2 42





ACS AUTHORCHOICE

Temperature-Dependent Optical Band Gap in CsPbBr₃, MAPbBr₃, and FAPbBr₃ Single Crystals

Giovanni Mannino, Ioannis Deretzis, Emanuele Smecca, Antonino La Magna, Alessandra Alberti,* Davide Ceratti,* and David Cahen



ABSTRACT: Single crystals represent a benchmark for understanding the bulk properties of halide perovskites. We have indeed studied the dielectric function of lead bromide perovskite single crystals (MAPbBr₃, CsPbBr₃ and for the first time FAPbBr₃) by spectroscopic ellipsometry in the range of 1-5 eV while varying the temperature from 183 to 440 K. An extremely low absorption coefficient in the sub-band gap region was found, indicating the high optical quality of all three crystals. We extracted the band gap values through critical point analysis showing that Tauc-based values are systematically underestimated. The two structural phase transitions, i.e., orthorhombic-tetragonal and tetragonal-cubic, show distinct optical behaviors, with the former having a discontinuous character. The cross-correlation of optical data with DFT calculations evidences the role of octahedral tilting in tailoring the value of the band gap at a given temperature, whereas differences in the thermal expansion affect the slope of the band gap trend as a function of temperature.

he strategy for choosing the lattice composition of photoactive halide perovskites is not unidirectional. It is sometimes based on the need of avoiding organic moieties in the composition, as this is thought to be a weak point for the decomposition of the materials through the formation of volatile species.¹⁻⁵ However, solar cells with the best performance still contain organic cations.^{6,7} It is at other times pushed by the need to increase the robustness of the inorganic lattice frame, with bromides preferred to iodides. Adding bromides increases the band gap compared to corresponding pure iodides, and this favors tandem coupling with silicon in combined photovoltaic technologies.^{8,9} Their relatively wide band gap is likewise exploited for other optoelectronic applications (LEDs and lasers). In addition to hybrid perovskites, recent developments push toward allinorganic or Cs-containing materials.^{10–12}

Single-crystal perovskites therefore represent benchmarks for the study of the intrinsic behavior of the bulk of those materials, free from morphological effects that are instead encountered in the polycrystalline counterparts.¹³

It was also disclosed that FA-based lead iodide and bromide single crystals exhibit diffusion lengths that are close or even above 10 μ m (respectively).¹⁴ Better carrier lifetime and lower dark carrier concentrations were also measured in FA-based lead iodides and bromides than in MAPbBr₃ single crystals. Furthermore, unlike the corresponding iodides, FA-based lead bromides take a stable cubic perovskite structure with space group $Pm\overline{3}m$ at room temperature.



CsPbBr_

Although large efforts were made to determine the UVvisible absorbance by spectrophotometric analyses, to the best of our knowledge very little is known about the optical and dielectric properties of single-crystal lead bromide perovskites.¹⁴⁻¹⁷ The literature on the optical constants of lead bromide perovskites is limited to CsPbBr₃ or MAPbBr₃ single crystals.¹⁸⁻²¹ In other cases, the study relies on nanocrystals rather than on millimeter-large single crystals.²²

Here we report a systematic study of the absorption coefficient and refractive index of bulk lead bromide perovskite single crystals (XPbBr₃ with $X = MA^+$, FA^+ , and Cs^+) through spectroscopic ellipsometry measurements (see Experimental Methods and the Supporting Information for further details). We show that their temperature-dependent optical properties are shaped by the cation type, which indirectly impacts on structural features like the octahedral tilting or the thermal expansion that are responsible for their optical response.

We first extract the real (ε_1) and imaginary (ε_2) part of the dielectric constant for all three perovskites (Figure 1a) from modeling the spectroscopic ellipsometry data (Figure SI-1). We identify some differences among the spectra, both in the

Received: January 29, 2020 Accepted: March 9, 2020 Published: March 9, 2020

👦 ACS Publications

pubs.acs.org/JPCL

Letter



Figure 1. (a) Real and imaginary parts of the dielectric constant of the three perovskites and (b) their absorption coefficient, as derived from the data in Figure SI-1. Estimates of the gap are shown in panels c-h, using (c-e) the Tauc plot and (f-h) the critical point analysis for (c and f) MAPbBr₃, (d and g) FAPbBr₃, and (e and h) CsPbBr₃. Values of the gap are given as labels within the panels.



Figure 2. Critical point energy (*E*), broadening (Γ), amplitude (*A*), and phase (Φ) as extracted from fitting of eq 2 for the three XPbBr₃ (FA in blue, MA in red, and Cs in green). Continuous vertical lines represent phase-change temperatures observed from data reported here whereas dashed vertical lines are from ref 20. In the figures, the labels are T for tetragonal, C for cubic, and O for orthorhombic phase.

value of the band gap (around 2.30 eV) as well as for the main absorption peak (see ε_2 curve) at ~4 eV. The absorption coefficient is calculated according to the equation

$$\alpha = \frac{2\omega}{c} \sqrt{\frac{\sqrt{(\varepsilon_1^2 + \varepsilon_2^2)} - \varepsilon_1}{2}}$$
(1)

where ε_1 and ε_2 are obtained from the optical modelm and ω is the light frequency. The values of the absorption coefficients

for MAPbBr₃ and FAPbBr₃ are very similar, whereas for CsPbBr₃ the main peak is blue-shifted by ~0.2 eV (Figure 1b). The fine differences in the gap value (E_g) may have multiple origins (e.g., the size of the X-site cations, the tilting of the inorganic octahedral network, the structural phase of each material at a given temperature, the thermal expansion coefficient) and will be hereafter discussed in detail.

