

Heterovalent Dopant Incorporation for Bandgap and Type Engineering of Perovskite Crystals

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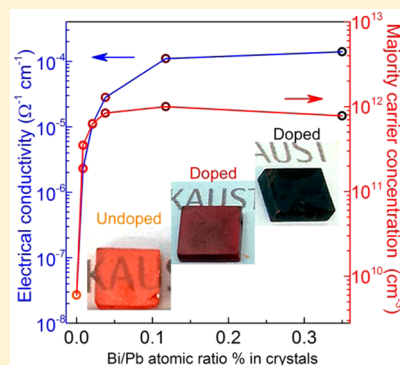
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Supporting Information

ABSTRACT: Controllable doping of semiconductors is a fundamental technological requirement for electronic and optoelectronic devices. As intrinsic semiconductors, hybrid perovskites have so far been a phenomenal success in photovoltaics. The inability to dope these materials heterovalently (or aliovalently) has greatly limited their wider utilizations in electronics. Here we show an efficient in situ chemical route that achieves the controlled incorporation of trivalent cations (Bi^{3+} , Au^{3+} , or In^{3+}) by exploiting the retrograde solubility behavior of perovskites. We term the new method dopant incorporation in the retrograde regime. We achieve Bi^{3+} incorporation that leads to bandgap tuning (~ 300 meV), 10^4 fold enhancement in electrical conductivity, and a change in the sign of majority charge carriers from positive to negative. This work demonstrates the successful incorporation of dopants into perovskite crystals while preserving the host lattice structure, opening new avenues to tailor the electronic and optoelectronic properties of this rapidly emerging class of solution-processed semiconductors.



Doping of semiconductors is fundamental to modern electronic and optoelectronic devices.¹ Doping enables manipulation of both the optical^{2,3} and the electrical properties of semiconductors—keys to device functionality.¹

The properties of the doped semiconductors strongly depend on the electronic levels introduced by the dopants.^{1,4–6} Upon increasing the dopant concentration, the discrete impurity levels in the band gap of the host semiconductor evolve into an impurity band that can overlap with the conduction/valence band in n-/p-type semiconductors, respectively,^{1,4,7} resulting in bandgap narrowing (BGN).^{1,5–7} In semiconductors, the bandgap is integral to device architecture and expected performance, such as governing the limits of power conversion efficiency (PCE) in solar cells.⁵ In the case of semiconductors, incorporating a high concentration of dopants, band tails appear as a consequence of the large disorder in the distribution of the density of states,^{4,7} and these can be useful in applications such as nonlinear optical switching.^{7,8}

Hybrid trihalide perovskites, especially MAPbX_3 ($\text{MA} = \text{CH}_3\text{NH}_3^+$, $\text{X} = \text{Br}^-$ or I^-), have seen intensive investigation,^{9–16} particularly in the context of photovoltaic applications following early studies beginning in 2009.¹⁷ In only a few years, the field has witnessed a remarkable increase in the PCE of

polycrystalline thin film perovskite-based solar cells, recently reaching certified efficiencies of 20.1%.¹⁸ The incorporation of dopants offers a route to tailor hybrid perovskites and endow them with new properties.

To date, MAPbX_3 has primarily been doped using elements that are isovalent with the anion (I^-/Cl^-)^{19–22} or with the metal cation $\text{Pb}^{2+}/\text{M}^{2+}$ ($\text{M}^{2+} = \text{Sn}^{2+}$, Sr^{2+} , Cd^{2+} or Ca^{2+}).²³ This limits dopants' capacity to impact the sign or concentration of the majority charge carriers. By contrast, heterovalent doping in semiconductors has a propensity to switch the sign of majority charge carrier from n- to p-type or vice versa and, if established in hybrid perovskites, could permit the fabrication of devices based on a p–n perovskite homojunction with minimal lattice mismatch. In addition, incorporation of heterovalent cations into the hybrid trihalide perovskite could potentially extend their spectral range to longer wavelengths. However, despite the promised benefits, the complete absence of reports on the heterovalent doping of hybrid trihalide perovskite polycrystalline films and, more importantly, crystals reflects the challenge

