum calculations and defect spectroscopy to identify and quantify recombination-active defects experimentally.

II. METHODS

We grew single crystals of BaZrS_3 with dimensions of approximately 100 μm using a flux method as reported previously [9]. We grew single crystals of CsPbBr_3 with dimensions on the order of 2 mm using the vapor saturation of an antisolvent method as reported previously [44].

We performed Raman scattering in a homebuilt system in backscattering geometry. We used a 1.58 eV CW pump-diode laser (Toptica Inc., USA), which is below the band gap of BaZrS_3 (1.9 eV) [9, 34] and CsPbBr_3

(2.32 eV) [52]. We performed PL spectroscopy using the same optical system and a 2.54 eV CW sapphire-pumped diode laser (Coherent Inc., USA). The signal was measured in a 1 m long spectrometer (FHR1000, Horiba Inc.) equipped with a holographic grating (1800 gr/mm for Raman and 150 gr/mm for PL) and a Synapse Plus CCD detector (Horiba Inc.).

We controlled the sample temperature using a liquid N_2 - or liquid He-cooled high-vacuum optical cryostat (Janis Inc., USA) for $T \leq 400$ K. For higher temperature measurements, we controlled the temperature in an optical furnace (Linkam TS1000) under N_2 flow. We performed measurements for a series of increasing temperatures. We took precautions to isolate the effect of varying sample temperature on the measured spectra by maintaining stable measurement conditions, refocusing the laser before every measurement, and taking repeated measurements across the whole temperature range. We verified sample integrity by the repeatability of the measured spectra and by optical microscope inspection after each measurement sequence. We did not observe evidence of sample damage [53, 54], except when the BaZrS_3 sample was heated to 850 K (consistent with reported thermal stability to at least 600 $^\circ\text{C}$). [14] The measurement system and protocols are further described in Refs. [55–59].

We calculate normalized PL yield (Y) by analyzing the integrated PL intensity, including both the band-to-band peaks and the shoulders. The PL data is measured in counts, and we compute intensity by dividing by the acquisition time. We define Y as the ratio between the PL intensity emitted from the sample (I_{PL} , measured in counts/sec) and the excitation laser intensity that reaches the interior of the sample (I_{in}):

$$Y = \frac{I_{\text{PL}}}{I_{\text{in}}} = \frac{I_{\text{PL}}}{I_0} (1 - R_s)^{-1}. \quad (1)$$

We measure the laser intensity I_0 (in photons/sec) at the microscope entrance. We compute I_{in} from I_0 by accounting for losses due to reflection from the cryostat windows and the sample surface. The same cryostat window reflection losses affect the collected PL intensity and cancel in the expression for Y , leaving only a dependence on the sample surface power reflection coefficient (R_s). Further details are presented in Sec. S1 of the Supplemental Material (SM) [60].

III. RESULTS

A. Photoluminescence and nonradiative recombination

In Fig. 1, we present temperature-dependent PL spectra of BaZrS_3 and CsPbBr_3 measured between 80–300 K. At low temperatures, spectra are dominated by band-edge recombination at $E_g \approx 1.96$ eV and 2.34 eV for BaZrS_3 and CsPbBr_3 , respectively. The low-temperature

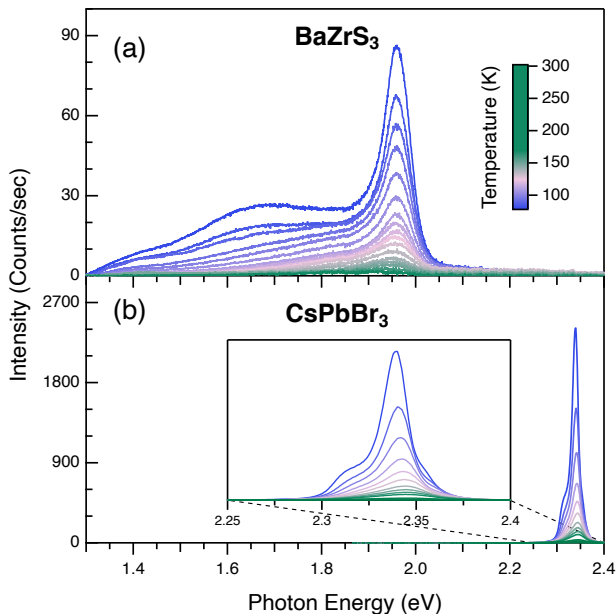


FIG. 1. Temperature-dependent PL spectra. PL spectra measured between 80 K and 300 K for (a) BaZrS₃ and (b) CsPbBr₃, after subtraction of the background spectra at 170 K and 300 K, respectively. The line color indicates temperature. BaZrS₃ and CsPbBr₃ were measured with different pump laser fluence: 4.3 MJ/cm² for BaZrS₃, and 2.7×10^{-4} MJ/cm² for CsPbBr₃.

spectra for both samples feature low-energy shoulders, which are quenched at elevated temperatures. The band-to-band peak and the shoulder are much broader in BaZrS₃ than in CsPbBr₃. In both materials, PL is quenched with increasing temperature, and for BaZrS₃, it becomes too weak to measure above 170 K. To eliminate external features in the PL spectra, the high-temperature spectra were subtracted from those in Fig. 1.

BaZrS₃ and CsPbBr₃ are direct band-gap semiconductors and strongly absorb the pump laser. At the pump laser energy of 2.54 eV, the absorption coefficient of BaZrS₃ is 1.68×10^5 cm⁻¹, and that of CsPbBr₃ is 4.04×10^5 cm⁻¹ [37, 61, 62]. Therefore, the pump laser absorption depth is much smaller than the thickness for both samples, and all the light entering the samples is absorbed. However, the PL emission intensity of CsPbBr₃ dwarfs that of BaZrS₃.

In Fig. 2(a), we present an Arrhenius plot of the normalized PL yield (Y) of the main band-to-band transition (deconvolution detailed in Sec. S1 of the SM [60]). We fit the data to a minimal model of thermally activated nonradiative recombination [63, 64]:

$$Y(T) = \frac{1}{1 + Ae^{-E_a/k_B T} + Be^{-E_b/k_B T}}, \quad (2)$$

where E_a and E_b are the activation energies of two non-radiative recombination mechanisms, k_B is the Boltzmann constant, and T is the temperature. $A = k_{nr,a}^0/k_r$

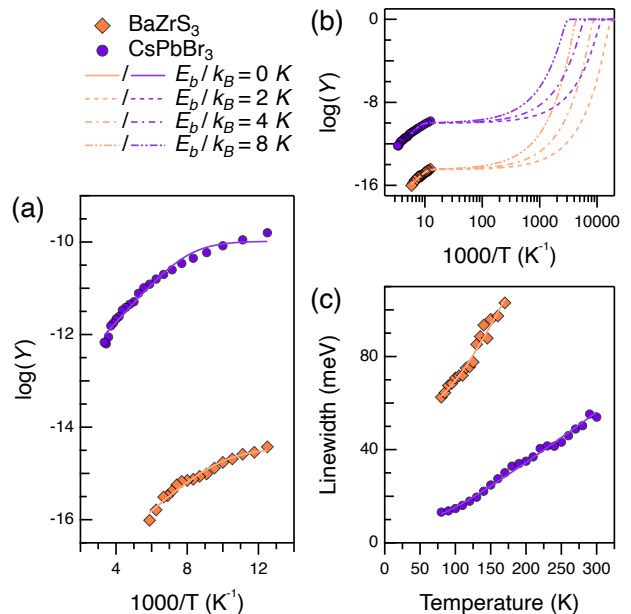


FIG. 2. Model-based analysis of normalized PL yield [Y , Eq. (2)] and linewidth (Γ_{PL}). (a) Y as a function of the inverse temperature. (b) Fit to a model with a second nonradiative recombination pathway. E_b/k_B fall below our measurement temperature window. (c) Γ_{PL} of the band-to-band peak as a function of the temperature. All fitted values can be found in Sec. S1 of the SM [60]. Purple circles and traces are for CsPbBr₃, and orange diamonds and traces are for BaZrS₃.

and $B = k_{nr,b}^0/k_r$ are ratios of exponential prefactors that compare the nonradiative ($k_{nr,a}^0$ and $k_{nr,b}^0$) to radiative (k_r) recombination coefficients at $T = 0$ K. As discussed below, two nonradiative recombination mechanisms are required for a minimal model of the data. This model assumes that all radiative recombination has a sufficiently small activation energy that appears barrierless within the measurement window. The effect of this assumption is that the PL internal quantum efficiency (IQE) approaches unity at low temperatures. The best-fit model parameters are presented in Table I.

