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Parallel evaluation of the BiI_3 , BiOI , and Ag_3BiI_6 layered photoabsorbers

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Abstract

The bismuth-based (oxy)iodides BiI_3 , BiOI and $\text{Ag}_x\text{BiI}_{x+3}$ share similar layered crystal structures, optimal band gaps for top absorbers in tandem solar cells, and moderate synthesis temperatures. Similarly to halide perovskite absorbers, they contain a heavy cation with a lone pair of electrons (Bi^{3+}) which has been proposed as an important feature enabling defect tolerance in perovskites. The aim of this work is to grow and characterize BiI_3 , BiOI , and Ag_3BiI_6 absorbers and solar cells using a consistent synthesis and analysis routine. In this way, the individual strengths and weaknesses of the three absorbers, as well as their common challenges, can be outlined. The proposed synthesis method based on (oxy)iodization of metallic precursor films results in similar room-temperature photoluminescence features in all three materials, possibly indicating a similar degree of defect tolerance. At the device level, the open circuit voltage of BiI_3 solar cells and the fill factor of BiOI solar cells are improved

compared to their respective state of the art. To improve short circuit currents, control of growth orientation should be a priority in view of the anisotropic properties of these compounds. P-type bulk doping and selection of hole transport layers with deep valence bands are also key areas for future work. Beyond photovoltaics, the very low (< 1.1) dark diode ideality factor in BiI_3 devices and the existence of both electronic and ionic conduction in Ag_3BiI_6 may open up applications in other areas of optoelectronics.

Introduction

An important reason behind the remarkable performance of methylammonium lead iodide (MAPbI_3) and related Pb-based halide perovskites as solar absorbers is their combination of high carrier lifetimes and relatively high mobilities, which together enable high minority carrier lifetimes and diffusion lengths even in solution-processed films.¹ These experimental features indicate a high degree of defect tolerance, which can be rationalized based on fundamental features in their band structure.²⁻⁴ In particular, it has been suggested⁴ that defect tolerance in halide perovskites may be linked to the presence of the heavy Pb^{2+} cation in a partially oxidized state, i.e., with the ns^2np^0 electron configuration retaining a lone pair of electrons. On the one hand, interaction between the cation(s) lone-pair orbital and anion(p) orbitals yields an antibonding valence band with high dispersion. These are prerequisites for defect tolerance towards cation vacancies and high hole mobility respectively.^{2,3} On the other hand, the large mass of Pb intensifies spin-orbit coupling, which broadens the conduction band (more dispersion) and pushes its minimum to a lower energy than the atomic Pb 6p states. These are prerequisites for high electron mobility and defect tolerance towards anion vacancies respectively.^{2,3} Besides their enhanced spin-orbit coupling, heavy cations have the additional advantage that the relative stability of the partially oxidized state versus the fully oxidized state typically increases down a column of the periodic table.

Since other materials containing a heavy, partially oxidized p-block element may exhibit similar optoelectronic properties to halide perovskites, increasing attention has been devoted

Figure 1: Crystal structures of BiI_3 ($R\bar{3}$), BiOI ($P4/nmm$), and ABI ($R\bar{3}m$). The latter is shown with the stoichiometry and occupations determined by Oldag *et al.*⁹ Note the completely disordered cation sublattice with fractional occupation by Ag and Bi, the small Ag population of normally vacant sites between the layers, and the absence of part of the Ag expected from the Ag_3BiI_6 stoichiometry. The missing Ag is either delocalized in the lattice or present in the form of a AgI secondary phase.^{9,10} Also note the similarity between the $R\bar{3}$ structure of BiI_3 , where every third possible cation site is not occupied, and the $R\bar{3}m$ structure of ABI , where all possible cation sites are fractionally occupied. Green: Bi; orange: Ag; purple: I; red: O; white: vacancies. Sites with more than one color are fractionally occupied.

to ns^2 -containing solar absorbers, which are the subject of a recent review.⁵ Among the heaviest cations (Tl^+ , Pb^{2+} , and Bi^{3+}), Bi^{3+} is especially interesting as Bi has no particular toxicity concerns,⁶ is relatively inexpensive,⁷ and its compounds have not been widely investigated as solar absorbers. The specific field of Bi-containing compounds for photovoltaics has been recently reviewed.^{7,8}

Among a number of possible candidates, BiI_3 , BiOI , and a range of $\text{Ag}_x\text{BiI}_{x+3}$ (ABI) compounds have potential applications as top absorbers in tandem solar cells, since their reported band gaps are in the 1.6-2.0 eV range.^{11,12,14,19,23-32} The highest single-junction cell efficiencies achieved until now are 1.2% for BiI_3 ,¹⁴ 1.8% for BiOI ,¹⁹ and 4.3% for ABI with $x = 3$ (Ag_3BiI_6).³⁰ The valence bands maximum (VBM) has predominantly I 5p character