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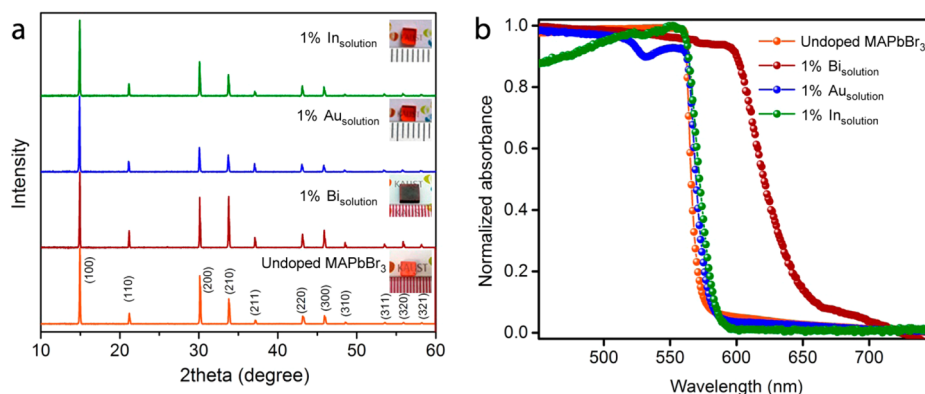


Figure 1. (a) Powder XRD of ground MAPbBr₃ and doped crystals prepared from solutions containing 1% dopant precursor. The inset above each XRD pattern shows the picture of the corresponding as-grown crystal. (b) Steady-state absorption spectra of MAPbBr₃ crystals with and without cation doping.

of incorporating differently charged cations into perovskites. This challenge derives from the demanding requirement that incorporated dopants satisfy both octahedral and tolerance factors while maintaining the same underlying crystal structure.

It is well documented that the introduction of Cl⁻ into perovskite precursors solutions can significantly alter the crystallinity, morphology, and grain size of the obtained thin films, the combined effects of which appreciably impact device performance.^{20,21,24,25} Given this combination of mechanisms, it has been difficult to isolate the specific role of the chloride additive on polycrystalline thin film properties.

Studying single crystals, which are not conflated by grain boundary and morphological effects, offers to put the focus on the role of dopants on the underlying properties of the material. There are, however, a number of constraints and challenges to classical crystal growth techniques associated with devising a general heterovalent doping approach of MAPbX₃ crystals. For example, employing antisolvent vapor-assisted crystallization²⁶ requires the choice of a solvent–antisolvent combination that is suitable for all precursors. Also, crystal growth by cooling from a saturated solution²⁷ occurs at temperatures that are likely too low to dissociate the dopant from its precursor state. Moreover, in each of these methods, crystallization occurs at a very slow rate, approaching the near-equilibrium conditions that militate against the incorporation of impurities into the host lattice.

We reasoned that the in situ incorporation of a dopant might be feasible using the inverse temperature solubility regime, a regime peculiar to hybrid perovskites. In this regime, crystallization occurs at astonishingly rapid rates at moderately elevated temperatures.^{28,29} The approach we explore herein, dopant incorporation in the retrograde regime (DIRR), offers advantages that overcome many of the shortcomings of other methods: it requires the use of only a single solvent; its rapidity provides a higher probability of incorporation of impurities; and its use of moderately elevated temperatures enhances the chances of dissociation of precursor–solvent complexes,²⁹ making the impurities more readily available for incorporation.

Additional consideration, beyond the suitable choice of reaction conditions, must be given to designing a heterovalent doping strategy. We tried various trivalent cations, focusing on Bi³⁺ (isoelectronic with Pb²⁺, i.e. having the same electronic structure), Au³⁺, or In³⁺, which fit into the perovskite tolerance factor.³⁰ Tolerance factors for Bi³⁺, Au³⁺, and In³⁺ were calculated to be 0.889, 0.946, and 0.963, respectively. These

values fall within the range (0.75–1.00) reported to allow the formation of perovskites.³⁰

As a result of the development of the DIRR process, we report herein an efficient in situ solution-processed method for the synthesis of heterovalent doped hybrid perovskite crystals. The successful incorporation of trivalent dopants (Bi³⁺, Au³⁺, or In³⁺) into MAPbBr₃ crystals demonstrates the flexibility of the perovskite structure to host a number of different heterovalent cations. Our studies also reveal the considerable influence of dopants on the properties of the underlying semiconductor. In particular, we achieved a high concentration of Bi³⁺ reaching $\sim 10^{19}$ cm⁻³, although the active carrier concentration was ~ 7 orders of magnitude less than this (but still ~ 100 fold greater than the undoped crystals) and we also showed conclusively that variation in bismuth concentration in the feed crystallization solution directly impacts both optical and electronic properties of MAPbBr₃. The introduction of Bi³⁺ as a dopant resulted in significant bandgap narrowing (~ 300 meV), an enhancement of charge carrier concentration, a 3 to 4 orders of magnitude increase in conductivity, and sign switching of the majority carriers. Based on our results, Bi may be of particular interest in ongoing efforts to narrow the bandgap of hybrid perovskites, including iodide perovskite crystals, in the direction of the 1.0–1.3 eV range optimal for single junction solar cells.³¹