We find that BaZrS₃ and CsPbBr₃ feature a nonradiative recombination process with similar activation energy $E_a = 68 \pm 7$ and 86 ± 5 meV, respectively. This is apparent by eye in the Arrhenius plot [Fig. 2(a)], as both data sets have similar curvature and a knee at approximately the same temperature. However, the PL yield of CsPbBr₃ is over four orders of magnitude larger than that of BaZrS₃, and the data do not extrapolate toward the same yield in the low-temperature limit. The presence of nonradiative recombination mechanisms with similar activation energy belies the difference in PL intensity.

To explain the divergence in PL intensity, we invoke a second nonradiative recombination mechanism in BaZrS₃, with activation energy E_b too low to be determined in our measurement window. We also assume a similar second mechanism in CsPbBr₃ for con-

TABLE I. Best-fit parameters for PL yield, Eq. (2). Results are presented here for $E_b/k_B = 0$ K. In Table S2 of the SM [60], we present results for other choices of E_b/k_B .

Material	I_0 (photons/sec)	E_a (meV)	E_b/k_B (K)	A	B
BaZrS ₃	6.7×10^{15}	68 ± 7	0	$(6.9 \pm 3.8) \times 10^{17}$	$(2.8 \pm 0.5) \times 10^{14}$
CsPbBr ₃	4.3×10^{11}	86 ± 5	0	$(2.8 \pm 0.8) \times 10^{13}$	$(9.6 \pm 1.4) \times 10^9$

sistency in the model function. By construction, the thermal scale E_b/k_B falls well below our experimental temperature window, and therefore, E_b cannot be determined by regression. This low-temperature process is saturated within the measured temperature range, and $e^{-E_b/k_B T} \approx 1$. With this assumption, we fix the temperature scale E_b/k_B at a low value and fit the data to determine B . In Fig. 2(b), we present a family of model functions with E_b varied manually; for E_b sufficiently small, its value has an insignificant impact on the fit results and our conclusions. The ratio $B_{\text{BZS}}/B_{\text{CPB}}$ is meaningful, as it determines the measured difference in low-temperature PL yield between BaZrS₃ (BZS) and CsPbBr₃ (CPB). We find that:

$$\frac{B_{\text{BZS}}}{B_{\text{CPB}}} = \frac{\left(\frac{k_{\text{nr,b}}^0}{k_r}\right)_{\text{BZS}}}{\left(\frac{k_{\text{nr,b}}^0}{k_r}\right)_{\text{CPB}}} = 28,181. \quad (3)$$

Both materials have comparable optical absorption coefficients near their band edge; therefore, we can approximate $(k_{r,\text{CPB}}/k_{r,\text{BZS}}) \approx \mathcal{O}(1)$. We therefore conclude that the rate constant $k_{\text{nr,b}}^0$ of low- (or zero-) barrier non-radiative recombination is $\mathcal{O}(10^4)$ times faster in BaZrS₃ than in CsPbBr₃.

We analyze the PL linewidth (Γ_{PL}) for insight into how excited states couple to lattice vibrations. In Fig. 2(b), we show the temperature dependence of Γ_{PL} of the main PL peak at the E_g for each material. We use multiple Gaussian peaks to fit the data, three for CsPbBr₃ and four for BaZrS₃. For both materials, the main PL peak is well modeled by two Gaussian peaks, and we determine Γ_{PL} numerically from the best-fit models. We fit Γ_{PL} to a relation describing thermal and non-thermal broadening, previously applied to halide perovskites [52]:

$$\Gamma_{\text{PL}}(T) = \Gamma_0 + \frac{\gamma}{e^{E_{\text{ph}}/k_B T} - 1}, \quad (4)$$

where Γ_0 represents temperature-independent contributions to Γ_{PL} , such as heterogeneous broadening due to quenched structural disorder. The second term describes broadening due to coupling between excited states and lattice vibrations with characteristic energy E_{ph} and electron-phonon coupling constant γ . These lattice vibrations are likely longitudinal optical phonons (see below), and the electron-phonon interactions can be described through deformation potentials.

We find that luminescent band-edge states couple to vibrations with characteristic energy that is similar

in both materials: $E_{\text{ph}} = 24 \pm 7$ meV for BaZrS₃, and 17 ± 4 meV for CsPbBr₃ (see below). The electron-phonon coupling constant γ is larger for BaZrS₃ (200 ± 100 meV) than for CsPbBr₃ (50 ± 10 meV). γ is related to deformation potentials and polar optical coupling. The higher value in BaZrS₃ may be related to the stronger covalent nature of the Zr-S bonds compared to Pb-Br bonds: 32% covalent for Zr-S, compared to 26% for Pb-Br, according to the Pauling scale. This implies enhanced sensitivity of electron energies to bond angles in the chalcogenide, as we have studied previously [13, 35]. We also see that BaZrS₃ has larger heterogeneous broadening, Γ_0 , than CsPbBr₃, reflecting a higher concentration of structural defects and other forms of non-thermal disorder. In addition to affecting the PL spectra, these factors affect how steeply optical absorption rises at the band gap, the width of the Urbach tail, and the phonon-limited charge transport mobility, and are therefore relevant to photovoltaic performance [65–67].

B. Raman Scattering and Phonon Dynamics

The lower luminescence yield and larger PL broadening in BaZrS₃, compared to CsPbBr₃, are related to differences in lattice vibrations. To better understand these relationships, we turn to theoretical and experimental studies of the phonon spectra. In Fig. 3, we present the total (black) and partial (orange, green, and blue) vibrational density of states of BaZrS₃ (top) and CsPbBr₃ (bottom), calculated *ab initio* using the temperature-dependent effective potential (TDEP) method at 300 K (details in Sec. S2 the SM [60, 68–83]). The optical vibrations in BaZrS₃ span frequencies up to 430 cm^{-1} (53 meV), while those in CsPbBr₃ peak at 160 cm^{-1} (20 meV). This is due to the higher mass of the atoms in CsPbBr₃ and the more covalent character of the bonds in BaZrS₃ [84].

Longitudinal optical (LO) phonons couple to electronic excitations and likely contribute most to the temperature-dependent PL linewidth broadening. In Fig. 3, the vertical red lines provide a measure of the phonon LO character: As detailed in Sec. S2 of the SM [60], the LO character is estimated by computing the longitudinal charges for optical vibrations from the mode eigenvectors and the atomic Born charge tensors, projected on the [101] excitation direction, and divided by the vibration frequency to account for the average mode amplitudes. We see that BaZrS₃ has many phonons with prominent LO character along the [101] excitation

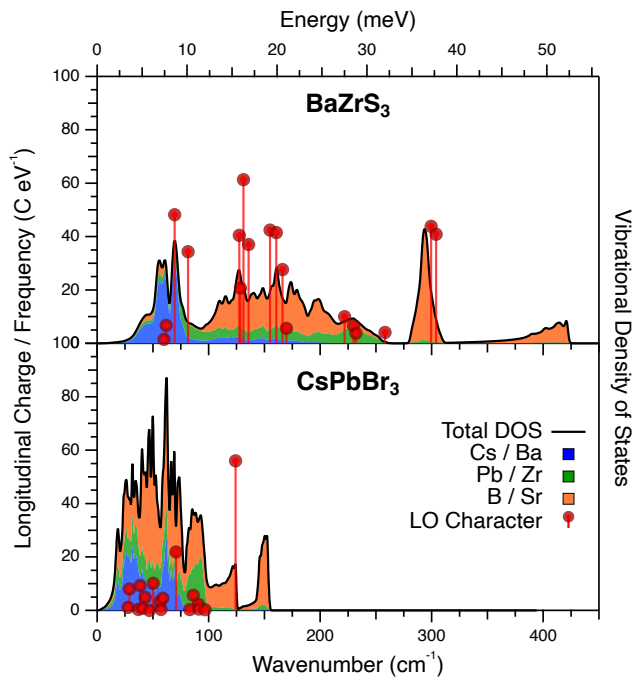


FIG. 3. Calculated room-temperature phonon density of states (DOS, right axis) of BaZrS_3 and CsPbBr_3 . The colors indicate the partial contribution of the A (blue), M (green), and X (orange) ions in the AMX_3 formula. The red lines are the measure (left axis) of the LO character. The top and bottom axes label the abscissa in energy and wavenumber, respectively.

direction, whereas CsPbBr_3 only shows one mode of appreciable LO character at $\approx 125 \text{ cm}^{-1}$. This factor likely contributes to the stronger temperature-dependent PL broadening in BaZrS_3 in addition to the higher deformation potentials.

