Temperature-Dependent Optical Band Gap in CsPbBr$_3$, MAPbBr$_3$, and FAPbBr$_3$ 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 (MAPbBr$_3$, CsPbBr$_3$, and for the first time FAPbBr$_3$) 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.

The 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. However, solar cells with the best performance still contain organic cations. 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. Their corresponding pure iodides, and this favors tandem coupling with silicon in combined photovoltaic technologies. In addition to relatively wide band gap is likewise exploited for other optoelectronic applications (LEDs and lasers). In addition to relatively wide band gap is likewise exploited for other optoelectronic applications (LEDs and lasers).

Although large efforts were made to determine the UV–visible 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. The literature on the optical constants of lead bromide perovskites is limited to CsPbBr$_3$ or MAPbBr$_3$ single crystals. In other cases, the study relies on nanocrystals rather than on millimeter-large single crystals.

Here we report a systematic study of the absorption coefficient and refractive index of bulk lead bromide perovskite single crystals (XPbBr$_3$ 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 ($\varepsilon_1$) and imaginary ($\varepsilon_2$) 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...
value of the band gap (around 2.30 eV) as well as for the main absorption peak (see $\varepsilon_2$ curve) at $\sim$4 eV. The absorption coefficient is calculated according to the equation

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

where $\varepsilon_1$ and $\varepsilon_2$ are obtained from the optical model and $\omega$ is the light frequency. The values of the absorption coefficients for MAPbBr$_3$ and FAPbBr$_3$ are very similar, whereas for CsPbBr$_3$ the main peak is blue-shifted by $\sim$0.2 eV (Figure 1b). The fine differences in the gap value ($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 in the absorption coefficient is a result of the change in the material's electronic structure. This region is critical for understanding the optical properties of perovskites and their potential applications in optoelectronic devices.

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) MAPbBr$_3$, (d and g) FAPbBr$_3$, and (e and h) CsPbBr$_3$. Values of the gap are given as labels within the panels.

Figure 2. Critical point energy ($E$), broadening ($\Gamma$), amplitude ($A$), and phase ($\Phi$) as extracted from fitting of eq 2 for the three XPbBr$_3$ (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.
below (at energies less than) \( E_{gpp} \) 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 FAPbB\(_3\) 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 (\( (Ea(E)n(E))^{2} \) 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:

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

(2)

where \( E, \Gamma, A, \Phi \), 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 \( E_{gpp} \) are shown in Figure 1f–h. By comparing these values with the ones obtained by the Tauc plot, we conclude that \( E_{g} \) is systematically underestimated by \( \sim 0.03 \) 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 X\( \text{PbBr}_3 \) samples undergo lattice changes at least from tetragonal to cubic (\( \sim 235 \) K for MAP\( \text{PbBr}_3 \) and \( \sim 265 \) K for FAP\( \text{PbBr}_3 \)).\(^{34}\) In the case of CsPb\( \text{Br}_3 \), an additional, orthorhombic–tetragonal transition is expected at \( \sim 361 \) K.\(^{35}\) We accordingly extended, in this case, the temperature window up to 440 K. In all explored cases, we used a dry N\(_2\) 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 \( E_{gpp} \) 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 \( E_{gpp} \) 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 MAP\( \text{PbBr}_3 \), 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 \( \Phi \), 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 \( E_{gpp} \) at \( \sim 255 \) K.

In the case of FAP\( \text{PbBr}_3 \), the \( A \) and \( \Phi \) 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 \( \sim 270 \) K. At the same time, the \( E_{gpp} \) increases linearly over the whole temperature range, and no discontinuity is observed at the transition temperature.

As a general paradigm, the FA- and MAP\( \text{PbBr}_3 \) show a unique and coherent picture of phase transition 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 CsPb\( \text{Br}_3 \), the crystal is in the orthorhombic phase in the low-temperature range. Its \( E_{gpp} \) undergoes a jump and a sudden change of slope when the lattice is transformed to tetragonal at \( \sim 380 \) K. In contrast to the slow (FA- and MAP\( \text{PbBr}_3 \)) and well-marked (MAP\( \text{PbBr}_3 \)) transitions from tetragonal to cubic phases, not much can be said about the same transition in CsPb\( \text{Br}_3 \). 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.\(^{34}\) 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 (\( \Phi \)) 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 FAP\( \text{PbBr}_3 \).

Although the trend of the \( E_{gpp} \) versus \( T \) and its value near 0 K are often fitted with the Bose–Einstein equation to account for electron–phonon interactions,\(^{27-30}\) MAP\( \text{PbBr}_3 \) and FAP\( \text{PbBr}_3 \) are still in the tetragonal phase within the investigated \( T \)-range while in Cs\( \text{PbBr}_3 \), the transition to orthorhombic is not linear (see also Figure SI-3).\(^{39,40}\) A linear fit in this region would overestimate \( E_{gpp}(0) \) 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.\(^{21,22,23,41}\) Under these circumstances, the relative weight of thermal expansion and electron–phonon coupling could be evaluated, as in the case of MAP\( \text{Bi}_3 \).\(^{42}\)

**Figure 3.** Temperature dependence of \( E_{gpp} \) 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 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 CsPbBr$_3$ show a linear behavior over the whole range of the tetragonal and cubic phases. The $E_g$ dependence of MAPbBr$_3$ 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 $E_{g\text{opt}}$. For MAPbBr$_3$, a phase transition from orthorhombic to tetragonal is expected at $\sim$150 K where, similar to CsPbBr$_3$, some discontinuity is expected. Therefore, data reported here and those in ref 21 are in excellent agreement. In the case of CsPbBr$_3$, 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 MAPbBr$_3$, which is higher than for FAPbBr$_3$.