We implemented in situ incorporation of dopants by adding a mixture of trivalent (Bi³⁺, Au³⁺, In³⁺) bromide salts and MABr into a crystallization solution containing a mixture of PbBr₂ and MABr in DMF, and then heating to the required temperature (synthesis is described in detail in the Methods section in the Supporting Information). After 3 h, bulk crystals—entirely lacking grain boundaries (Figure S1, Supporting Information)—of parallelepiped shape (the same as undoped MAPbBr₃) were formed. We observed a color change, from orange to deep red, in Bi-doped crystals, but not for other dopants (inset in Figure 1a). In the case of Au-doped crystals, the dark color of the solution (which is due to the presence of AuBr₃) became much lighter (Figure S2, Supporting Information). This color fading could be attributed to either the incorporation of the Au³⁺ ions in the perovskite crystal or to the reduction of Au³⁺ to Au⁺.

The exact dopant content in the crystals grown by DIRR was quantified using inductively coupled plasma optical emission spectrometry (ICP-OES). The dopant/Pb atomic ratio % in crystals synthesized from a feed solution containing 1%

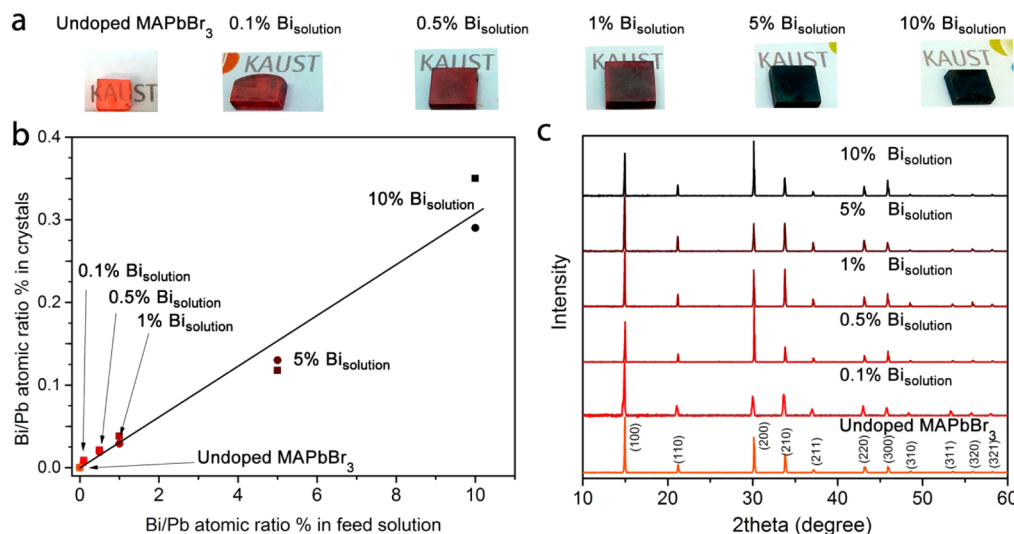


Figure 2. (a) Photographs showing MAPbBr₃ crystals having various Bi incorporation levels. (b) ICP measurement for Bi/Pb atomic ratio % as a function of feed solution atomic ratio %. (c) Powder XRD of ground MAPbBr₃ crystals with various Bi% doping.

dopant/Pb atomic ratio % was determined to be 0.029%, 0.020%, and 0.004% for Bi³⁺, Au³⁺, and In³⁺, respectively. The Au³⁺ content measured by ICP indicates successful incorporation of the Au ions. Low In³⁺ content could be due to the large difference in ionic radii between lead and indium.³² X-ray diffraction (XRD) patterns of powders made by grinding each type of crystal showed no extra peaks compared to the undoped crystal, indicating a single-phase material (Figure 1a) that retains the structural framework of pure MAPbBr₃ crystals. The preservation of the host perovskite structure, especially the inorganic framework, is important since this substructure is associated with the semiconducting properties of the organic–inorganic hybrids.³³