The characteristic energy of lattice vibrations responsible for PL broadening in CsPbBr_3 , $E_{\text{ph}} \simeq 17 \text{ meV}$ ($\approx 140 \text{ cm}^{-1}$) is comparable to the most prominent LO phonon in the calculated spectrum. For BaZrS_3 , $E_{\text{ph}} \simeq 24 \text{ meV}$ ($\approx 190 \text{ cm}^{-1}$) falls roughly in the middle of the calculated spectrum. Likely, band-edge states couple to a diversity of lattice vibrations in both materials through polar-optical coupling and deformation potentials, and the characteristic energy determined by PL broadening represents a distribution of processes. Similar conclusions have been reached in studies of ultrafast lattice rearrangement following optical excitation of halide perovskites, including CsPbBr_3 [85].

In Fig. 4, we present the low-frequency Raman spectra of BaZrS_3 and CsPbBr_3 measured in the temperature range 80–350 K. The spectra of BaZrS_3 and CsPbBr_3 are consistent with previous reports [58, 86], and mode assignments can be found in Ref. [56, 87]. In Sec. S3 of the SM [60], we present the Raman spectra of BaZrS_3 measured over a wider temperature range, from 10 to 875 K, showing no indication of a phase transition [14,

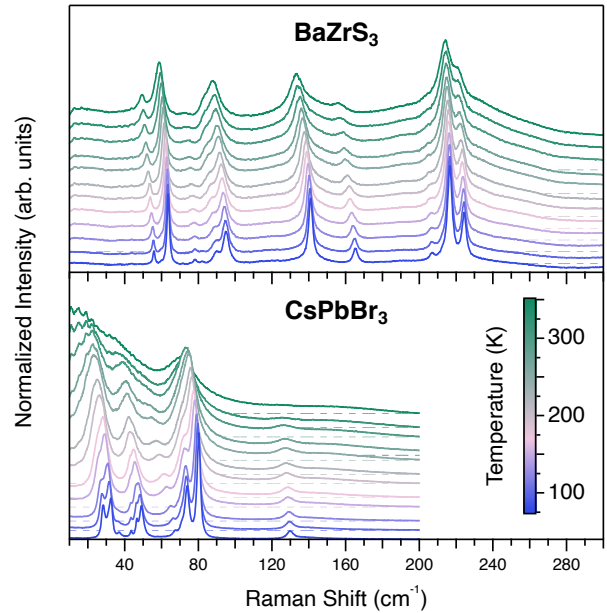


FIG. 4. Temperature-dependent Raman scattering spectra of BaZrS_3 and CsPbBr_3 . Temperature is indicated by color. The individual data sets are shifted vertically for clarity; the dashed horizontal lines indicate the zero level for each data set.

88, 89].

The Raman spectra of CsPbBr_3 exhibit sharp first-order peaks (one photon scattered by one vibration) [90] at low temperatures, which shift and broaden significantly with increasing temperature. These structural dynamics are characteristic of halide and certain oxide perovskites [53, 91–93]. The broad, featureless spectra at high temperatures, combined with a rapid decrease in vibrational lifetime (evidenced by peak broadening), indicate the impact of anharmonic vibrational dynamics [23, 52].

At low temperatures, the Raman spectra of BaZrS_3 resemble those of CsPbBr_3 and other halide perovskites [55, 94], with a similar number of prominent peaks divided into doublets and triplets. The vibrations in BaZrS_3 are higher in frequency than those in CsPbBr_3 . Unlike CsPbBr_3 , the Raman peaks in BaZrS_3 remain sharp and distinct with increasing temperature, and even at 350 K, there is a scant signature of anharmonic dynamics. The harmonic dynamics in BaZrS_3 recall those in tetrahedrally bonded semiconductors (e.g., GaAs), in which vibrations along the stiff covalent bonds do not interact and change little with temperature [95, 96].

We can more quantitatively compare the structural dynamics of BaZrS_3 and CsPbBr_3 by considering the temperature dependence of the phonon frequencies and linewidths. We model the Raman spectra as a convolution of pseudo-Voigt peaks multiplied by the Bose-

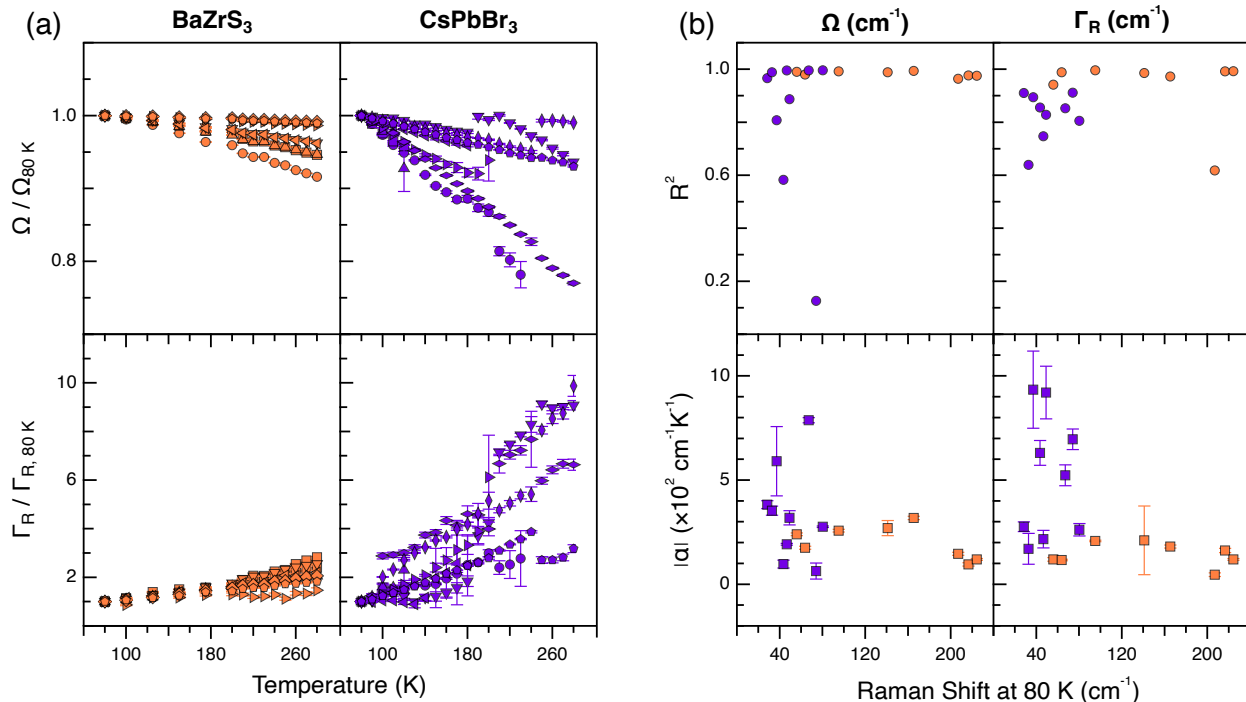


FIG. 5. Analysis of Raman Spectra: (a) Frequencies (Ω , top) and linewidths (Γ_R , bottom) of the first-order peaks of BaZrS₃ (left) and CsPbBr₃ (right) as a function of temperature, relative to the value at 80 K. Different markers mark different peaks. (b) Linear regression results (R^2 , top, and slopes α , bottom) of the temperature-dependent frequencies (left) and linewidths (right) of BaZrS₃ and CsPbBr₃, between 80 and 280 K. The results are plotted as a function of peak frequency at 80 K. Orange and purple markers are for BaZrS₃ and CsPbBr₃, respectively. Error bars indicate one standard deviation as determined by the numerical fitting process.

Einstein occupation factor [97–99] (see Sec. S3 of the SM [60]). We focus on the prominent peaks because they yield the most confident fits. In Fig. 5(a) we present the vibrational frequency (Ω) and linewidth (Γ_R) of the prominent first-order peaks of BaZrS₃ (left panel, orange) and CsPbBr₃ (right panel, purple). The frequency and linewidth data are divided by their values at 80 K for ease of comparison (for original values, see Sec. S3 of the SM [60]). The Raman peaks of BaZrS₃ red shift and broaden linearly with increasing temperature, as is expected from perturbation theory for weak anharmonic effects [100, 101]. A slight change in slope near 200 K may relate to the observed increase in the low-frequency dielectric susceptibility in this same temperature range [12].