The second issue regards the slope of the band gap temperature dependence. Here, when considering equivalent phases for the three materials (either tetragonal or cubic), FAPbBr$_3$ shows the steepest band gap increase with increasing temperature, followed by CsPbBr$_3$ and then MAPbBr$_3$ (cubic phase).

The third issue that deserves discussion is the quasi-continuous 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 CsPbBr$_3$ 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.

The first can be evaluated following ref 42 and using the thermal parameters (the volumetric expansion coefficient ($\alpha_v$) and the bulk modulus ($\beta$) where available) reported in refs 40 and 45–51.

As we can see from the calculated data (compare $\frac{\partial E_g}{\partial T}$ 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 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, $\varphi$, for the [PbBr$_6^{2-}$] octahedra! which is higher for the orthorhombic phase. Figure SI-4 shows the impact of either octahedral tilting (cubic → orthorhombic) or isotropic volume variation (of the cubic phase) on the band edge energies of the CsPbBr$_3$ 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 XPbBr$_3$, 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.

It is therefore important to keep in mind that the band gap of a XPbBr$_3$ 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 CsPbBr$_3$ and cubic for MAPbBr$_3$ and FAPbBr$_3$) by means of the DFT calculations (Figure 4b). We find the result of our calculations to agree with the experimental data that CsPbBr$_3$ has the smallest volume per formula unit, followed by MAPbBr$_3$ and then FAPbBr$_3$, reflecting the X-cation sizes. 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 $\varphi$ (Figure 4b). Here, the highest value is obtained for CsPbBr$_3$, followed by MAPbBr$_3$ and FAPbBr$_3$. 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 values for the three perovskites and explains the differences observed in Figure 3.
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.

In conclusion, we studied the phase transition of three $\text{XPbBr}_3$ single crystals, namely, $\text{MaPbBr}_3$, $\text{CsPbBr}_3$, and (for the first time) $\text{FAPbBr}_3$, 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 $\text{XPbBr}_3$: 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.** $\text{MAPbBr}_3$, $\text{FAPbBr}_3$, and $\text{CsPbBr}_3$ 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, $60^\circ$–$65^\circ$–$70^\circ$–$75^\circ$, 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. We used the Perdew–Burke–Ernzerhof (PBE) implementation of the generalized gradient approximation for exchange and correlation along with scalar relativistic ultrasoft pseudopotentials. 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)
Corresponding Authors
Alessandra Alberti — CNR-IMM, 95121 Catania, Italy;
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
Emanuele Smecca — CNR-IMM, 95121 Catania, Italy
Antonio La Magna — CNR-IMM, 95121 Catania, Italy
David Cahen — Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel;
Email: orcid.org/0000-0001-7252-1831

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcllett.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 G06J1700350007). 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. Atomic origins of CH3NH3PbI3 degradation to PbI2 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 2013, 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. Photovolt. Res. Appl. 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. 2017, 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.; Murai, 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, A.; Weber, O. J.; Yao, J.; Bryant, D.; Wellner, 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.; McCull, K. M.; Chen, M.; Stoumpos, C. C.; Liu, J.; 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 wanner-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

(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) Jiay, 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 CH₃NH₃PbI₃ optical constants improvement in a N₂ environment in the range 40–80 °C. J. Phys. Chem. C 2017, 121, 7703.

(34) Wurmbrand, M.; Küchler, R.; Yuan, H.; Debeye, E.; Steele, J. A.; Martens, J.; Hussey, N. E.; Brehmholm, M.; Roelfsma, M. B. J.; Hofkens, J.; et al. Tracking structural phase transitions in lead-halide perovskites by synchrotron X-ray diffraction. RSC Adv. 2019, 9, 11051–11159.

(35) Stoumpos, C. C.; Mallikas, 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.

(36) Lehmann, F.; Franz, A.; Többens, D. M.; Levengo, S.; Unold, T.; Tautz, A.; Schorr, S. The phase diagram of a mixed halide (Br, I) hybrid perovskite obtained by synchrotron X-ray diffraction. Phys. Rev. Lett. 2019, 123, 256102–256102.

(37) Effimioopoulos, 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, 5227–5273.

(38) Prasanna, R.; Gold-Parker, A.; Leijtens, T.; Conings, B.; Babayigit, A.; Boyen, H.-G.; Toney, M. F.; McGeehan, M. D. Band gap tuning via lattice contraction and octahedral tilting in perovskite materials for photovoltaics. J. Am. Chem. Soc. 2017, 139, 11117–11124.