As evidenced from the color of the crystals, the absorption edge of the Bi-doped crystal was red-shifted, while Au- and In-doped crystals showed no obvious spectral change from the undoped crystal (Figure 1b). This is consistent with prior reports that BGN is dependent on the nature of the dopant.⁶ The BGN observed only in the case of Bi-doped crystals is in agreement with theoretical studies suggesting that the outer *ns*² electrons play a critical role in bandgap modulation.³⁴ Our density functional theory (DFT) calculations show that Au and In create deeper, more localized, and less interacting states than Bi, consistent with the failure of Au and In incorporation to produce notable BGN (Figure S3, Supporting Information).

The trivalent bismuth cation and Pb²⁺ have very similar ionic radii and are isoelectronic (6s²), and this may explain the similarities in chemical behavior for these cations.³² Previous reports have found that the bismuth cation forms regular chains built of nearly regular octahedra with halide anions;^{35,36} in particular, the Bi–Br bond length³⁵ (axial: 2.926, equatorial: 2.849 and 2.826 Å) in the octahedron BiBr₆^{3–} closely matches that of the Pb–Br bond (2.95 Å)²⁶ in the corresponding octahedral structure. Mitzi reported bismuth perovskites, yet with a distorted octahedral coordination leading to a lower-dimensionality material.³⁷ The degree of distortion of an octahedron in hybrid perovskites is dependent on the size of the organic cation, the inorganic cation, and the halide.¹⁴ In addition, bismuth has been previously used to dope PbS in both thin films³⁸ and quantum dots,³⁹ converting them from p-type to n-type semiconductors. The lattice mismatch between PbS³⁹

and MAPbBr₃²⁸ is less than 1%, which may suggest Bi³⁺ could be incorporated into the bromide-based perovskites crystal as well.

Motivated by this remarkable resemblance of Bi and Pb, as well as our findings of effective incorporation—BGN and preservation of the lattice structure of the perovskite—we further explored the effect of bismuth concentration on crystal optoelectronic properties. The color of the crystal was readily tuned by controlling the concentration of Bi³⁺ in the feed solution, as seen in Figure 2a. The Bi content in the obtained crystals, identified using ICP-OES, was found to be substantially lower than the nominal precursor amount in the feed solution. However, the Bi content obtained by ICP still indicates a moderate-to-heavy doping regime.⁴⁰ Table 1 shows

Table 1. Bi and Pb Atomic % in the Feed Solution and Obtained Crystals

Bi% in feed solution	Bi%	Pb%	~number of Bi atoms per cm ³ of crystal
0 (undoped)	–	42.7 ± 0.7	–
0.1	0.0026 ± 0.0005	40.6 ± 0.7	4 × 10 ¹⁷
0.5	0.0072 ± 0.0007	41.1 ± 0.7	1 × 10 ¹⁸
1	0.0120 ± 0.0006	41.5 ± 0.7	2 × 10 ¹⁸
5	0.055 ± 0.016	38.3 ± 0.6	6 × 10 ¹⁸
10	0.120 ± 0.038	37.5 ± 0.6	2 × 10 ¹⁹

the Bi and Pb percentages in both the feed solution and the obtained crystals. Hereafter, for simplicity, we refer to the crystals by the Bi% in the feed solution. Figure 2b shows the measured Bi/Pb atomic ratio % as a function of Bi/Pb atomic ratio % in the feed solution. The reduction in the Pb% (Table 1) is not fully compensated by an equal increase in the Bi%, and this could be indicating the formation of Pb vacancies. Previous works reported that, in doped materials, the structure stabilizes through the formation of vacancies.^{41,42} Our DFT studies (Figure S4, Supporting Information) indicate that Pb vacancies may also contribute to BGN. Although the position of the Bi atoms in the structure was not determined, the decrease in Pb content and the similarity in the ionic radii might suggest substitutional doping, and this is also consistent with our DFT calculations (Figure S5, Supporting Information). Figure 2c