Another important feature to highlight is the region where the absorption coefficient is extremely low. The sudden drop below (at energies less than) $E_{\rm gap}$ occurs where the material is transparent and light travels for millimeters, thus indicating the high optical quality of the prepared materials. The finding is consistent with the long diffusion length of carriers, as found for FAPbB₃ crystals.¹⁴

A precise evaluation of the band gap value is a major anchor for theoretical models and for comparing experimental data to judge their relevance for photonic and photovoltaic devices. A simple way to determine the gap consists of using the absorption coefficient from eq 1 and the refractive index in Tauc plots $(E\alpha(E)n(E))^2$ versus E (see Figure 1c–e).

A more accurate determination of the gap value is obtained by using the critical point (CP) analysis.^{23–26} This analysis relies on the densities of states of electron and phonon bands possessing singularities corresponding to critical points in the dielectric function (see the Supporting Information for further information).^{27–30} These points are better identified by calculating the second derivative of the measured dielectric function and finding the simultaneous best fit to the real and imaginary parts of the dielectric function, using a least-squares procedure, with the following equation:

$$\frac{\partial^2 \varepsilon}{\partial \omega^2} = n(n-1)Ae^{i\Phi}(\omega - E + i\Gamma)^{(n-2)}$$
(2)

where E, Γ , A, Φ , and n describe the shape (energy threshold, amplitude, broadening, excitonic phase angle, and singularity dimension) of the dielectric function around the band gap energy point (see Figure 1f–h). If the gap is a discrete excitonic transition, n = -1.^{31–33} The fitting results of $E_{\rm gap}$ are shown in Figure 1f–h. By comparing these values with the ones obtained by the Tauc plot, we conclude that $E_{\rm g}$ is systematically underestimated by ~0.03 eV in the latter.

We then explored the optical behavior of the materials as a function of temperature to measure the band gap values over a wide range from 183 to 363 K, wherein it is expected that the XPbBr₃ samples undergo lattice changes at least from tetragonal to cubic (~235 K for MAPbBr₃ and ~265 K for FAPbBr₃).³⁴ In the case of CsPbBr₃, an additional, orthorhombic-tetragonal transition is expected at ~361 K.35 We accordingly extended, in this case, the temperature window up to 440 K. In all explored cases, we used a pure dry N₂ environment to prevent sample degradation due to humid air.^{5,36} The data have been rationalized using the CP analysis for better estimating not only of the E_{gap} position but also other parameters that provide important complementary information on the material evolution with temperature. The results for all fitting parameters are shown in Figure 2. A comparison of the $E_{\rm gap}$ position extracted from CP analysis and Tauc plots as a function of the temperature is also given in Figures SI-2 and SI-3.

Each material's data has specific features that will be discussed separately.

In the case of MAPbBr₃, the tetragonal-cubic transition signed by the band gap is continuous. Notwithstanding this, a well-marked discontinuity is observed in the broadening A and excitonic phase Φ , whereas a drastic change of slope (from decreasing to increasing) is observed in the amplitude parameter. These significant modifications are also visible in the change of slope of the $E_{\rm gap}$ at ~255 K. In the case of FAPbBr₃, the A and Φ discontinuity is less

In the case of FAPbBr₃, the A and Φ discontinuity is less evident but still present as corroborated by a discontinuity in the broadening parameter. Moreover, the amplitude, constant for lower temperatures, starts increasing at the same temperature of the discontinuity in the broadening parameter, at ~270 K. At the same time, the $E_{\rm gap}$ increases linearly over the whole temperature range, and no discontinuity is observed at the transition temperature.

As a general paradigm, the FA- and MAPbBr₃ show a unique and coherent picture of phase transformation from tetragonal to cubic by increasing the temperature. The parameter continuity is a typical behavior observed in order–disorder phase transitions in halide perovskites.^{37,38}

In the case of CsPbBr₃, the crystal is in the orthorhombic phase in the low-temperature range. Its $E_{\rm gap}$ undergoes a jump and a sudden change of slope when the lattice is transformed to tetragonal at ~380 K. In contrast to the slow (FA- and MAPbBr₃) and well-marked (MAPbBr₃) transitions from tetragonal to cubic phases, not much can be said about the same transition in CsPbBr₃. The upper bound of the temperature window for the tetragonal phase is only 20 K before the lattice becomes cubic, and such an interval is too narrow to extract accurate fitting parameters considering that intermediate phases might exist.⁵⁴ However, for the sake of completeness, we added the expected transition point from literature data at 403 K.²⁰

Besides the highlighted differences, a common feature to all three materials is that the excitonic phase (Φ) decreases with temperature, empirically indicating a decrease of excitonic interactions.^{27–30} Finally, we observe that, compared to literature data, the phase-change temperatures provided by spectroscopic ellipsometry are shifted upwards by 20 K for MA- and Cs- and by 5 K for FAPbBr₃.