CsPbBr₃ exhibits a similar monotonic and linear trend in frequency and linewidth with increasing temperature up to 280 K, above which the data deviate substantially, including sharp blue shifts and rapidly increasing linewidth (see Fig. S8 in the SM [60]). We attribute these changes to two causes: (1) the thermal population of all the optical phonons above $T_{\text{Debye}} \approx 250$ K, and (2) the incipient orthorhombic-to-tetragonal phase transition at $T \approx 360$ K. Peak broadening with increasing temperature is attributed to the shortening of vibrational lifetime due to phonon-phonon scattering [98, 100, 101]. It

is apparent that the structural dynamics of BaZrS₃ exhibit minor thermal effects and are less impacted by anharmonic vibrational interactions than the dynamics of CsPbBr₃ [100, 101].

The extent of anharmonicity in the phonon dynamics can be further quantified by analyzing the deviation from linearity of the temperature dependence of the phonon frequencies and linewidths. A linear temperature dependence is expected within perturbation theory for weak phonon-phonon interactions. Therefore, strong and anharmonic interactions are indicated by deviations from linearity. In Fig. 5(b), we present the R^2 parameter and the absolute value of the slope ($|\alpha|$) of linear regression to the $\Omega(T)$ and $\Gamma_R(T)$ (for mean values, see Sec. S3 of the SM [60]). For CsPbBr₃, the R^2 values are far from unity, and the slopes are much larger than for BaZrS₃. This analysis further supports the conclusion that anharmonic effects in BaZrS₃ can be modeled as a weak perturbation, whereas in CsPbBr₃, they substantially change the lattice vibrational properties.

IV. DISCUSSION

Lead halide perovskites excel as PV absorbers largely due to their slow rates of defect-assisted Shockley-Read-

Hall (SRH) nonradiative free energy loss. Electron-phonon interactions mediate SRH recombination processes, converting excited-state energy into phonons and heat [25, 27, 31, 102]. Therefore, by focusing on vibrational properties and electron-phonon interactions, we can better understand the origin of the excellent PV performance of the halides and identify promising new semiconductors for thin-film PV.

Chalcogenide perovskites have an untested potential for PV mainly due to challenges in thin-film synthesis. There are few published measurements of the optoelectronic properties of chalcogenide perovskites, and the results are ambiguous. We reported time-resolved PL (TRPL) data that suggest long radiative lifetimes in BaZrS_3 and the Ruddlesden-Popper compound $\text{Ba}_3\text{Zr}_2\text{S}_7$, comparable to lead halides and other high-performing PV materials such as CIGS [19]. Several research groups have reported band-edge PL measured from BaZrS_3 samples of various form factors, including solution-processed nanoparticles and thin films made by sulfurizing oxide precursors [16, 18, 20, 21]. However, quantitative PL measurements (albeit on early-stage powder samples) suggest low quantum efficiency and low quasi-Fermi level splitting (i.e., open-circuit voltage potential) [9]. Our experience of measuring PL on BaZrS_3 single crystals is that many samples have weak or no measurable band-edge PL and that the band-edge PL can be strongly position dependent. To this point, the BaZrS_3 crystals used in our prior TRPL study were produced by the same process as the crystal studied here, but were prepared in different batches. We have observed similar variability in measuring PL on epitaxial thin films (unpublished). Substantial sample-to-sample variation, combined with challenges in synthesis and defect control, makes it difficult to assess the technological potential of chalcogenide perovskites.

We also note that the presence of long-lived traps in the detailed balance with only one band edge (e.g., electron traps with vanishing hole capture likelihood) would slow the decay to equilibrium after pulsed excitation. For a direct band-gap semiconductor such as BaZrS_3 , this would be observed as a long TRPL lifetime that could coexist with a low PL quantum yield.

SRH recombination is much faster in BaZrS_3 than in CsPbBr_3 due to an unidentified recombination pathway that is active even at low temperatures, implying that it has a very low thermal activation energy [Fig. 2(b)]. The theory of multiphonon nonradiative recombination highlights the importance of the overlap between the vibrational wavefunctions of the initial and final electronic states, consistent with the Franck-Condon principle [50]. Model calculations for a harmonic lattice indicate a steep dependence of SRH recombination rate on phonon energy [102]. Lower phonon energy means more phonons are needed to participate in nonradiative recombination processes. Within this model, the overlap of vibrational wavefunctions is suppressed with increasing phonon number. Therefore, the lower phonon frequency in CsPbBr_3

compared to BaZrS_3 may explain the difference in SRH recombination rates, even if the concentration and properties of defects are similar.

The same harmonic model also predicts that SRH recombination rates increase with the extent of lattice distortion accompanying defect charge capture; this distortion can be parameterized by the Huang-Rhys factor [50, 102]. These lattice distortions often result in long-lived charge trapping and are responsible for persistent photoconductivity in many semiconductors; it is related to DX-center phenomena in III-V compounds, and we termed it defect-level switching in the context of resistive switches [103–106]. There have been many studies of persistent photoconductivity in halide perovskites. Still, there is no clear model for defects in CsPbBr_3 [107–110]. The timescale of photoconductivity decay in BaZrS_3 crystals depends on sample polishing, suggesting that defects introduced during plastic deformation (e.g., dislocations) may be effective charge traps with large Huang-Rhys factors [36]. However, these observations may not be directly relevant to the Huang-Rhys factors of recombination-active defects, which may differ from the traps that influence photoconductivity decay. Further, it has been suggested that polaronic effects resulting from strong charge-lattice coupling – including Fröhlich (i.e., large effective mass states) polarons and defect-localized polarons – may suppress SRH recombination rates by screening dissimilar charges [111, 112]. It is likely that a full quantum calculation of electron-phonon interactions, combined with first-principles modeling of the known crystal structures and the most likely recombination-active defects, will be required to resolve these questions over the role of strong electron-phonon coupling on SRH recombination rates.

The effect of anharmonic phonon-phonon interactions on SRH recombination remains an open question. It would be enlightening to compare a model calculation of vibrational wavefunction overlap during multiphonon recombination with and without anharmonic lattice vibrations and for varying Huang-Rhys factor for otherwise similar phonon energies. Model system calculations could help to understand the conflated effects of low-phonon energy, lattice distortion at defects, and anharmonic vibrations on SRH recombination rates. However, full quantum calculations are likely needed to accurately model the differences in carrier capture rates between halide and chalcogenide perovskites.

The discussion to this point has focused on the effects of lattice vibrations on SRH recombination rates via the carrier capture processes. However, another significant unknown is the concentration of recombination-active defects. Anharmonic vibrations in halide perovskites indicate rather soft bonds, a pliable crystal lattice, and low activation energy for ionic diffusion [113–115]. Therefore, anharmonic vibration in lead halide perovskites may improve optoelectronic performance by accelerating the elimination of point defects by annealing, even at room temperature (termed “self-healing”) [51, 116–119]. The

same accelerated mass transport may hasten degradation mechanisms. BaZrS_3 , in contrast, requires a high temperature to form and, therefore, is likely to retain quenched-in defects (e.g., chemical impurities). This suggests that the PL yield and PV performance of chalcogenide perovskites will depend more strongly on defect control during sample processing than the performance of halide perovskites.

Defect characterization by methods such as deep-level transient spectroscopy (DLTS) and related forms of impedance spectroscopy could directly measure defect concentrations and quantify the extent of self-healing [120–126]. Interpretation of DLTS data is challenging for halide perovskites due to mixed ionic-electronic conduction, but progress has been reported [127]. Similar studies have not yet been undertaken for chalcogenide perovskites.

V. CONCLUSIONS

We have presented a detailed spectroscopic comparison between two perovskite semiconductors, the chalcogenide BaZrS_3 and the well-studied halide CsPbBr_3 . We find that the PL emission yield of CsPbBr_3 is over four orders of magnitude higher than that of BaZrS_3 for the single-crystal samples considered here, indicative of a far higher concentration of very low-barrier, nonradiative recombination centers in BaZrS_3 . *Ab initio* simulations show that BaZrS_3 exhibits higher LO vibrational frequencies than CsPbBr_3 : this may increase carrier capture cross sections due to Franck-Condon effects [50]. Raman scattering results suggest that the strongly anharmonic structural dynamics in CsPbBr_3 , relative to BaZrS_3 , may reduce defect concentration through accelerated solid-state diffusion and annealing [51].

We are optimistic that the fast SRH recombination rates observed here for BaZrS_3 can be reduced through sample processing. Large sample-to-sample variability, and preliminary results on BaZrS_3 epitaxial thin films (not shown), suggest that low PL yield may not be intrinsic to BaZrS_3 . The usefulness of BaZrS_3 (and likely other chalcogenide perovskites) for optoelectronic applications will hinge on continued progress in defect control during synthesis and processing – as has been historically required for other semiconductors.