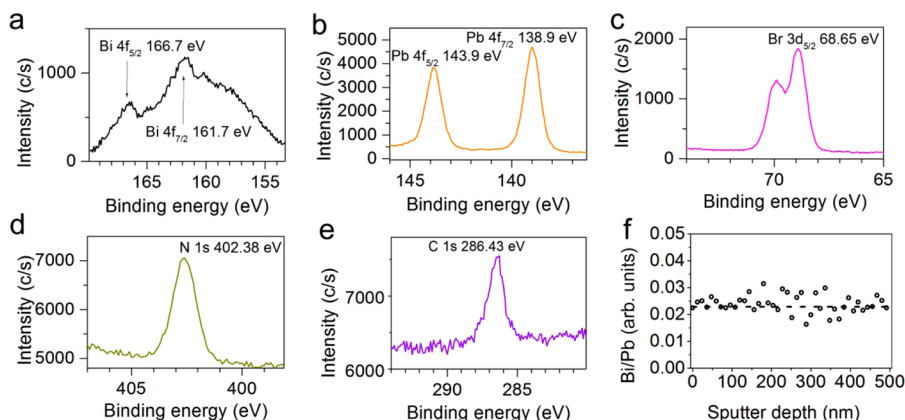


Figure 3. High-resolution XPS spectra of (a) Bi 4f, (b) Pb 4f, (c) Br 3d, (d) N 1s, (e) C 1s after single sputtering cycle and (f) sputter depth profile for the Bi/Pb ratio. A 500 eV Ar-ion beam was used for 2 min in a single sputtering cycle.

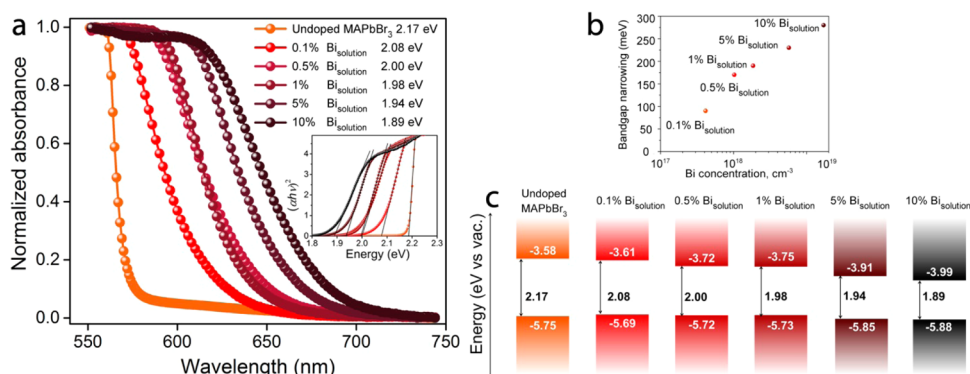


Figure 4. (a) Steady-state absorption spectra of MAPbBr₃ crystals with various Bi%. Inset: corresponding Tauc plots. (b) Bandgap narrowing as a function of Bi concentration in the crystal. (c) Bandgap alignment of MAPbBr₃ crystals with various Bi%.

shows XRD patterns of undoped and Bi-doped MAPbBr₃ crystals. Even at the highest doping level, the XRD pattern confirmed a single phase of the host cubic perovskite structure. Careful XRD analysis revealed no differences between the lattice parameters (5.92 Å) in both doped and undoped crystals. Similarly, there is no change in the full width at half maxima before and after doping (Table 1, Supporting Information).

Next, we inserted a number of freshly cleaved crystal surfaces with different Bi doping levels into an X-ray photoelectron spectroscopy (XPS) chamber and, following a single cycle of gentle sputtering, performed high-resolution XPS on each sample. The spectrometer dispersion was adjusted to give a binding energy of 284.8 eV for the C 1s line of adventitious (aliphatic) carbon presented on the non-sputtered samples (Figure S6, Supporting Information, and Table S2, Supporting Information). Figure 3 shows the representative high-resolution XPS spectra for the regions of interest of the most highly Bi-doped sample. The Bi 4f doublet is clearly resolved at the 161.7 eV (Bi 4f_{7/2}) and 166.7 eV (Bi 4f_{5/2}) binding energies (Figure 3a), slightly higher than the reported values for Bi³⁺ ions, which might suggest a different chemical environment.⁴³ The expected ratio of 4/3 for the spin-orbit split f-levels is in good agreement with the experimental data (Figure S7, Supporting Information and Table S3, Supporting Information). The Pb 4f doublet and Br 3d binding energies, shown in Figure 3b and 3c, respectively, are also slightly higher than the reported values for MAPbBr₃ thin films.⁴⁴ N 1s, and C 1s core level peaks are observed at 402.38 and 286.43 eV, respectively