Absorber material	m_e^* (m_0)	m_h^* (m_0)	CBM	VBM	ϵ_r	doping type	main defects (I-rich region)
BiI ₃	$\parallel \mathbf{c}$: >1.8 ¹¹	$\parallel \mathbf{c}$: >10 ¹¹	Bi 6p ($\sim 60\%$)	I 5p ($>90\%$) ¹²	$\parallel \mathbf{c}$: 9 ¹³	p ^{12,14}	$V_{\text{Bi}}, I_{\text{Bi}}$ (deep) ¹⁵
	$\perp \mathbf{c}$: 0.75 ¹⁶	$\perp \mathbf{c}$: $1.0-3.9$ ¹⁶	I 5p ($\sim 40\%$)	Bi 6s ($<10\%$)	$\perp \mathbf{c}$: 54 ¹³	n ¹⁷	V_I (shallow)
BiOI	$\parallel \mathbf{c}$: >1 ¹⁸	$\parallel \mathbf{c}$: 1.9 ¹⁸	Bi 6p ($\sim 60\%$)	I 5p ($\sim 70\%$) ¹⁸	46 ^{11,19}	n ^{20,21}	V_{Bi} (shallow) ¹⁹
	$\perp \mathbf{c}$: ~ 0.3 ¹⁸	$\perp \mathbf{c}$: 1.9 ¹⁸	O 2p $\sim$ I 5p	O 2p $>$ Bi 6s		p ²²	V_I (shallow)
ABI ($R\bar{3}m$)	$\parallel \mathbf{c}$: $1.8?$ ¹⁷	$\parallel \mathbf{c}$: $1.3?$ ¹⁷	Bi 6p ($\sim 50\%$)	I 5p ($>60\%$) ¹⁷	N.A.	p ¹⁷	N.A
	$\perp \mathbf{c}$: $0.4?$ ¹⁷	$\perp \mathbf{c}$: $0.4?$ ¹⁷	I 5p ($\sim 50\%$)	Bi 6s? Ag 4d?		n ²³	

Table 1: Electronic properties of BiI₃, BiOI, and Ag₃BiI₆. All properties are calculated except for doping type. m_0 , m_e^* , and m_h^* are the electron mass and the effective masses of electrons and holes respectively. $\parallel \mathbf{c}$ and $\perp \mathbf{c}$ refer to effective masses along the $\mathbf{c}$ axis and on the $\mathbf{ab}$ plane respectively, as shown in Fig. 1. The VBM and CBM columns refer to the orbital character of the valence band maximum and conduction band minimum respectively. ϵ_r is the static (zero-frequency) relative permittivity. The listed defects are those with the lowest calculated formation energy under I-rich growth conditions. Some properties of ABI are labeled with a question mark, signaling a higher uncertainty due to the more approximate computational approach used to calculate those quantities. Although data for the relative permittivity and defects in ABI are not available, the situation is likely similar to the case of BiI₃ due to the similarity of the two compounds.

in all three compounds, with a small contribution from Bi 6s states as expected from the discussion above (Table 1). The overlap between Bi 6s and I 5p states is however not large enough for the $6s^2$ lone pair to be stereochemically active,³³ so Bi retains an undistorted octahedral coordination in all compounds.^{11,18,30} For the case of BiOI, O 2p states also contribute to the VBM (Table 1). In all cases, the conduction band maximum (CBM) consists of a roughly equal mix of Bi 6p and I 5p states. Interestingly, these materials share quite similar anisotropic crystal structures with layers held together by weak van der Waals forces along the **c** axis (Fig. 1). It can be argued that layered structures are not optimal for carrier transport as they tend to exhibit low band dispersion and high carrier effective masses along the **c** axis due to poor orbital overlap. Indeed, first-principles calculations predict relatively high effective masses along **c** for both carrier types in all three compounds (Table 1). Despite this potential disadvantage, recent work on other layered compounds (particularly Sb_2Se_3 and 2D perovskites)^{34,35} has shown that high photovoltaic efficiencies are still possible if film growth can be controlled so that the **c** axis is oriented in the plane of the substrate and, thus, not in the main transport direction.

Among the three Bi-based compounds, ABI is the photoabsorber with the largest number of papers reporting solar cell fabrication and with the highest reported efficiency. However, ABI is also the most poorly understood of the three, since it features a wide range of possible compositions ($0.5 < x < 3$),¹⁰ two possible crystal structures (cubic $Fd\bar{3}m$ and rhomboedral $R\bar{3}m$),^{10,17,36} complete disorder in the Ag/Bi sublattice,^{9,30} partial occupation of (nominally vacant) lattice sites between layers (Fig. 1),⁹ and a relatively low activation energy for Ag migration (0.44 eV)⁹ implying potential ionic conduction. Possibly due to the structural and compositional flexibility of the material, as well as to challenges related to modeling disordered structures, detailed computational work on ABI using state-of-the-art methods is lacking. Calculations on the cubic phase using hybrid functionals and spin-orbit coupling dealt mainly with structural aspects.³⁶ More detailed calculations were carried out recently for both crystal structures of AgBiI_4 , but they relied on the less accurate generalized gradient