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- [1] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, Hybrid organic—inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties, *Nature Reviews Materials*, 16011 (2016).
- [2] M. Grätzel, The light and shade of perovskite solar cells, *Nature Materials* **13**, 838 (2014).
- [3] S. D. Stranks and H. J. Snaith, Metal-halide perovskites for photovoltaic and light-emitting devices, *Nature Nanotechnology* **10**, 391 (2015).
- [4] H. He, Q. Yu, H. Li, J. Li, J. Si, Y. Jin, N. Wang, J. Wang, J. He, X. Wang, Y. Zhang, and Z. Ye, Exciton localization in solution-processed organolead trihalide perovskites, *Nature Communications* **7**, 1 (2016).
- [5] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, and O. M. Bakr, Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals, *Science* **347**, 519 (2015).
- [6] S. D. Stranks, V. M. Burlakov, T. Leijtens, J. M. Ball, A. Goriely, and H. J. Snaith, Recombination Kinetics in Organic-Inorganic Perovskites: Excitons, Free Charge, and Subgap States, *Physical Review Applied* **2**, 1 (2014).
- [7] Y. Yamada, T. Yamada, L. Q. Phuong, N. Maruyama, H. Nishimura, A. Wakamiya, Y. Murata, and Y. Kanemitsu, Dynamic Optical Properties of CH₃NH₃PbI₃ Single Crystals As Revealed by One- and Two-Photon Excited Photoluminescence Measurements, *Journal of the American Chemical Society* **137**, 10456 (2015).
- [8] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, and L. M. Herz, High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites, *Adv. Mater.* **26**, 1584 (2014).
- [9] S. Niu, H. Huyan, Y. Liu, M. Yeung, K. Ye, L. Blanke-meier, T. Orvis, D. Sarkar, D. J. Singh, R. Kapadia, and J. Ravichandran, Bandgap Control via Structural and Chemical Tuning of Transition Metal Perovskite Chalcogenides, *Advanced Materials* **29**, 16 (2017).
- [10] R. Jaramillo and J. Ravichandran, In praise and in search of highly-polarizable semiconductors: Technological promise and discovery strategies, *APL Materials* **7**, 100902 (2019).
- [11] Y.-Y. Sun, M. L. Agiorgousis, P. Zhang, and S. Zhang, Chalcogenide Perovskites for Photovoltaics, *Nano Letters* **15**, 581 (2015).
- [12] S. Filippone, B. Zhao, S. Niu, N. Z. Koocher, D. Silevitch, I. Fina, J. M. Rondinelli, J. Ravichandran, and R. Jaramillo, Discovery of highly polarizable semiconductors BaZrS₃ and Ba₃Zr₂S₇, *Physical Review Materials* **4**, 10.1103/PhysRevMaterials.4.091601 (2020).
- [13] K. Ye, N. Z. Koocher, S. Filippone, S. Niu, B. Zhao, M. Yeung, S. Bone, A. J. Robinson, P. Vora, A. Schleife, L. Ju, A. Boubnov, J. M. Rondinelli, J. Ravichandran, and R. Jaramillo, Low-energy electronic structure of perovskite and Ruddlesden-Popper semiconductors in the Ba-Zr-S system probed by bond-selective polarized x-ray absorption spectroscopy, infrared reflectivity, and Raman scattering, *Physical Review B* **105**, 195203 (2022).
- [14] S. Niu, J. Milam-Guerrero, Y. Zhou, K. Ye, B. Zhao, B. C. Melot, and J. Ravichandran, Thermal stability study of transition metal perovskite sulfides, *Journal of Materials Research* **33**, 4135 (2018).
- [15] I. Sadeghi, K. Ye, M. Xu, Y. Li, J. M. LeBeau, and R. Jaramillo, Making BaZrS₃ Chalcogenide Perovskite Thin Films by Molecular Beam Epitaxy, *Advanced Functional Materials* **31**, 2105563 (2021).
- [16] X. Wei, H. Hui, C. Zhao, C. Deng, M. Han, Z. Yu, A. Sheng, P. Roy, A. Chen, J. Lin, D. F. Watson, Y.-Y. Sun, T. Thomay, S. Yang, Q. Jia, S. Zhang, and H. Zeng, Realization of BaZrS₃ chalcogenide perovskite thin films for optoelectronics, *Nano Energy* **68**, 104317 (2020).
- [17] M. Surendran, H. Chen, B. Zhao, A. S. Thind, S. Singh, T. Orvis, H. Zhao, J.-K. Han, H. Htoon, M. Kawasaki, R. Mishra, and J. Ravichandran, Epitaxial Thin Films of a Chalcogenide Perovskite, *Chemistry of Materials* **33**, 7457 (2021).
- [18] C. Comparotto, A. Davydova, T. Ericson, L. Riekehr, M. V. Moro, T. Kubart, and J. Scragg, Chalcogenide Perovskite BaZrS₃: Thin Film Growth by Sputtering and Rapid Thermal Processing, *ACS Applied Energy Materials* **3**, 2762 (2020).
- [19] K. Ye, B. Zhao, B. T. Diroll, J. Ravichandran, and R. Jaramillo, Time-resolved photoluminescence studies of perovskite chalcogenides, *Faraday Discussions* **239**, 146 (2022).
- [20] A. Pradhan, M. Uible, S. Agarwal, J. Turnley, S. Khandelwal, J. Peterson, D. Blach, R. Swope, L. Huang, S. Bart, and R. Agrawal, *Angew Chem Int Ed - 2023 - Pradhan - Synthesis of BaZrS₃ and BaHfS₃ Chalcogenide Perovskite Films Using Single-Phase-2.pdf*, *Angewandte Chemie International Edition* **62**, e202301049 (2023).
- [21] R. Yang, A. D. Jess, C. Fai, and C. J. Hages, Low-Temperature, Solution-Based Synthesis of Luminescent Chalcogenide Perovskite BaZrS₃ Nanoparticles, *Journal of the American Chemical Society* **144**, 15928 (2022).
- [22] R. Sharma, Z. Dai, L. Gao, T. M. Brenner, L. Yadgarov, J. Zhang, Y. Rakita, R. Korobko, A. M. Rappe, and O. Yaffe, Elucidating the atomistic origin of anharmonicity in tetragonal ch₃nh₃pbi₃ with raman scattering, *Phys. Rev. Mater.* **4**, 092401 (2020).
- [23] O. Yaffe, Y. Guo, L. Z. Tan, D. A. Egger, T. D. Hull, C. C. Stoumpos, F. Zheng, T. F. Heinz, L. Kronik, M. G. Kanatzidis, J. S. Owen, A. M. Rappe, M. A. Pimenta, and L. E. Brus, Local Polar Fluctuations in Lead Halide Perovskite Crystals, *Physical Review Letters* **118**, 1 (2017).
- [24] Y. Guo, O. Yaffe, D. W. Paley, A. N. Beecher, T. D. Hull, G. Szpak, J. S. Owen, L. E. Brus, and M. A. Pi-