Although the trend of the E_{gap} versus T and its value near 0 K are often fitted with the Bose–Einstein equation to account for electron–phonon interactions,^{27–30} MAPbBr₃ and FAPbBr₃ are still in the tetragonal phase within the investigated T-range while in CsPbBr₃ the transition to orthorhombic is not linear (see also Figure SI-3).^{39,40} A linear fit in this region would overestimate $E_{gap}(0)$ and would contradict what was reported in ref 22 (see Figure 3). To properly apply the Bose–Einstein equation, the sample should be cooled down near 0 K.^{21,22,41} Under these circumstances, the relative weight of thermal expansion and electron–phonon coupling could be evaluated, as in the case of MAPbI₃.⁴²



Figure 3. Temperature dependence of E_{gap} in comparison with data from Wei et al.²² and Tilchin et al.²¹ The labels are T for tetragonal, C for cubic, and O for orthorhombic phase as in Figure 2.

The Journal of Physical Chemistry Letters

The temperature dependence of the bad gap was fitted using $E_g(T) = A + B \cdot T$. All the fitting values are summarized in Table 1. FA- and CsPbBr₃ show a linear behavior over the whole

Table 1. Values of Parameters Used to Fit Data in Figure $3a-c^{a}$

T-C phases	A (eV)	$B \ (\times 10^{-4} \ \text{eV} \ \text{K}^{-1})$
FAPbBr ₃	2.154 ± 0.001	4.98 ± 0.04
MAPbBr ₃ (183–255 K)	2.279 ± 0.001	1.91 ± 0.04
MAPbBr ₃ (255–363 K)	2.256 ± 0.001	2.75 ± 0.03
CsPbBr ₃ (380–435 K)	2.242 ± 0.001	3.41 ± 0.1

^{*a*}Values refer to the interval wherein each XPbBr₃ is in the tetragonal (T) and cubic (C) phases.

range of the tetragonal and cubic phases. The E_g dependence of MAPbBr₃ deviates from linearity at the transition temperature from tetragonal to cubic, making necessary the use of two distinct linear equations.

Finally, we compare our data to the very few other data available in the literature dealing with the specific task of evaluating the $E_{\rm gap}$.^{21,22} For MAPbBr₃, a phase transition from orthorhombic to tetragonal is expected at ~150 K where, similar to CsPbBr₃, some discontinuity is expected. Therefore, data reported here and those in ref 21 are in excellent agreement. In the case of CsPbBr₃, data collected in ref 22 obtained on quantum dots have been shifted to match our data in order to account for the effect of quantum confinement.

As discussed earlier, the origins of the fine differences in the band gap, optical constants, and temperature behavior of the three $XPbBr_3$ can be attributed to structural features related to the X-site cations. There are three characteristics of the band gap behavior of Figure 3 that are of interest.

The first one regards the value of the band gap, which appears to be higher for the $CsPbBr_3$ perovskite than for MAPbBr₃, which is higher than for FAPbBr₃.

The second issue regards the slope of the band gap's temperature dependence. Here, when considering equivalent phases for the three materials (either tetragonal or cubic), FAPbBr₃ shows the steepest band gap increase with increasing temperature, followed by CsPbBr₃ and then MAPbBr₃ (cubic phase).

The third issue that deserves discussion is the quasicontinuous behavior of the band gap trend at the tetragonal– cubic phase transition, in contrast with the discontinuous behavior of the orthorhombic–tetragonal transition (seen here for the CsPbBr₃ perovskite within the studied temperature range).

We now discuss these aspects in detail. It is already known from lead iodide perovskites that two main factors affect the value of the band gap: the change in the unit cell volume (through a variation of the lattice constants) and the octahedral tilting of the inorganic framework.^{43,44} The first can be evaluated following ref 42 and using the thermal parameters (the volumetric expansion coefficient (α_v) and the bulk modulus (β) where available) reported in refs 40 and 45–51.

As we can see from the calculated data (compare $\begin{bmatrix} \frac{\partial E_g}{\partial T} \end{bmatrix}_{TE}$ in Table 2 with *B* in Table 1), the variation of the band gap due to the temperature-related volume increase is not sufficient to explain our findings. We indeed evaluate the contribution of the octahedral tilting with the aid of the density functional

Table 2. Literature Values Used to Estimate the Variation of the Band Gap Due to the Thermal Expansion^a