(Figure 3d,e, respectively). A possible explanation for the slightly higher binding energy values of Bi, Pb, and Br is that XPS measurements were conducted on bulk crystals rather than the commonly reported thin films. The sputtering regime we chose can be concluded to be a largely nondestructive, consistent with the stable surface chemical composition observed up to 500 nm in depth (see depth profiles in Figure 3f) of the crystal. The initial drop in carbon content and the increase in lead and bromine atomic concentrations can be attributed to the removal of surface contamination. This is supported by the significant reduction in the total carbon component due to its aliphatic component removal observed after the very first sputtering cycles. At the later stages, the intensity of the Bi and Pb signals remained essentially constant, indicating a uniform distribution of Bi, and also confirming the effectiveness of doping.

The normalized absorbance spectra of Bi-doped crystals exhibit a red-shift proportional to the Bi content (Figure 4a). The absolute absorbance spectra of the crystals are provided in Figure S8, Supporting Information. Figure 4b shows the BGN as a function of Bi concentration in the crystal. Even a much lower Bi percentage in solution (0.01%) can result in BGN (Figure S9, Supporting Information). The band edge shifted from 570 nm for the undoped crystal to 680 nm in the case of the highest Bi%. This latter corresponds to a bandgap value of 1.89 eV. BGN in doped semiconductors is caused by the interaction of the electrons with positive impurities, altering the density of states.^{6,7} BGN may also be explained by the higher electronegativity of Bi compared to Pb, leading to more

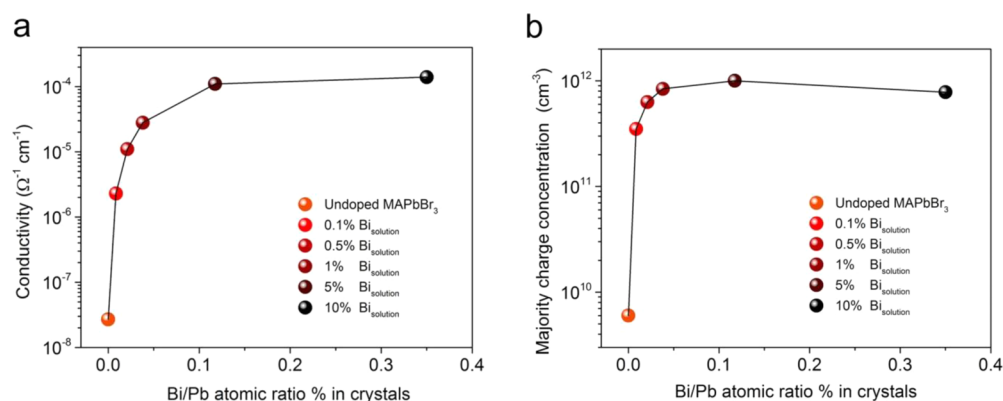


Figure 5. (a) Conductivity and (b) majority charge concentration of the different crystals as a function of Bi/Pb atomic ratio % in the crystals.

covalent bonding with bromide. This is consonant with the previously reported decrease in bandgap from Pb to Sn and Ge perovskites due to the difference in their electronegativity.¹⁴ The relatively shallow (in comparison to Au and In) and delocalized Bi states, as determined using DFT, facilitate the mutual interaction of nearby Bi dopants—a condition required for bandgap narrowing (Figure S10, Supporting Information). We note that the band edge is not as sharp as in the undoped crystal, with tail states in the absorption. Such Urbach tails have been exploited in other doped semiconductors for nonlinear optical switching.⁷ Notable bandtailing was also observed in mixed I/Br perovskite films;⁴⁵ nevertheless, they have been used successfully in optoelectronic devices.⁴⁶ It is worth mentioning that incorporating Bi³⁺ into the perovskite crystal quenches the photoluminescence, which is similar to what is observed in Bi-doped PbS quantum dots³⁹ and other doped quantum dots systems⁴⁷ and could be attributed to carrier capture into Bi-related energy band which is optically inactive.