- menta, Interplay between organic cations and inorganic framework and incommensurability in hybrid lead-halide perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$, *Phys. Rev. Mater.* **1**, 042401 (2017).
- [25] M. Mayers, L. Z. Tan, D. A. Egger, A. M. Rappe, and D. R. Reichman, How Lattice and Charge Fluctuations Control Carrier Dynamics in Halide Perovskites, *Nano Letters* **18**, acs.nanolett.8b04276 (2018).
- [26] L. D. Whalley, J. M. Skelton, J. M. Frost, and A. Walsh, Phonon anharmonicity, lifetimes, and thermal transport in $\text{CH}_3\text{NH}_3\text{PbI}_3$ from many-body perturbation theory, *Phys. Rev. B* **94**, 220301 (2016).
- [27] D. A. Egger, A. Bera, D. Cahen, G. Hodes, T. Kirchartz, L. Kronik, R. Lovrincic, A. M. Rappe, D. R. Reichman, and O. Yaffe, What Remains Unexplained about the Properties of Halide Perovskites?, *Adv. Mater.* **30**, 1800691 (2018).
- [28] F. Panzer, C. Li, T. Meier, A. Köhler, and S. Huettnner, Impact of Structural Dynamics on the Optical Properties of Methylammonium Lead Iodide Perovskites, *Adv. Energy Mater.* **7**, 1700286 (2017).
- [29] S. A. Seidl, X. Zhu, G. Reuveni, S. Aharon, C. Gehrman, S. Caicedo-Dávila, O. Yaffe, and D. A. Egger, Anharmonic Fluctuations Govern the Band Gap of Halide Perovskites, *Phys. Rev. Mater.* **7**, L092401 (2023).
- [30] C. Gehrman and D. A. Egger, Dynamic shortening of disorder potentials in anharmonic halide perovskites, *Nature Communications* **10**, 3141 (2019).
- [31] M. J. Schilcher, P. J. Robinson, D. J. Abramovitch, L. Z. Tan, A. M. Rappe, D. R. Reichman, and D. A. Egger, The Significance of Polarons and Dynamic Disorder in Halide Perovskites, *ACS Energy Letters* **6**, 2162 (2021).
- [32] S. Niu, B. Zhao, K. Ye, E. Bianco, J. Zhou, M. E. McConney, C. Settens, R. Haiges, R. Jaramillo, and J. Ravichandran, Crystal growth and structural analysis of perovskite chalcogenide BaZrS_3 and Ruddlesden-Popper phase $\text{Ba}_3\text{Zr}_2\text{S}_7$, *Journal of Materials Research* **34**, 3819 (2019).
- [33] T. Lanigan-Atkins, X. He, M. J. Krogstad, D. M. Pajerowski, D. L. Abernathy, G. N. Xu, Z. Xu, D. Y. Chung, M. G. Kanatzidis, S. Rosenkranz, R. Osborn, and O. Delaire, Two-dimensional overdamped fluctuations of the soft perovskite lattice in CsPbBr_3 , *Nature Materials* **20**, 977 (2021).
- [34] Y. Nishigaki, T. Nagai, M. Nishiwaki, T. Aizawa, M. Kozawa, K. Hanzawa, Y. Kato, H. Sai, H. Hiramatsu, H. Hosono, and H. Fujiwara, Extraordinary Strong Band-Edge Absorption in Distorted Chalcogenide Perovskites, *Solar RRL* **4**, 1900555 (2020).
- [35] W. Li, S. Niu, B. Zhao, R. Haiges, Z. Zhang, J. Ravichandran, and A. Janotti, Band gap evolution in Ruddlesden-Popper phases, *Physical Review Materials* **3**, 101601 (2019).
- [36] B. Zhao, H. Chen, R. Ahsan, F. Hou, E. R. Hoglund, S. Singh, M. Shanmugasundaram, H. Zhao, A. V. Krayev, H. Htoon, P. E. Hopkins, J. Seidel, R. Kapadia, and J. Ravichandran, Photoconductive effects in single crystals of bazrs_3 , *ACS Photonics* **11**, 1109 (2024).
- [37] I. Sadeghi, J. Van Sambeek, T. Simonian, M. Xu, K. Ye, T. Cai, V. Nicolosi, J. M. LeBeau, and R. Jaramillo, Expanding the Perovskite Periodic Table to Include Chalcogenide Alloys with Tunable Band Gap Spanning 1.5–1.9 eV, *Advanced Functional Materials* **33**, 2304575 (2023).
- [38] K. Ye, I. Sadeghi, M. Xu, J. Van Sambeek, T. Cai, J. Dong, R. Kothari, J. M. LeBeau, and R. Jaramillo, A processing route to chalcogenide perovskites alloys with tunable band gap via anion exchange, *Advanced Functional Materials* , 2405135.
- [39] N. Kumar, J. Rani, and R. Kurchania, Advancement in csppbr_3 inorganic perovskite solar cells: Fabrication, efficiency and stability, *Solar Energy* **221**, 197 (2021).
- [40] S. Ullah, J. Wang, P. Yang, L. Liu, S.-E. Yang, T. Xia, H. Guo, and Y. Chen, All-inorganic csppbr_3 perovskite: a promising choice for photovoltaics, *Materials Advances* **2**, 646 (2021).
- [41] L. Clinckemalie, D. Valli, M. B. Roeffaers, J. Hofkens, B. Pradhan, and E. Debroye, Challenges and opportunities for csppbr_3 perovskites in low- and high-energy radiation detection, *ACS Energy Letters* **6**, 1290 (2021).
- [42] J. Yu, G. Liu, C. Chen, Y. Li, M. Xu, T. Wang, G. Zhao, and L. Zhang, Perovskite csppbr_3 crystals: growth and applications, *Journal of Materials Chemistry C* **8**, 6326 (2020).
- [43] P. Cheng, Z. Liu, R. Kang, J. Zhou, X. Wang, J. Zhao, and Z. Zuo, Growth and high-performance photodetectors of csppbr_3 single crystals, *ACS Omega* **8**, 26351 (2023).
- [44] Y. Rakita, N. Kedem, S. Gupta, A. Sadhanala, V. Kalchenko, M. L. Böhm, M. Kulbak, R. H. Friend, D. Cahen, and G. Hodes, Low-Temperature Solution-Grown CsPbBr_3 Single Crystals and Their Characterization, *Crystal Growth and Design* **16**, 5717 (2016).
- [45] Y. He, L. Matei, H. J. Jung, K. M. McCall, M. Chen, C. C. Stoumpos, Z. Liu, J. A. Peters, D. Y. Chung, B. W. Wessels, M. R. Wasielewski, V. P. Dravid, A. Burger, and M. G. Kanatzidis, High spectral resolution of gamma-rays at room temperature by perovskite csppbr_3 single crystals, *Nature Communications* **9**, 1609 (2018).
- [46] M. Zhang, Z. Zheng, Q. Fu, Z. Chen, J. He, S. Zhang, L. Yan, Y. Hu, and W. Luo, Growth and characterization of all-inorganic lead halide perovskite semiconductor csppbr_3 single crystals, *CrystEngComm* **19**, 6797 (2017).
- [47] J. Cheng, Z. Fan, and J. Dong, Research progress of green solvent in csppbr_3 perovskite solar cells, *Nanomaterials* **13**, 991 (2023).
- [48] Y. Feng, L. Pan, H. Wei, Y. Liu, Z. Ni, J. Zhao, P. N. Rudd, L. R. Cao, and J. Huang, Low defects density csppbr_3 single crystals grown by an additive assisted method for gamma-ray detection, *Journal of Materials Chemistry C* **8**, 11360 (2020).
- [49] D. N. Dirin, I. Cherniukh, S. Yakunin, Y. Shynkarenko, and M. V. Kovalenko, Solution-grown csppbr_3 perovskite single crystals for photon detection, *Chemistry of Materials* **28**, 8470 (2016).
- [50] B. Das, I. Aguilera, U. Rau, and T. Kirchartz, What is a deep defect? Combining Shockley-Read-Hall statistics with multiphonon recombination theory, *Physical Review Materials* **4**, 024602 (2020).
- [51] D. Cahen, L. Kronik, and G. Hodes, Are Defects in Lead-Halide Perovskites Healed, Tolerated, or Both?, *ACS Energy Letters* **6**, 4108 (2021).
- [52] Y. Guo, O. Yaffe, T. D. Hull, J. S. Owen, D. R. Reichman, and L. E. Brus, Dynamic Emission Stokes Shift and Liquid-Like Dielectric Solvation of Band Edge Car-