	$(\times 10^{6} \text{ K}^{-1})$	β (GPa)	$\frac{\partial E_{g}}{\partial P}$ (eV/GPa)	$ \begin{bmatrix} \frac{\partial E_g}{\partial T} \end{bmatrix}_{TE} \\ (\times 10^{-4} \text{ eV} \end{cases} $	K ⁻¹)				
FAPbBr ₃	150	12.3	-0.20	3.6	9				
MAPbBr ₃	33	19.6	not available	-					
CsPbBr ₃	50	15.8	-0.28	2.2	1				
^{<i>a</i>} The relationship used is $\left[\frac{\partial E_g}{\partial T}\right]_{TE} = -\alpha_v \beta \frac{\partial E_g}{\partial P}$. In the case of									
MAPbBr ₃ the value of $\frac{\partial E_g}{\partial P}$ is not reported. MAPbBr ₃ has a phase									
transition at 0.1 GPa which do not allow obtaining accurate data.									

theory (DFT, see the Supporting Information). Figure 4a shows the band structures of $CsPbBr_3$ in the cubic and the orthorhombic phase at 0 K, where we observe an increase in the band gap value for the orthorhombic symmetry.

We note that the main geometrical feature distinguishing the two phases is the tilt angle, φ , for the [PbBr₆⁴⁻] octahedra, which is higher for the orthorhombic phase. Figure SI-4 shows the impact of either octahedral tilting (cubic \rightarrow orthorhombic) or isotropic volume variation (of the cubic phase) on the band edge energies of the CsPbBr₃ perovskite, relative to the vacuum level. An isotropic expansion of the unit cell volume increases both the ionization potential and electron affinity, i.e., shifts the valence band maximum (VBM) and conduction band minimum (CBM) toward more negative energies relative to the vacuum level. However, because the VBM changes more than the CBM, the band gap increases. Similarly, an isotropic compression of the unit cell reduces the band gap value. Octahedral tilting increases the band gap by shifting the VBM away from the vacuum level, toward more negative energies, and the CBM toward more positive energies. We expect that these are general trends for both hybrid and inorganic XPbBr₃, as the band gap in all cases is defined by antibonding Pb and halogen orbitals, whereas states that derive from the X-cations are well-removed in energy from the band gap region.⁵² It is therefore important to keep in mind that the band gap of a XPbBr₃ sample can increase by either an isotropic volume expansion or by the tilting of the $[PbBr_6^{4-}]$ octahedra.

We now compare the structural parameters of all three perovskites in their corresponding room-temperature phases (i.e., orthorhombic for CsPbBr₃ and cubic for MAPbBr₃ and FAPbBr₃) by means of the DFT calculations (Figure 4b). We find the result of our calculations to agree with the experimental data that CsPbBr3 has the smallest volume per formula unit, followed by $MAPbBr_3$ and then $FAPbBr_3$, reflecting the X-cation sizes.^{40,53-56} On the basis of the volumetric data, it is not possible to explain the differences of the experimental band gap values for the three perovskites (Figure 3). We then observe the tilting angle φ (Figure 4b). Here, the highest value is obtained for CsPbBr₃, followed by MAPbBr₃ and FAPbBr₃. We note that a local tilting of the $[PbBr_6^{4-}]$ octahedra can take place also in the cubic phase. Macroscopically though its effect is canceled out because of the random orientations or positions of the X-cations within the inorganic cage. Considering these results, it appears that octahedral tilting has a primary role in shaping the band gap value for the three perovskites and explains the differences observed in Figure 3.

pubs.acs.org/JPCL



Figure 4. (a) Differences in the calculated band gap of CsPbBr₃ in the cubic (left) and orthorhombic (right) phase for models representing the structures at T = 0 K. (b) Calculated octahedral tilting angle φ (columns) and volume per formula unit (points) for orthorhombic CsPbBr₃, cubic MAPbBr₃, and cubic FAPbBr₃ (corresponding to the phases of each material at room temperature).

The slope of the band gap value as a function of the temperature cannot be deduced by our DFT calculations, as these reflect a "frozen" static picture. It is most likely related to the thermal expansion of the three perovskites (considering the volumetric data reported in refs 53, 54, and 40), if we consider separately each perovskite phase. Here, it is important to note that the optically continuous tetragonal–cubic transition (at least for the band gap value, see Figure 2) indicates also a structural relationship between the two phases. In contrast, the discontinuity in the orthorhombic–tetragonal transition denotes a sharp structural change related to the X-cations, which influences the vibrational properties of the system.⁵⁷

In conclusion, we studied the phase transition of three XPbBr₃ single crystals, namely, MaPbBr₃, CsPbBr₃, and (for the first time) FAPbBr₃ in the range of temperature 183-440 K by spectroscopic ellipsometry under nitrogen atmosphere. Optical data were extracted by applying the critical point analysis, with special regard to the band gap region. The extremely low value of the absorption coefficient in the subgap region certifies a small scattering inside the crystal and indeed the high optical quality of the materials. We propose a close relationship connecting the structural parameters with the optoelectronic properties of the three kinds of crystals. The combined experimental-theoretical analysis indicates two important parameters for the band gap determination in XPbBr₃: octahedral tilting, which is fundamental for the band gap value, and the thermal expansion, which likely impacts the slope of the band gap as a function of the temperature.