approximation, thus yielding drastically underestimated band gaps.¹⁷

In this work, we synthesize BiI_3 , BiOI , and ABI thin films under anion-rich conditions using a two-step process, i.e., sputter deposition of metallic precursors followed by (oxy)iodization at moderate temperatures. The motivation for employing a two-step process is that anion-rich growth conditions can be realized in the second step by performing the iodization process at atmospheric pressure. According to calculations, anion-rich conditions should ensure a lower concentration of deep defects (V_O in BiOI ; Bi_I and Bi interstitials in BiI_3) which can be effective recombination centers.^{15,19} Since the effective masses in these materials are generally lower for electrons than for holes (Table 1) the p-type conductivity favored under anion-rich conditions^{15,19} is another possible advantage. To our knowledge, a synthesis route based on (oxy)iodization of metallic precursors has not been explored for BiI_3 , BiOI , or ABI. By employing a consistent synthesis and characterization routine for BiI_3 , BiOI , and ABI, it is hoped that the present study can provide useful information for (i) comparing the three absorbers on a fair basis and (ii) evaluating advantages and drawbacks of the proposed two-step synthesis method for this class of materials.

Experimental details

Metallic Bi precursor films for BiI_3 and BiOI were sputter-deposited from a Bi target. Metallic precursor films for ABI were deposited by co-sputtering individual Bi and Ag targets at suitable powers for obtaining an Ag-Bi alloy with Ag_2Bi composition according to energy dispersive x-ray spectroscopy (EDX). This particular precursor stoichiometry is appropriate for obtaining a final ABI stoichiometry around Ag_3BiI_6 , due to some BiI_3 losses during iodization. Following the device structures proposed in previous work,^{12,23} the precursor films for BiI_3 and ABI were deposited on a glass/FTO/ TiO_2 substrate, whereas the precursor films for BiOI were deposited on a glass/ITO/ NiO substrate.¹⁹ Iodization of BiI_3 and ABI was carried out at atmospheric pressure by subliming I_2 lumps within a Petri dish

Figure 2: (a-c): Top-view SEM images of BiI₃ (a), Ag₃BiI₆ (b), and BiOI (c). (d-f): Cross-sectional SEM images of solar cells based on BiI₃ (d), Ag₃BiI₆ (e), and BiOI absorbers (f).

placed upside down on a hotplate where the precursor films were also located (Fig. S1(a), Supporting Information). Unless otherwise specified, BiI₃ and ABI were iodized at 100°C for 15 min and 150°C for 60 min respectively. Oxyiodization of BiOI was carried out at 300°C for 10 min, using a tube furnace flushed with 100 sccm O₂ and roughly 0.1 sccm I₂ at atmospheric pressure (Fig. S1(a), Supporting Information). The absorber thicknesses after (oxy)iodization are ~200 nm for BiI₃, ~500 nm for BiOI, and ~500 nm for ABI (Fig. 2). Note that the absorbers were processed in air, unless otherwise specified. Further details on absorber growth, device fabrication, and characterization are available in the Supporting Information.

Results and discussion

Growth of BiI₃ and BiOI

EDX measurements performed after the (oxy)iodization step show a stoichiometric composition for BiI₃ and BiOI within the uncertainty of the measurement (Fig. S2, Supporting

Information). X-ray diffraction (XRD) patterns are consistent with the rhombohedral $R\bar{3}$ structure of BiI_3 and the tetragonal $P4/nmm$ structure of BiOI (Fig. 1), with additional peaks corresponding to the FTO and ITO substrate respectively (Fig. 3(a,b)). Within the detection limit of the XRD measurement, the films appear to be single-phase. The morphology of BiI_3 grown at 100°C is shown in Fig. 2(a). Its morphology evolution with growth temperature is shown in Fig. S3, Supporting information. BiI_3 formation starts at around 70°C , with the growth of small, isotropic grains. As the reaction temperature is increased, some grains become more elongated until, at a temperature around 150°C , a platelet morphology with increasing c -axis texture begins to develop as observed by others.^{11,37,38} If the reaction temperature is too low, the XRD peaks of BiI_3 are weak and broad, and metallic Bi remains as a secondary phase. If the reaction temperature is too high, BiI_3 solar cells exhibit very low photocurrents, presumably due to the presence of large, poorly connected BiI_3 platelets and the unfavorable transport properties along the c axis. A higher growth temperature might, however, present other advantages, such as a higher photoluminescence quantum yield,²⁷ signaling a higher intrinsic material quality with a more favorable defect landscape. A strong dependence of BiI_3 material properties on growth temperature is reflected in their corresponding device properties. As will be shown later, BiI_3 films grown at 100°C yield the most efficient solar cells, but the films grown at 180°C result in very low diode ideality factors in the dark despite their poor photovoltaic performance.