- riers in Lead-Halide Perovskites, *Nature Communications* **10**, 1175 (2019).
- [53] M. Menahem, N. Benshalom, M. Asher, S. Aharon, R. Korobko, O. Hellman, and O. Yaffe, Disorder origin of Raman scattering in perovskite single crystals, *Physical Review Materials* **7**, 044602 (2023).
- [54] D. Han, K. Yang, C. Bai, F. Chen, Z. Sun, Y. Wang, H. Ji, Z. Yang, and X. Tang, Thermal and chemical durability of metal halide perovskite CsPbBr_3 single crystals, *Chemical Engineering Journal* **475**, 146209 (2023).
- [55] M. Menahem, Z. Dai, S. Aharon, R. Sharma, M. Asher, Y. Diskin-Posner, R. Korobko, A. M. Rappe, and O. Yaffe, Strongly Anharmonic Octahedral Tilting in Two-Dimensional Hybrid Halide Perovskites, *ACS Nano* **15**, 10153 (2021).
- [56] R. Sharma, M. Menahem, Z. Dai, L. Gao, R. Korobko, I. Pinkas, A. M. Rappe, O. Yaffe, T. M. Brenner, L. Yadgarov, J. Zhang, Y. Rakita, R. Korobko, I. Pinkas, A. M. Rappe, and O. Yaffe, Lattice mode symmetry analysis of the orthorhombic phase of methylammonium lead iodide using polarized Raman, *Physical Review Materials* **4**, 051601 (2020).
- [57] M. Asher, D. Angerer, R. Korobko, Y. Diskin-Posner, D. A. Egger, and O. Yaffe, Anharmonic Lattice Vibrations in Small-Molecule Organic Semiconductors, *Advanced Materials* **32**, 10.1002/adma.201908028 (2020).
- [58] A. Cohen, T. M. Brenner, J. Klarbring, R. Sharma, D. H. Fabini, R. Korobko, P. K. Nayak, O. Hellman, and O. Yaffe, Diverging expressions of anharmonicity in halide perovskites, *Advanced Materials* **34**, 2107932 (2022).
- [59] M. Asher, M. Bardini, L. Catalano, R. Jouclas, G. Schweicher, J. Liu, R. Korobko, A. Cohen, Y. Geerts, D. Beljonne, and O. Yaffe, Mechanistic View on the Order-Disorder Phase Transition in Amphidynamic Crystals, *The Journal of Physical Chemistry Letters* **14**, 1570 (2023).
- [60] See Supplemental Material at <https://link.aps.org/supplemental/> for additional Raman spectra and fitting, derivations of the equations for the numerical simulation and additional results, and fit results to the model.
- [61] J. W. Bennett, I. Grinberg, and A. M. Rappe, Effect of substituting of S for O: The sulfide perovskite BaZrS_3 investigated with density functional theory, *Physical Review B* **79**, 235115 (2009).
- [62] G. Ermolaev, A. P. Pushkarev, A. Zhizhchenko, A. A. Kuchmizhak, I. Iorsh, I. Kruglov, A. Mazitov, A. Ishteev, K. Konstantinova, D. Saranin, A. Slavich, D. Stosic, E. S. Zhukova, G. Tselikov, A. Di Carlo, A. Arsenin, K. S. Novoselov, S. V. Makarov, and V. S. Volkov, Giant and Tunable Excitonic Optical Anisotropy in Single-Crystal Halide Perovskites, *Nano Letters* **23**, 2570 (2023).
- [63] D. Bimberg, M. Sondergeld, and E. Grobe, Thermal dissociation of excitons bounds to neutral acceptors in high-purity GaAs, *Physical Review B* **4**, 3451 (1971).
- [64] J. D. Lambkin, L. Considine, S. Walsh, G. M. O'Connor, C. J. McDonagh, and T. J. Glynn, Temperature dependence of the photoluminescence intensity of ordered and disordered $\text{In}_{0.48}\text{Ga}_{0.52}\text{P}$, *Applied Physics Letters* **65**, 73 (1994).
- [65] M. H. Wolter, R. Carron, E. Avancini, B. Bissig, T. P. Weiss, S. Nishiwaki, T. Feurer, S. Buecheler, P. Jackson, W. Witte, and S. Siebentritt, How band tail recombination influences the open-circuit voltage of solar cells, *Prog Photovolt Res Appl.* **30**, 702 (2022).
- [66] X. Wang, D. Yu, and S. Xu, Determination of absorption coefficients and Urbach tail depth of ZnO below the bandgap with two-photon photoluminescence, *Optics Express* **28**, 13817 (2020).
- [67] N. Falsini, G. Roini, A. Ristori, N. Calisi, F. Biccari, and A. Vinattieri, Analysis of the Urbach tail in cesium lead halide perovskites, *Journal of Applied Physics* **131**, 010902 (2022).
- [68] F. Knoop, N. Shulumba, A. Castellano, J. P. A. Batista, R. Farris, M. J. Verstraete, M. Heine, D. Broido, D. S. Kim, J. Klarbring, I. A. Abrikosov, S. I. Simak, and O. Hellman, TDEP: Temperature Dependent Effective Potentials, *Journal of Open Source Software* **9**, 6150 (2024).
- [69] N. Benshalom, G. Reuveni, R. Korobko, O. Yaffe, and O. Hellman, Dielectric response of rock-salt crystals at finite temperatures from first principles, *Physical Review Materials* **6**, 033607 (2022).
- [70] A. v. Roekeghem, J. Carrete, and N. Mingo, Quantum Self-Consistent Ab-Initio Lattice Dynamics, *Computer Physics Communications* **263**, 107945 (2021).
- [71] P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. d. Gironcoli, P. Delugas, F. F. Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, and S. Baroni, Quantum ESPRESSO toward the exascale, *The Journal of Chemical Physics* **152**, 154105 (2020).
- [72] R. Bianco, I. Errea, L. Paulatto, M. Calandra, and F. Mauri, Second-order structural phase transitions, free energy curvature, and temperature-dependent anharmonic phonons in the self-consistent harmonic approximation: Theory and stochastic implementation, *Physical Review B* **96**, 014111 (2017).
- [73] N. Shulumba, O. Hellman, and A. J. Minnich, Intrinsic localized mode and low thermal conductivity of PbSe , *Physical Review B* **95**, 014302 (2017).
- [74] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. d. Gironcoli, P. Delugas, R. A. D. Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. Otero-de-la Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, *Journal of Physics: Condensed Matter* **29**, 465901 (2017).
- [75] M. Schlipf and F. Gygi, Optimization algorithm for the generation of ONCV pseudopotentials, *Computer Physics Communications* **196**, 36 (2015).
- [76] O. Hellman and I. A. Abrikosov, Temperature-dependent effective third-order interatomic force constants from first principles, *Physical Review B* **88**, 144301 (2013).
- [77] D. R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, *Physical Review B* **88**, 085117 (2013).

- [78] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, *APL Materials* **1**, 011002 (2013).
- [79] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. d. Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *Journal of Physics: Condensed Matter* **21**, 395502 (2009).
- [80] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Ab initio molecular simulations with numeric atom-centered orbitals, *Computer Physics Communications* **180**, 2175 (2009).
- [81] A. E. Mattsson, R. Armiento, J. Paier, G. Kresse, J. M. Wills, and T. R. Mattsson, The AM05 density functional applied to solids, *The Journal of Chemical Physics* **128**, 084714 (2008).
- [82] R. Armiento and A. E. Mattsson, Functional designed to include surface effects in self-consistent density functional theory, *Physical Review B* **72**, 085108 (2005).
- [83] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Physical Review Letters* **77**, 3865 (1996), pBE.
- [84] M. Fox, Phonons, in *Optical Properties of Solids* (Oxford University Press, New York, USA, 2010) pp. 273–276, 2nd ed.
- [85] N. Yazdani, M. I. Bodnarchuk, F. Bertolotti, N. Masciocchi, I. Furera, B. Guzelturk, B. L. Cotts, M. Zajac, G. Rainò, M. Jansen, S. C. Boehme, M. Yarema, M. F. Lin, M. Kozina, A. Reid, X. Shen, S. Weathersby, X. Wang, E. Vauthey, A. Guagliardi, M. V. Kovalenko, V. Wood, and A. M. Lindenberg, Coupling to octahedral tilts in halide perovskite nanocrystals induces phonon-mediated attractive interactions between excitons, *Nature Physics* **20**, 47 (2024).
- [86] S. Perera, H. Hui, C. Zhao, H. Xue, F. Sun, C. Deng, N. Gross, C. Milleville, X. Xu, D. F. Watson, B. Weinstein, Y.-Y. Sun, S. Zhang, and H. Zeng, Chalcogenide Perovskites – an Emerging Class of Ionic Semiconductors, *Nano Energy* **22**, 129 (2016).
- [87] N. Gross, Y.-Y. Sun, S. Perera, H. Hui, X. Wei, S. Zhang, H. Zeng, and B. A. Weinstein, Stability and Band-Gap Tuning of the Chalcogenide Perovskite BaZrS₃ in Raman and Optical Investigations at High Pressures, *Physical Review Applied* **8**, 044014 (2017).
- [88] J. Xu, Y. Fan, W. Tian, L. Ye, Y. Zhang, Y. Tian, Y. Han, and Z. Shi, Enhancing the optical absorption of chalcogenide perovskite BaZrS₃ by optimizing the synthesis and post-processing conditions, *Journal of Solid State Chemistry* **307**, 122872 (2022).
- [89] Z. Yu, X. Wei, Y. Zheng, H. Hui, M. Bian, S. Dhole, J.-H. Seo, Y.-Y. Sun, Q. Jia, S. Zhang, S. Yang, and H. Zeng, Chalcogenide perovskite BaZrS₃ thin-film electronic and optoelectronic devices by low temperature processing, *Nano Energy* **85**, 105959 (2021).
- [90] M. Cardona and G. Guntherodt, *Light Scattering in Solids II - Basic Concepts and Instrumentation* (Springer-Verlag, Berlin, 1982) pp. 1–252.
- [91] C. H. Perry, J. H. Fertel, and T. F. McNelly, Temperature dependence of the Raman spectrum of SrTiO₃ and KTaO₃, *The Journal of Chemical Physics* **47**, 1619 (1967).
- [92] P. McMillan and N. Ross, The Raman spectra of several orthorhombic calcium oxide perovskites, *Physics and Chemistry of Minerals* **16**, 21 (1988).
- [93] R. Ouillon, J.-P. Pinan-Lucarre, P. Ranson, P. Pruzan, S. K. Mishra, R. Ranjan, and D. Pandey, A Raman scattering study of the phase transitions in SrTiO₃ and in the mixed system (Sr_{1-x}Ca_x)TiO₃ at ambient pressure from T = 300 K down to 8 K, *Journal of Physics: Condensed Matter* **14**, 2079 (2002).
- [94] G. Reuveni, Y. Diskin-Posner, C. Gehrman, S. Godse, G. G. Gkikas, I. Buchine, S. Aharon, R. Korobko, C. C. Stoumpos, D. A. Egger, and O. Yaffe, Static and Dynamic Disorder in Formamidinium Lead Bromide Single Crystals, *The Journal of Physical Chemistry Letters* **14**, 1288 (2023).
- [95] M. Born and M. Bradburn, The theory of the Raman effect in crystals, in particular rocksalt., *Proceedings of the Royal Society A* **188**, 161 (1947).
- [96] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors, Physics and Materials Properties*, 4th ed. (Springer, Berlin/Heidelberg, 2010) p. 775.
- [97] P. C. Kwok, Green's function method in lattice dynamics (Academic Press, New York, USA, 1968) pp. 213–303.
- [98] A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press, New York, USA, 1971) pp. 1–67, 2nd ed.
- [99] S. A. Safra, G. Dresselhaus, and B. Lax, Theory of spin-disorder Raman scattering in magnetic semiconductors, *Phys. Rev. B* **16**, 2749 (1977).
- [100] E. Haro, M. Balkanski, R. F. Wallis, and K. H. Wanser, Theory of the anharmonic damping and shift of the Raman mode in silicon, *Physical Review B* **34**, 5358 (1986).
- [101] J. Menéndez and M. Cardona, Temperature dependence of the first-order Raman scattering by phonons in Si, Ge, and α -Sn: Anharmonic effects, *Physical Review B* **29**, 2051 (1984).
- [102] T. Kirchartz, T. Markvart, U. Rau, and D. A. Egger, Impact of Small Phonon Energies on the Charge-Carrier Lifetimes in Metal-Halide Perovskites, *Journal of Physical Chemistry Letters* **9**, 939 (2018).
- [103] D. V. Lang and R. A. Logan, Large-Lattice-Relaxation Model for Persistent Photoconductivity in Compound Semiconductors, *Physical Review Letters* **39**, 635 (1977).
- [104] P. M. Mooney, Deep donor levels (DX centers) in III-V semiconductors, *Journal of Applied Physics* **67**, R1 (1990).
- [105] H. Yin, A. Akey, and R. Jaramillo, Large and persistent photoconductivity due to hole-hole correlation in CdS, *Physical Review Materials* **2**, 084602 (2018).
- [106] H. Yin, A. Kumar, J. M. LeBeau, and R. Jaramillo, Defect-Level Switching for Highly Nonlinear and Hysteretic Electronic Devices, *Physical Review Applied* **15**, 014014 (2021).