EXPERIMENTAL METHODS

Sample Preparation. MAPbBr₃, FAPbBr₃, and CsPbBr₃ single crystals were grown by the method reported in the supplementary information of ref 13. We add here details of the synthesis that help to obtain with the antisolvent method crystals larger than those created before. To that end, we cover the container of the perovskite precursors with filtering paper. This avoids unwanted dropping of antisolvent that condensed on the crystallization chamber walls. Any antisolvent drop falling in the precursor solution induces the formation of multiple seeds, which reduces average crystal size. The crystals

were conserved in boxes containing nitrogen with silica gel. See the Supporting Information for details.

Spectroscopic Ellipsometry. We used a V-VASE, J. A. Woollam spectroscopic ellipsometry instrument for optical characterization. Measurements were collected at four angles, 60° – 65° – 70° – 75° , below and above the Brewster angle, over a wide range of wavelengths 245–1240 nm (1–5 eV). We explored also a wide temperature range (180–440 K) varying the temperature with an Instec MK100 heater/cooler system with an accuracy of 0.1 °C. See the Supporting Information for further setup details and data modeling.

X-ray Diffraction. High-resolution X-ray diffraction analyses have been performed on single-crystal perovskite samples using a D8Discover Bruker AXS diffractometer by focusing the beam over an area of 2 mm in diameter and using a Ge022 monochromator to remove the k_2 component. Data are shown in the Supporting Information (Figure SI-5).

Density Functional Theory. We performed density functional theory calculations as implemented in the plane-wave Quantum Espresso code.⁵⁸ We used the Perdew–Burke–Ernzerhof (PBE) implementation of the generalized gradient approximation for exchange and correlation along with scalar relativistic ultrasoft pseudopotentials.⁵⁹ See the Supporting Information for details.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00295.

Method details (section 1); ellipsometric data treatment (section 2 and related figures (Figures SI-1 and SI-2); comparison between Tauc and CP gap values (Figure SI-3); theoretical evaluation of valence and conduction band variation due to compression and expansion in different bromides lattices (Figure SI-4); diffraction pattern of the FAPbBr3 bulk crystal (Figure SI-5) (PDF)

The Journal of Physical Chemistry Letters

pubs.acs.org/JPCL

AUTHOR INFORMATION

Corresponding Authors

Alessandra Alberti – CNR-IMM, 95121 Catania, Italy; orcid.org/0000-0002-4103-6208;

Email: alessandra.alberti@imm.cnr.it

Davide Ceratti – Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel; Email: davide-raffaele.ceratti@weizmann.ac.il

Authors

Giovanni Mannino – CNR-IMM, 95121 Catania, Italy Ioannis Deretzis – CNR-IMM, 95121 Catania, Italy; orcid.org/0000-0001-7252-1831

Emanuele Smecca – CNR-IMM, 95121 Catania, Italy Antonino La Magna – CNR-IMM, 95121 Catania, Italy

 David Cahen – Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel;
orcid.org/0000-0001-8118-5446

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.0c00295

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This activity was partially supported at CNR by the national project BEYOND NANO Upgrade (CUP G66J17000350007). CNR also gratefully acknowledges the project PON entitled "Tecnologia per celle solari bifacciali ad alta Efficienza a 4 terminali per utility scale", called BEST-4U, financed by the Italian Ministry MIUR (CUP B88D19000160005). At the Weizmann Institute this work was supported by a research grant from the YOTAM project. D.R.C. acknowledges support from the Weizmann Institute's Sustainability And Energy Research Initiative, SAERI.

REFERENCES

(1) Deretzis, I.; Alberti, A.; Pellegrino, G.; Smecca, E.; Giannazzo, F.; Sakai, N.; Miyasaka, T.; La Magna, A. Atomistic origins of $CH_3NH_3PbI_3$ degradation to PbI_2 in vacuum. *Appl. Phys. Lett.* **2015**, *106*, 131904.

(2) Smecca, E.; Numata, Y.; Deretzis, I.; Pellegrino, G.; Boninelli, S.; Miyasaka, T.; La Magna, A.; Alberti, A. Stability of solution-processed MAPbI₃ and FAPbI₃ layers. *Phys. Chem. Chem. Phys.* **2016**, *18*, 13413–13422.

(3) Alberti, A.; Bongiorno, C.; Smecca, E.; Deretzis, I.; La Magna, A.; Spinella, C. Pb clustering and PbI₂ nanofragmentation during methylammonium lead iodide perovskite degradation. *Nat. Commun.* **2019**, *10*, 2196.

(4) Deretzis, I.; Smecca, E.; Mannino, G.; La Magna, A.; Miyasaka, T.; Alberti, A. Stability and degradation in hybrid perovskites: is the glass half-empty or half-full? *J. Phys. Chem. Lett.* **2018**, *9*, 3000–3007.

(5) Alberti, A.; Deretzis, I.; Mannino, G.; Smecca, E.; Giannazzo, F.; Listorti, A.; Colella, S.; Masi, S.; La Magna, A. Nitrogen soaking promotes lattice recovery in polycrystalline hybrid perovskites. *Adv. Energy Mater.* **2019**, *9*, 1803450.