BiOI growth proceeds first by conversion of Bi into BiI_3 , starting at around 100°C . As long as the I_2 and O_2 partial pressures are appropriate, conversion of BiI_3 into BiOI begins near the sublimation point of BiI_3 (237°C).¹⁵ If the I_2 partial pressure is too high, BiI_3 sublimates instead of forming BiOI . If the I_2 partial pressure is too low, the reaction product is Bi_2O_3 instead of BiOI . In practice, we found that BiOI processed at less than 280°C still contained spurious peaks in its XRD pattern. Since BiOI starts decomposing at 300°C ,³⁹ the accessible temperature window for converting BiI_3 into BiOI is rather narrow ($\sim 280\text{--}300^\circ\text{C}$). This is a disadvantage of the proposed two-step growth method, and is related to the fact

that any Bi lost due to decomposition cannot be recovered. Conversely, growth techniques in which Bi, I, and O are supplied simultaneously (such as chemical vapor transport) can maintain the substrate at higher temperatures as long as the deposition rate is higher than the decomposition rate. In fact, the best BiOI cells by chemical vapor transport were made at 350°C.¹⁹ Similarly to previous reports using other deposition techniques^{19,40} BiOI films made by oxyiodization of Bi precursors grow in the form of thin platelets that are often oriented perpendicularly to the substrate plane (Fig. 2(c)). The BiOI platelets are generally more densely packed than the BiI₃ platelets obtained at high reaction temperatures, which may be an advantage for carrier transport.

BiOI films grown by oxyiodization of metallic precursors suffer from poor adhesion of BiOI on the hole transport layer, often resulting in BiOI peeling off during the cooling phase. Adhesion properties are clearly influenced by the nature of the underlying layer, as BiOI films grown on bare quartz and on MoS₂ had a much higher peel-off rate than films grown on NiO. It would be interesting to grow BiOI by direct conversion of metallic Bi without the BiI₃ intermediate, or by conversion of Bi₂O₃. The former option is, however, hindered by the low melting point of Bi (271°C) and by the ease of formation of BiI₃ even at very low I₂ partial pressures. The latter option was attempted in this work but resulted in only partial iodization of Bi₂O₃ and no single-phase BiOI could be obtained (more details in the Supporting Information).

Growth of Ag₃BiI₆

Before describing the growth of ABI, it is worth discussing some of its compositional and structural aspects. The occurrence of the rhomboedral $R\bar{3}m$ and cubic $Fd\bar{3}m$ crystal structures of ABI as a function of composition x has been the subject of some debate.^{9,10,17,30,36,41} The only possible stoichiometry in either structure that is compatible with both charge neutrality and with the absence of vacancies and interstitials is AgBiI₄ ($x = 1$). However, it was shown by two independent studies that, for $x = 1$, a mix of the two $R\bar{3}m$ and $Fd\bar{3}m$

structures is obtained.^{10,41} For $x > 1$, the $R\bar{3}m$ structure is favored and it appears as a single phase at compositions close to Ag_2BiI_5 . For higher values of x , the $R\bar{3}m$ phase is present together with a AgI secondary phase. The most efficient ABI cells to date,³⁰ as well as the films produced in this work ($x \sim 3$), fall into this category. For $x < 1$, the $Fd\bar{3}m$ structure is favored and it appears as a single phase at compositions close to AgBi_2I_7 . For lower values of x , the $Fd\bar{3}m$ phase is present together with a BiI_3 secondary phase. As mentioned above, all stoichiometries for which $x \neq 1$ must contain a certain combination of vacancies and/or interstitials to be compatible with any of the two crystal structures. For the $R\bar{3}m$ single phase, Ag interstitials between the **ab** planes were identified by Rietveld refinement,^{9,10} and those are shown in Fig. 1. For the $Fd\bar{3}m$ single phase, vacancies in the Ag/Bi sublattice were identified.¹⁰ Furthermore, a fraction of Ag was found to be completely delocalized in the lattice.⁹ This is a hint that the performance of ABI solar cells may be influenced by mobile ions, as in halide perovskite solar cells.