Generally, time-resolved laser spectroscopy provides direct information about the carrier dynamics in organic and semiconductor materials.^{48–50} In this study, nanosecond time-resolved transient absorption experiments reveal an extended carrier lifetime in crystals following Bi³⁺ incorporation. In addition to two time constants of tens and hundreds of nanoseconds (these are commonly observed for the undoped single crystals^{26,28}), a new component with a characteristic time constant of several tens to hundreds of microseconds is observed for Bi-doped MAPbBr₃ crystals. The contribution of this component increases as the doping concentration (Figure S11, Supporting Information). Reduced recombination rates and longer lifetimes has been previously reported for mixed halide perovskites.⁵¹

The band positions of crystals were identified by combination of Photoelectron spectroscopy in air (PESA) and optical bandgap.⁵² PESA was used to obtain the valence band maximum (VBM) from the onset energy value of the spectra (Figure S12, Supporting Information). Using the optical bandgaps (E_g), we deduced the conduction band minimum (CBM) from the relationship $\text{VBM} + E_g = \text{CBM}$, as previously reported by McGehee et al.⁵² Figure 4c shows the values calculated for VBM and CBM. The conduction band moves downward considerably in energy, hinting that Bi doping may be prone to produce n-type semiconductors.

The sizable dimensions of the crystals synthesized using DIRR enabled the deposition of ohmic contacts for the study of electronic parameters such as conductivity (σ) and charge concentration (n) (Figure S13, Supporting Information, 10% Bi

as an example). The four point probe method allows measurement of conductivity in semiconductor materials.⁵³ Using this method, we observed an increase in conductivity of as much as 4 orders of magnitude, from $\sim 10^{-8} \Omega^{-1} \text{cm}^{-1}$ for the undoped crystal to $\sim 10^{-4} \Omega^{-1} \text{cm}^{-1}$ for the highest-conductivity Bi-doped crystals (Figure 5a). As in Bi-doped PbS thin films reported previously,³⁸ a rapid and abrupt increase in conductivity is first observed, followed by a gradual saturation as higher dopant concentrations are approached.

Hall Effect studies revealed that free carrier concentration within Bi-doped crystals increases to $\sim 10^{11}$ – 10^{12}cm^{-3} compared to $\sim 10^9 \text{cm}^{-3}$ for undoped crystals (Figure 5b). This indicates that, of the $\sim 10^{19} \text{cm}^{-3}$ impurity atoms introduced, only a certain fraction contribute free carriers.

MAPbBr₃ is an intrinsic p-type semiconductor.²⁶ Through Hall Effect measurements (Figure S13, Supporting Information), we were able to demonstrate the change in the sign of majority carriers from p- to n-type through converting the intrinsic perovskite semiconductor to an extrinsic one, which is in line with values obtained from simple semiconductor physics considerations (Note 1, Supporting Information). The change in the sign of charge carriers is in agreement with our measurements of VBM and CBM discussed earlier. This switching in behavior from p- to n-type has been reported for the Bi-doping of other materials systems such as PbS thin films³⁸ and quantum dots.³⁹ The mobility of charge carriers was coarsely estimated from $\mu = en/\sigma$ (e is the electron charge) to be an order of magnitude larger in doped compared to in undoped crystals. Although such an increase was previously observed in prior studies of certain materials systems,⁵⁴ it is usually the case that mobility decreases when high concentrations of impurities are introduced to the semiconductor.

Bandgap tailoring is clearly of interest across the family of hybrid perovskites, including in MAPbI₃. Although Bi-doped MAPbBr₃ crystals were used for many of the key studies herein, Bi-doped MAPbI₃ crystals also show a single phase material (Figure S14, Supporting Information) with BGN that depends systematically on the Bi%. The bandgap of MAPbI₃ is reduced from its intrinsic value of 1.51 eV⁵⁸ to as low as 1.28 eV (Figures S15 and S16, Supporting Information and Table 4, Supporting Information), a value of interest in photovoltaics.

In summary, we demonstrated herein an efficient in situ chemical route for the incorporation of heterovalent dopants into hybrid perovskite crystal through the DIRR technique. Trivalent metals such as Bi, Au, and In were successfully introduced while preserving the structure of the host perovskite. Our results suggest that Bi is a potential candidate

for tuning a number of optical and electronic properties in the hybrid perovskite crystal. The performance of hybrid perovskite-based optoelectronic devices such as solar cells and photodetectors mainly rely on bandgap, conductivity, charge carrier concentration, and mobility of the semiconductor. The observed BGN upon doping, as well as the increase in the charge carrier concentration and conductivity, and notably the change in the majority charge carrier sign, suggest promise in a diverse set of perovskite-based optoelectronic devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b02681.

Materials, synthesis, measurements, and characterization, along with the UV-photodetector setup (PDF)

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Notes

The authors declare no competing financial interest.

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