(6) Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface passivation of perovskite film for efficient solar cells. *Nat. Photonics* **2019**, *13*, 460–466.

(7) Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T.-Y.; Noh, J. H.; Seo, J. Efficient, stable and scalable perovskite solar cells using poly (3-hexylthiophene). *Nature* **2019**, *567*, 511– 515.

(8) Bett, A. J.; Schulze, P. S.C.; Winkler, K. M.; Kabakli, O. S.; Ketterer, I.; Mundt, L. E.; Reichmuth, S. K.; Siefer, G.; Cojocaru, L.; Tutsch, L.; Bivour, M.; Hermle, M.; Glunz, S. W.; Goldschmidt, J. C.; et al. Two-terminal Perovskite silicon tandem solar cells with a high-Bandgap Perovskite absorber enabling voltages over 1.8 V. *Prog. Photovoltaics* **2020**, *28*, 99–110.

(9) Dewi, H. A.; Wang, H.; Li, J.; Thway, M.; Sridharan, R.; Stangl, R.; Lin, F.; Aberle, A. G.; Mathews, N.; Bruno, A.; Mhaisalkar, S. Highly efficient semitransparent perovskite solar cells for four terminal perovskite-silicon tandems. *ACS Appl. Mater. Interfaces* **2019**, *11*, 34178–34187.

(10) Shibayama, N.; Kanda, H.; Yusa, S.; Fukumoto, S.; Baranwal, A. K.; Segawa, H.; Miyasaka, T.; Ito, S. All-inorganic inverse perovskite solar cells using zinc oxide nanocolloids on spin coated perovskite layer. *Nano Converg.* **201**7, *4*, 18.

(11) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide perovskite photovoltaics: background, status, and future prospects. *Chem. Rev.* **2019**, *119*, 3036–3103.

(12) Miyasaka, T.; Kulkarni, A.; Kim, G. M.; Öz, S.; Jena, A. K. Perovskite solar cells: Can we go organic-free, lead-free, and dopant-free? *Adv. Energy Mater.* **2019**, 1902500.

(13) Ceratti, D. R.; Rakita, Y.; Cremonesi, L.; Tenne, R.; Kalchenko, V.; Elbaum, M.; Oron, D.; Potenza, M. A. C.; Hodes, G.; Cahen, D. Self-healing inside APbBr₃ halide perovskite crystals. *Adv. Mater.* **2018**, *30*, 1706273.

(14) Haque, M. A.; Alarousu, E.; Sarmah, A. P.; Murali, B.; Dursun, I.; Miao, X.-M.; Abdelhady, A. L.; Wu, T.; Mohammed, O. F.; Bakr, O. F.; et al. Formamidinium lead halide perovskite crystals with unprecedented long carrier dynamics and diffusion length. *ACS Energy Lett.* **2016**, *1*, 32–37.

(15) Walters, G.; Sutherland, B. R.; Hoogland, S.; Shi, D.; Comin, R.; Sellan, D. P.; Bakr, O. M.; Sargent, E. H. Two-photon absorption in organometallic bromide perovskites. *ACS Nano* **2015**, *9*, 9340–9346.

(16) Zhang, F.; Yang, B.; Zheng, K.; Yang, S.; Li, Y.; Deng, W.; He, R. Formamidinium lead bromide (FAPbBr₃) perovskite microcrystals for sensitive and fast photodetectors. *Nano-Micro Lett.* **2018**, *10*, 43.

(17) Alonso, M. I.; Campoy-Quiles, M.; Weber, O. J.; Yao, J.; Bryant, D.; Weller, M. T.; Nelson, J.; Walsh, A.; van Schilfgaarde, M.; Barnes, P. R. F.; et al. Experimental and theoretical optical properties of methylammonium lead halide perovskites. *Nanoscale* **2016**, *8*, 6317–6327.

(18) Zhao, M.; Shi, Y.; Dai, J.; Lian, J. Ellipsometric study of the complex optical constants of a CsPbBr₃ perovskite thin film. *J. Mater. Chem. C* **2018**, *6*, 10450–10455.

(19) Chen, X.; Wang, Y.; Song, J.; Li, X.; Xu, J.; Zeng, H.; Sun, H. J. Temperature dependent reflectance and ellipsometry studies on a CsPbBr₃ single crystal. *J. Phys. Chem. C* **2019**, *123*, 10564–10570.

(20) He, Y.; Matei, L.; Jung, H. J.; McCall, K. M.; Chen, M.; Stoumpos, C. C.; Liu, Z.; Peters, J. A.; Chung, D. Y.; Wessels, B. W.; Wasielewski, M. R.; Dravid, V. P.; Burger, A.; Kanatzidis, M. G.; et al. High spectral resolution of gamma-rays at room temperature by perovskite CsPbBr₃ single crystals. *Nat. Commun.* **2018**, *9*, 1609.

(21) Tilchin, J.; Dirin, D. N.; Maikov, G. I.; Sashchiuk, A.; Kovalenko, M. V.; Lifshitz, E. Hydrogen-like wannier-mott excitons in single crystal of methylammonium lead bromide perovskite. *ACS Nano* **2016**, *10*, 6363–6371.