In the two-step process proposed in this work, Ag in Ag_2Bi films reacts with I_2 already at room temperature to form AgI. From around $\sim 70^\circ\text{C}$, Bi starts reacting both with I_2 and with AgI to form a mix of BiI_3 and ABI. As the temperature is increased, the BiI_3 impurity content decreases. At a growth temperature of 150°C , a hold time of 1 hour is necessary to completely remove the BiI_3 XRD peaks (Fig. S4, Supporting Information). The film morphology consists of densely packed and rather isotropic crystal grains up to 500 nm in diameter (Fig. 2(b)). Due to some loss of BiI_3 during the hold step at 150°C , the composition of ABI films after iodization is usually close to the desired Ag_3BiI_6 stoichiometry according to EDX (Fig. S2, Supporting Information).²³ Employing iodization temperatures significantly higher than 150°C is challenging because the increasing BiI_3 loss would have to be finely counterbalanced either by more Bi-rich precursors or by a significant BiI_3 partial pressure during iodization. The XRD pattern of the iodized film (Fig. 3(c)) indicates that ABI in the $R\bar{3}m$ structure is present together with AgI secondary phases as expected from the $x \sim 3$ ABI stoichiometry. Thus, the present ABI films have similar composition and structure

Figure 3: Bragg-Brentano XRD patterns of a BiOI film on a NiO/ITO/glass substrate (a), a BiI₃ film on a TiO₂/FTO/glass substrate (b), and a Ag₃BiI₆ film on a TiO₂/FTO/glass substrate (c). The patterns at the bottom of each subfigure are reference patterns for randomly oriented films with collection codes 391354 (BiOI), 78791 (BiI₃), 414635 (AgBiI₄) and 56552 (γ -AgI secondary phase) in the Inorganic Crystal Structure Database (ICSD). The peak positions expected for the ITO and FTO transparent contacts are also shown. The experimental peaks assigned to the transparent contacts and to AgI are labeled with asterisks and circles respectively. Note that the strongest peak expected for TiO₂ overlaps with the (006) peaks of BiI₃ and Ag₃BiI₆. The (00X) peaks labeled in bold font arise from crystallites with the *c* axis oriented perpendicularly to the substrate plane, which are expected to be low-mobility paths. The peaks labeled in blue or red are the dominant peaks in the highest efficiency BiI₃ and BiOI absorbers reported by others.^{14,19}

to the ABI films from the highest efficiency solar cells to date.³⁰ It is perhaps surprising that those cells were based on an impure absorber containing AgI secondary phases. AgI in the α phase is one of the best-known ion conductors, but the α phase is only stable above 150°C. As expected, the AgI peaks present in the room-temperature XRD pattern of ABI (Fig. 3(c)) can be attributed to either the wurtzite β phase or the γ zincblende phase, but not to the ion-conducting α phase. Nevertheless, a certain fraction of Ag in ABI appears to be delocalized according to detailed XRD studies⁹ so it is conceivable that a Ag-rich stoichiometry may promote not only the formation of AgI secondary phases, but also a

higher fraction of delocalized Ag in ABI. Therefore, mobile ions such as Ag^+ in the $x = 3$ stoichiometry may have a beneficial rather than a detrimental effect, possibly due to an increased carrier selectivity of the absorber/transport layer interfaces where they are likely to accumulate.⁴²

The stability of BiI_3 , BiOI , and ABI was not studied systematically in this work. At a purely visual level, BiOI appears to be the most stable of the three compounds with respect to both air/moisture exposure and light. While BiOI does not change appearance after several months of storage in ambient conditions, BiI_3 turns yellow (Bi_2O_3)²⁶ within some weeks of storage in ambient air – a process that is accelerated by light exposure. Full Ag_3BiI_6 solar cells undergo a noticeable color change within about a week, possibly due to Ag migration or to other forms of interdiffusion across the layers. Ag_3BiI_6 is also unstable under electron beam exposure in the SEM. Surface reactions and changes in the measured compositions are clearly observed under high beam doses (Fig. S5, Supporting Information).

Texture

(001) and higher-order (00X) peaks are present in the XRD patterns of all three absorbers (Fig. 3). Those peaks originate from crystallites having the **c** axis oriented perpendicularly to the substrate plane (**c**-axis texturing). Since minority carriers must be transported in that direction, **c**-axis texturing is likely associated with suboptimal carrier collection due to high effective masses along the **c** axis (Table 1). By comparing the relative intensity of the (00X) peaks with the intensity of other strong diffraction peaks in the experimental and reference diffraction patterns (Fig. 3) it is straightforward to see that the trend in **c**-axis texturing is $\text{Ag}_3\text{BiI}_6 > \text{BiOI} > \text{BiI}_3$, with Ag_3BiI_6 (BiI_3) being more (less) textured than a randomly oriented film. Interestingly, the (00X) peaks in BiOI are broader than the peaks related to any other orientation. As the peak width is inversely related to crystallite size, this fact indicates that BiOI platelets are quite thin in the direction of the **c** axis, which can be easily related to the morphology observed in SEM images (Fig. 2(c)).