- [107] Z. Liu, J. A. Peters, K. S. Bayikadi, V. Klepov, L. Pan, I. R. Pandey, M. G. Kanatzidis, and B. W. Wessels, Defects of perovskite semiconductor CsPbBr₃ investigated via photoluminescence and thermally stimulated current spectroscopies, *Journal of Applied Physics* **134**, 245101 (2023).
- [108] A. V. Cohen, D. A. Egger, A. M. Rappe, and L. Kronik, Breakdown of the Static Picture of Defect Energetics in Halide Perovskites: The Case of the Br Vacancy in CsPbBr₃, *Journal of Physical Chemistry Letters* **10**, 4490 (2019).
- [109] J. Kang and L. W. Wang, High Defect Tolerance in Lead Halide Perovskite CsPbBr₃, *Journal of Physical Chemistry Letters* **8**, 489 (2017).
- [110] M. Sebastian, J. A. Peters, C. C. Stoumpos, J. Im, S. S. Kostina, Z. Liu, M. G. Kanatzidis, A. J. Freeman, and B. W. Wessels, Excitonic emissions and above-band-gap luminescence in the single-crystal perovskite semiconductors CsPbBr₃ and CsPbI₃, *Physical Review B - Condensed Matter and Materials Physics* **92**, 235210 (2015).
- [111] D. Emin, Barrier to recombination of oppositely charged large polarons, *Journal of Applied Physics* **123**, 055105 (2018).
- [112] C. Franchini, M. Reticcioli, M. Setvin, and U. Diebold, Polarons in materials, *Nature Reviews Materials* **6**, 560 (2021).
- [113] T. M. Brenner, C. Gehrman, R. Korobko, T. Livneh, D. A. Egger, and O. Yaffe, Anharmonic host-lattice dynamics enable fast ion conduction in superionic AgI, *Physical Review Materials* **4**, 115402 (2020).
- [114] D. T. Limmer and N. S. Ginsberg, Photoinduced phase separation in the lead halides is a polaronic effect, *The Journal of Chemical Physics* **152**, 230901 (2020).
- [115] Y.-C. Zhao, W.-K. Zhou, X. Zhou, K.-H. Liu, D.-P. Yu, and Q. Zhao, Quantification of light-enhanced ionic transport in lead iodide perovskite thin films and its solar cell applications, *Science & Applications* **6**, 10.1038/lsa.2016.243 (2016).
- [116] S. Aharon, D. R. Ceratti, N. P. Jasti, L. Cremonesi, Y. Feldman, M. A. C. Potenza, G. Hodes, and D. Cahen, 2d pb-halide perovskites can self-heal photodamage better than 3d ones, *Advanced Functional Materials* **32**, 2113354 (2022).
- [117] B. P. Finkenauer, Akriti, K. Ma, and L. Dou, Degradation and Self-Healing in Perovskite Solar Cells, *ACS Applied Materials and Interfaces* **14**, 24073 (2022).
- [118] D. R. Ceratti, Y. Rakita, L. Cremonesi, R. Tenne, V. Kalchenko, M. Elbaum, D. Oron, M. A. C. Potenza, G. Hodes, and D. Cahen, Self-healing inside apbbr₃ halide perovskite crystals, *Advanced Materials* **30**, 1706273 (2018).
- [119] S. Parida, S. Kumar, S. Cherf, S. Aharon, D. Cahen, and B. Eren, Self-healing and -repair of nanomechanical damages in lead halide perovskites, *Advanced Functional Materials* **33**, 2304278 (2023).
- [120] E. M. Hutter, G. E. Eperon, S. D. Stranks, and T. J. Savenije, Charge Carriers in Planar and Meso-Structured Organic-Inorganic Perovskites: Mobilities, Lifetimes, and Concentrations of Trap States, *The Journal of Physical Chemistry Letters* **6**, 3082 (2015).
- [121] Y. Bi, E. M. Hutter, Y. Fang, Q. Dong, J. Huang, and T. J. Savenije, Charge Carrier Lifetimes Exceeding 15 μ s in Methylammonium Lead Iodide Single Crystals, *J. Phys. Chem. Lett* **7**, 45 (2016).
- [122] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, and T. C. Sum, Low-temperature solution-processed wavelength-tunable perovskites for lasing, *Nature Materials* **13**, 476 (2014).
- [123] Y. Lei, Y. Xu, M. Wang, G. Zhu, Z. Jin, Y. Lei, Y. Xu, M. Wang, Z. Jin, and G. Zhu, Origin, Influence, and Countermeasures of Defects in Perovskite Solar Cells, *Small* **17**, 2005495 (2021).
- [124] V. M. Le Corre, E. A. Duijnste, O. El Tambouli, J. M. Ball, H. J. Snaith, J. Lim, and L. J. A. Koster, Revealing Charge Carrier Mobility and Defect Densities in Metal Halide Perovskites via Space-Charge-Limited Current Measurements, *ACS Energy Letters* **6**, 1087 (2021).
- [125] L. M. Herz, Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites, *Annual Review of Physical Chemistry* **67**, 65 (2016).
- [126] J. W. Rosenberg, M. J. Legodi, Y. Rakita, D. Cahen, and M. Diale, Laplace current deep level transient spectroscopy measurements of defect states in methylammonium lead bromide single crystals, *Journal of Applied Physics* **122**, 145701 (2017).
- [127] S. Reichert, Q. An, Y.-W. Woo, A. Walsh, Y. Vaynzof, and C. Deibel, Probing the ionic defect landscape in halide perovskite solar cells, *Nature Communications* **11**, 6098 (2020).