(22) Wei, K.; Xu, Z.; Chen, R.; Zheng, X.; Cheng, X.; Jiang, T. Temperature-dependent excitonic photoluminescence excited by two-photon absorption in perovskite CsPbBr₃ quantum dots. *Opt. Lett.* **2016**, *41* (16), 3821–3824.

(23) Cardona, M. Modulation Spectroscopy Supplement 11 to Solid State Physics, Advances in Research and Applications; Seitz, F. et al. Eds.; Academic: New York, 1969; pp 15–25.

(24) Cardona, M.; Yu, P. Fundamentals of semiconductors. *Physics* and materials properties Springer-Verlag **2010**, 243-344.

(25) Aspnes, D. E. Modulation spectroscopy/electric field effects on the dielectric function of semiconductors. In *Handbook on Semiconductors*; Optical Properties of Solids; Moss, T. S., Balkanski, M., Eds.; North-Holland: Amsterdam, 1980; Vol. 2, pp 123–133.

The Journal of Physical Chemistry Letters

pubs.acs.org/JPCL

(26) Lynch, D. W. Interband absorption-mechanisms and interpretation Handbook of Optical Constants of Solids; Palik, E. D. Ed.; Academic: Orlando, FL, 1985; pp 189-212.

(27) Vina, L.; Logothetidis, S.; Cardona, M. Temperature dependence of the dielectric function of germanium. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1984**, 30, 1979–1991.

(28) Logothetidis, S.; Via, L.; Cardona, M. Temperature dependence of the dielectric function and the interband critical points of InSb. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1985**, *31*, 947–957.

(29) Lautenschlager, P.; Garriga, M.; Cardona, M. Temperature dependence of the interband critical-point parameters of InP. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1987**, *36*, 4813–4820.

(30) Lautenschlager, P.; Garriga, M.; Vina, L.; Cardona, M. Temperature dependence of the dielectric function and interband critical points in silicon. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1987**, *36*, 4821–4830.

(31) Fano, U. Effects of configuration interaction on intensities and phase shifts. *Phys. Rev.* **1961**, *124*, 1866–1878.

(32) Jiang, Y.; Soufiani, A. M.; Gentle, A.; Huang, F.; Ho-Baillie, A.; Green, M. A. Temperature dependent optical properties of CH₃NH₃PbI₃ perovskite by spectroscopic ellipsometry. *Appl. Phys. Lett.* **2016**, *108*, No. 061905.

(33) Mannino, G.; Alberti, A.; Deretzis, I.; Smecca, E.; Sanzaro, S.; Numata, Y.; Miyasaka, T.; La Magna, A. First evidence of $CH_3NH_3PbI_3$ optical constants improvement in a N_2 environment in the range 40–80 °C. *J. Phys. Chem. C* **2017**, *121*, 7703.

(34) Wharmby, M.; Küchler, R.; Yuan, H.; Debroye, E.; Steele, J. A.; Martens, J.; Hussey, N. E.; Bremholm, M.; Roeffaers, M. B. J.; Hofkens, J.; et al. Tracking structural phase transitions in lead-halide perovskites by means of thermal expansion. *Adv. Mater.* **2019**, *31*, 1900521.

(35) Hirotsu, S.; Harada, J.; Iizumi, M.; Gesi, K. structural phase transitions in CsPbBr₃. J. Phys. Soc. Jpn. **1974**, 37, 1393–1398.

(36) Alberti, A.; Smecca, E.; Sanzaro, S.; Mannino, G.; Deretzis, I.; La Magna, A. Hybrid perovskites for photovoltaics: Story, challenges and opportunities. *Riv. Nuovo Cimento* **2019**, *7*, 301–366.

(37) Deretzis, I.; Di Mauro, B. N.; Alberti, A.; Pellegrino, G.; Smecca, E.; La Magna, A. Spontaneous bidirectional ordering of $CH_3NH_3^+$ in lead iodide perovskites at room temperature: The origins of the tetragonal phase. *Sci. Rep.* **2016**, *6*, 24443.

(38) Alberti, A.; Deretzis, I.; Mannino, G.; Smecca, E.; Sanzaro, S.; Numata, Y.; Miyasaka, T.; La Magna, A. Revealing a discontinuity in the degradation behavior of $CH_3NH_3PbI_3$ during thermal operation. *J. Phys. Chem. C* **2017**, *121*, 13577–13585.

(39) Gao, Z.-R.; Sun, X.-F.; Wu, Y.-Y.; Wu, Y.-Z.; Cai, H.-L.; Wu, X. S. Ferroelectricity of the orthorhombic and tetragonal MAPbBr₃ single crystal. *J. Phys. Chem. Lett.* **2019**, *10*, 2522–2527.

(40) Schueller, E. C.; Laurita, G.; Fabini, D. H.; Stoumpos, C. C.; Kanatzidis, M. G.; Seshadri, R. crystal structure evolution and notable thermal expansion in hybrid perovskites formamidinium tin iodide and formamidinium lead bromide. *Inorg. Chem.* **2018**, *57*, 695–701.