Using the chemical vapor transport growth method,¹⁹ **c**-axis texturing of BiOI on NiO was suppressed almost completely, possibly due to the higher achievable growth temperature and to the highly tunable deposition rate. Due to the limited growth temperature window of the two-step method (see previous section) it is unclear whether this method can achieve the same level of texture control as chemical vapor transport. Orientation control in BiI₃ and ABI appears in general to be more challenging than in BiOI, as indicated by the significant **c**-axis texturing present in nearly all BiI₃ and Ag₃BiI₆ cells reported in the literature, including the ones with the highest efficiency.^{14,28,29}

Some differences in the most successful device architectures for each absorber can be rationalized in terms of how challenging it is to obtain a **c**-axis-free texture in each material. For ideally-oriented BiOI films on NiO, a conventional planar solar cell structure with a relatively thick absorber (~ 900 nm) was found to be appropriate. For the case of BiI₃, **c**-axis texturing is usually more pronounced at high growth temperatures, so a low absorber thickness (~ 200 nm) is typically chosen to obtain shorter collection paths and at the same time allow the film to fully react at low process temperatures. Suppression of **c**-axis texturing seems to be most challenging for ABI, hence the preference for a mesoporous device architecture with very short collection paths in ABI solar cells. It must be emphasized that a number of growth techniques which have enabled texture control in other layered materials (vapor transport,⁴³ closed-space sublimation,³⁴ hot casting³⁵) have not been widely explored for BiI₃ and ABI, so there may be opportunities for substantially improved texture control.

Band gaps

BiI₃ and Ag₃BiI₆ films are dark grey in color, whereas BiOI is deep red (Fig. 4(a)). BiI₃ and BiOI are predicted to have indirect band gaps of 1.93 eV (BiI₃)¹² and 2.0 eV (BiOI)¹⁸ using high-level computational methods with hybrid exchange correlation functionals and spin-orbit coupling. However, the energy difference between the direct and indirect band gap is small (0.1 eV or less) for both compounds.^{12,18} The band structure and optical properties

Figure 4: Optical properties of BiI_3 , BiOI , and Ag_3BiI_6 absorbers. (a): Visual appearance and absorption coefficient α . (b,c): Normalized Tauc plots for direct (b) and indirect (c) band gap materials ($h\nu$ is the photon energy). (d,e): Normalized (d) and not normalized (e) PL spectra.

of ABI in the rhombohedral $R\bar{3}m$ structure have only been calculated for $x = 1$ under the generalized gradient approximation, which is prone to band gap underestimation.¹⁷ Nevertheless, significant similarities to rhombohedral BiI_3 are expected, as the crystal symmetry and bond lengths are nearly the same,^{10,36} and systematic characterization of ABI over a wide range of x showed that crystal structure has a much stronger influence than composition on the optical properties of this material system.¹⁰

Although the synthesized films are too rough for performing spectroscopic ellipsometry measurements, the absorption coefficient α of the three compounds can be roughly estimated

from transmission spectra since their thickness is known.²⁴ The absorption coefficients of BiI₃ and Ag₃BiI₆ (Fig. 4(a)) rise steeply to over 10⁵ cm⁻¹ and have a small dip between 2.0 eV and 2.2 eV. In BiI₃, those features are due to strongly bound excitons (180 meV binding energy)^{44,45} that are mobile along the **ab** planes.⁴⁵ As mentioned above, structural similarity between Ag₃BiI₆ and BiI₃ suggests that absorption features in Ag₃BiI₆ may be due to similar excitonic effects. Conversely, absorption in BiOI is weaker (Fig. 4(a)), even at higher photon energies than its presumed direct band gap energy. Weak absorption above the direct band gap can be due to a number of electronic structure features, such as a low joint density of states or dipole-forbidden transitions.^{46,47} Tauc plots for direct- and indirect band gap materials (Fig. 4(b,c)) yield direct (indirect) band gap values of 1.85 eV (1.79 eV) for BiI₃, 2.13 eV (2.05 eV) for BiOI, and 1.89 eV (1.83 eV) for Ag₃BiI₆. Since the indirect and direct band gaps are expected to be close in energy for all materials, it may be difficult to distinguish the weak indirect absorption from band tails just below the direct band gap, especially in thin-film samples. Thus, the values of the direct band gaps will be quoted from now on.

Photoluminescence

Room-temperature photoluminescence (PL) spectra of BiI₃, BiOI, and Ag₃BiI₆ films are shown in Fig. 4(d,e). The PL peak energy is 1.85 eV in BiI₃, 1.99 eV in BiOI, and 1.72 eV in Ag₃BiI₆. The peaks are rather broad for all materials. The full width at half maximum (FWHM) is 0.23 eV for BiI₃, 0.25 eV for BiOI, and 0.21 eV for Ag₃BiI₆. The BiI₃ peak is broadened more on the low-energy side, whereas the BiOI and Ag₃BiI₆ peaks are nearly symmetric. The (detrimental) Stokes shift between band gap and PL peak is largest for Ag₃BiI₆ ($\sim$ 0.15 eV) and smallest for BiI₃, where it is close to zero. The PL intensity, which is related to quasi-Fermi level splitting in the absorber, does not vary dramatically from one material to another. The BiI₃ peak is $\sim$ 4 times more intense than the BiOI and Ag₃BiI₆ peaks, which have approximately equal intensities at equal excitation levels. Note that the

differences in PL intensity measured here cannot be rigorously converted into implied open circuit voltage differences⁴⁸ because an excitation intensity significantly higher than 1 sun was necessary to obtain PL spectra of sufficient quality (see characterization details in the Supporting Information). The doping type of these materials is unclear, as contradicting reports of n- and p-type doping exist for each compound (see Table 1). There is some consensus, however, on the fact that their native doping levels are low and their resistivity is high. In fact, the doping densities of the three absorbers grown in this work were too low to be unambiguously determined by either Hall, thermovoltage, capacitance, or Kelvin probe techniques. Thus, the high iodine chemical potential employed during growth was likely not sufficient to obtain significantly higher doping levels than in previous studies. In weakly doped absorbers, high carrier lifetimes are particularly important to sustain a sufficiently high excess carrier density and minimize series resistance.¹¹ If very high lifetimes cannot be obtained, p-type doping through extrinsic impurities could be a viable strategy. Extrinsic doping would also ensure that electrons are the minority carriers in the device, thus minimizing the detrimental effect of high hole effective masses.

Review of band positions

The absolute band positions of the three absorbers are reviewed graphically in Fig. 5. BiI₃ and ABI are relatively well aligned to each other both in the valence band and in the conduction band. Therefore, it is reasonable to assume that most electron- and hole transport layers (ETL and HTL respectively) should be interchangeable between BiI₃ and ABI. However, the VBMs of BiI₃ and ABI are clearly deeper than the VBM of the archetypical hybrid perovskite absorber methylammonium lead iodide (MAPbI₃). The inadequacy of HTLs borrowed from perovskite technology has been recognized for BiI₃¹² and, in fact, a large fraction of the V_{oc} deficit with respect to the implied V_{oc} derived from PL yield measurements may be due to a large valence band cliff at the interface with the HTL.

While the CBMs of ABI and MAPbI₃ are reasonably well aligned to each other (Fig. 5),

Figure 5: Mini-review of the absolute band positions of BiI_3 , BiOI , and ABI , compared to the band positions of the hybrid perovskite MAPbI_3 and of the transport layers employed in this study. The mean band positions and their standard deviations are shown for each material. For the case of ABI , the statistical values are based on data from the $R\bar{3}m$ structure only. Both experimental and computational data are included. ^{4,10,12,14,18,19,23,26,31,38,49,50,53}

the CBM of BiI_3 lies somewhat deeper. The resulting electron barrier at the interface between BiI_3 and the perovskite-borrowed TiO_2 ETL could cause large fill factor (FF) losses or even block the photocurrent altogether.⁵¹ Although this possible issue has been discussed,^{15,38} only one study found a blocking $\text{BiI}_3/\text{TiO}_2$ interface.⁴⁵ Since the band positions and work function of TiO_2 are, to some extent, tunable by controlling the O chemical potential during growth,⁵² it is plausible that details of the TiO_2 growth process have a significant influence on the feasibility of carrier transport at the $\text{BiI}_3/\text{TiO}_2$ interface. We note that, for materials with a large exciton binding energy such as BiI_3 (and probably also ABI) a flat conduction band offset with the ETL may not be sufficient to dissociate excitons,⁴⁸ and an alternative ETL with a deeper CBM than TiO_2 may be necessary to improve the short circuit current (J_{sc}). We are, however, not aware of any study reporting BiI_3 solar cells with an electron transport layer other than TiO_2 . Previous attempts to grow BiI_3 films on ZnO , a potential ETL with a lower conduction band than TiO_2 ,⁵³ resulted in poor BiI_3 morphology.²⁷

It is more difficult to draw robust conclusions on the band positions of BiOI due to large

scattering in the reported values (Fig. 5). The overall trend, however, is a deeper location of both the VBM and the CBM. Compatibly with this trend, the ETL in the best BiOI cell to date¹⁹ is ZnO. BiOI cells with a TiO₂ electron transport layer exhibited a roll-over effect¹⁹ which is a typical symptom of a barrier to carrier transport.⁵⁴ Considering the average VBM position reported for BiOI (Fig. 5), identification of a new HTL with a deep VBM seems to be even more urgent for BiOI solar cells than for BiI₃ and ABI cells.

Photovoltaic properties

Single-junction BiI₃ and Ag₃BiI₆ solar cells are completed by sputtering a NiO HTL and a Au hole contact (Fig. 2(a,b)). Single-junction BiOI solar cells are completed by depositing a ZnO ETL by atomic layer deposition and an Al electron contact by sputtering (Fig. 2(c)). All three types of solar cells are illuminated through the glass substrate. However, BiOI cells have the hole contact on the illuminated side, whereas BiI₃ and Ag₃BiI₆ cells have the electron contact on the illuminated side. Since the goal of this study is to evaluate the two-step absorber growth method rather than experiment with alternative contact materials and layer thicknesses, device structures are intentionally similar to the structures of the highest-efficiency cells reported for each absorber material.