(41) Leguy, A. M. A.; Goni, A. R.; Frost, J. M.; Skelton, J.; Brivio, F.; Rodriguez-Martinez, X.; Weber, O. J.; Pallipurath, A.; Alonso, M. I.; Campoy-Quiles, M.; Weller, M. T.; Nelson, J.; Walsh, A.; Barnes, P. R. F.; et al. Dynamic disorder, phonon lifetimes, and the assignment of modes to the vibrational spectra of methylammonium lead halide perovskites. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27051–27066.

(42) Francisco-Lopez, A.; Charles, B.; Weber, O. J.; Alonso, M. I.; Garriga, M.; Campoy-Quiles, M.; Weller, M. T.; Goni, A. R. Equal footing of thermal expansion and electron-phonon interaction in the temperature dependence of lead halide perovskite band gaps. *J. Phys. Chem. Lett.* **2019**, *10*, 2971–2977.

(43) Prasanna, R.; Gold-Parker, A.; Leijtens, T.; Conings, B.; Babayigit, A.; Boyen, H.-G.; Toney, M. F.; McGehee, M. D. Band gap tuning via lattice contraction and octahedral tilting in perovskite materials for photovoltaics. *J. Am. Chem. Soc.* **2017**, *139*, 11117– 11124. (44) Mosconi, E.; Umari, P.; De Angelis, F. Electronic and optical properties of MAPbX₃ perovskites (X = I, Br, Cl): a unified DFT and GW theoretical analysis. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27158.

(45) Rakita, Y.; Cohen, S. R.; Kedem, N. K.; Hodes, G.; Cahen, D. Mechanical properties of APbX 3 (A = Cs or CH_3NH_3 ; X = I or Br) perovskite single crystals. *MRS Commun.* **2015**, *5*, 623–629.

(46) Sun, S.; Isikgor, F. H.; Deng, Z.; Wei, F.; Kieslich, G.; Bristowe, P. D.; Ouyang, J.; Cheetham, A. K. Factors influencing the mechanical properties of formamidinium lead halides and related hybrid perovskites Chem. *ChemSusChem* **2017**, *10*, 3740.

(47) Wang, L.; Wang, K.; Zou, B. Pressure-induced structural and optical properties of organometal halide perovskite-based formamidinium lead bromide. J. Phys. Chem. Lett. **2016**, 7 (13), 2556–2562.

(48) Sun, S.; Fang, Y.; Kieslich, G.; White, T. J.; Cheetham, A. K. Mechanical properties of organic-inorganic halide perovskites, $CH_3NH_3PbX_3$ (X = I, Br and Cl), by nanoindentation. *J. Mater. Chem. A* **2015**, 3 (36), 18450–18455.

(49) Rodovà, M.; Brozek, J.; Knizek, K.; Nitsch, K. Phase transition in ternary caesium lead bromide. *J. Therm. Anal. Calor.* **2003**, *71*, 667–673.

(50) Zhang, L.; Zeng, Q.; Wang, K. Pressure-induced structural and optical properties of inorganic halide perovskite CsPbBr₃. *J. Phys. Chem. Lett.* **2017**, *8*, 3752–3758.

(51) Wang, Y.; Liu, X.; Wen, T.; Yang, L.; Ren, X.; Wang, L.; Lin, Z.; Zhao, Y. Pressure-induced phase transformation, reversible amorphization, and anomalous visible light response in organolead bromide perovskite. *J. Am. Chem. Soc.* **2015**, *137*, 11144–11149.

(52) Goyal, A.; McKechnie, S.; Pashov, D.; Tumas, W.; Van Schilfgaarde, M.; Stevanović, V. Origin of pronounced nonlinear band gap behavior in lead-tin hybrid perovskite alloys. *Chem. Mater.* **2018**, *30*, 3920–3928.

(53) Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; et al. Crystal growth of the perovskite semiconductor CsPbBr₃: A new material for high-energy radiation detection. *Cryst. Growth Des.* **2013**, *13*, 2722–2727.

(54) Lehmann, F.; Franz, A.; Többens, D. M.; Levcenco, S.; Unold, T.; Taubert, A.; Schorr, S. The phase diagram of a mixed halide (Br, I) hybrid perovskite obtained by synchrotron X-ray diffraction. *RSC Adv.* **2019**, *9*, 11151–11159.

(55) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, 32, 751–767.

(56) Kieslich, G.; Sun, S.; Cheetham, A. K. Solid-state principles applied to organic-inorganic perovskites: new tricks for an old dog. *Chem. Sci.* **2014**, *5*, 4712–4715.

(57) Schuck, G.; TÖbbens, D. M.; Koch-Müller, M.; Efthimiopoulos, I.; Schorr, S. infrared spectroscopic study of vibrational modes across the orthorhombic-tetragonal phase transition in methylammonium lead halide single crystals. *J. Phys. Chem.* C 2018, 122, 5227-5237.

(58) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Guido, L. C.; Cococcioni, M.; Dabo, I.; et al. Quantum espresso: A modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.

(59) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.