The highest power conversion efficiency in this work ($\eta = 0.66\%$) is achieved by BiOI solar cells, primarily due to a much higher J_{sc} and, secondarily, to a higher FF compared to BiI₃ and Ag₃BiI₆ solar cells (Fig. 6(a)). Considering that BiOI has a higher band gap and weaker absorption than the other two absorbers (Fig. 4), the lower J_{sc} recorded in BiI₃ and Ag₃BiI₆ cells should be attributed to poor carrier collection rather than to a lower absorbed photon flux. The J_{sc} trend across the three absorbers (BiOI > BiI₃ > Ag₃BiI₆) can be related to various factors limiting carrier collection, such as differences in **c**-axis texturing and morphology of the films, as well as differences in band alignment with the ETL. Ag₃BiI₆ is the absorber with the highest degree of **c**-axis texturing (Fig. 3), which is expected to be detrimental for both J_{sc} and FF due to collection losses associated with crossing the

Absorber material	Growth T (°C)	Crystal space group	Band gap (eV)	PL max. (eV)	PL FWHM (eV)	η (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)
BiI ₃ , best	100	$R\bar{3}$	1.85(1.79)	1.85	0.23	0.16	0.63	0.80	32
BiI ₃ , average						0.11 ± 0.04	0.59 ± 0.04	0.61 ± 0.14	30 ± 3
BiI ₃ , Refs. 11,14	200	$R\bar{3}$	(1.80)	1.80	0.18	1.21	0.61	5.28	38
BiOI, best	300	$P4/nmm$	2.13(2.05)	1.99	0.25	0.66	0.46	2.74	49
BiOI, average						0.53 ± 0.09	0.45 ± 0.01	2.50 ± 0.39	47 ± 3
BiOI, Ref. 19	350	$P4/nmm$	(1.93)	1.90	0.3-0.4	1.82	0.75	6.3	39
Ag ₃ BiI ₆ , best	150	$R\bar{3}m$ (+AgI)	1.89(1.83)	1.72	0.21	0.08(0.04)	0.65(0.55)	0.36(0.26)	33(25)
Ag ₃ BiI ₆ , average						0.05 ± 0.01	0.64 ± 0.01	0.23 ± 0.05	35 ± 2
Ag ₃ BiI ₆ , Ref. 30	150	$R\bar{3}m$ (+AgI)	1.83	1.74	0.28	4.31	0.63	10.7	64

Table 2: Properties of BiI₃, BiOI, and Ag₃BiI₆ films grown by (oxy)iodization of metallic precursors, and photovoltaic device parameters of the corresponding solar cells presented in this work. Data from the best cell is shown together with average and standard deviation data for the 4 cells on the chip. Those values are compared to the highest efficiency solar cells found in the literature for each absorber material. In the band gap column, the direct band gap is quoted first, followed by the indirect band gap (in parentheses). When only one value is present in the device parameter columns, the JV characteristic does not depend noticeably on scan direction. When two values are present, the first value is recorded under reverse voltage scanning, and the second value (in parenthesis) is recorded under forward voltage scanning. The numbers in bold indicate improvement of a certain photovoltaic parameter with respect to the highest efficiency device from the literature.

Figure 6: (a,b): JV characteristics of the single-junction BiI₃, BiOI, and Ag₃BiI₆ solar cells produced in this work, recorded in the dark and under 1 sun illumination. (b) is a zoomed-in view of (a), showing significant hysteresis in the illuminated JV characteristic of the Ag₃BiI₆ solar cell. For all cells, the reverse JV scan is plotted as a solid line and the forward JV scan is plotted as a dotted line. The hysteresis characteristics of each type of cell are representative of all cells fabricated with the processes described in this paper. (c): Dark and illuminated JV characteristics (solid and dashed line respectively) of a separate BiI₃ solar cell, where BiI₃ was grown at 180°C instead of at 100°C. The value of the dark diode ideality factor n is obtained by a least-squares fit of the dark JV characteristic with the single-diode equation (Fig. S6, Supporting Information). The value is confirmed by an alternative analysis method (Fig. S7, Supporting Information) and is a general characteristic of BiI₃ diodes grown at 180°C (Fig. S8, Supporting Information).

layer planes. Although BiOI has more pronounced *c*-axis texturing than BiI₃ (Fig. 3), most BiOI platelets extend from top to bottom of the film, whereas the BiI₃ crystallites are smaller (compare Fig. 2(d) and Fig. 2(f)). Furthermore, an electron barrier may exist at the BiI₃/TiO₂ interface depending on the TiO₂ preparation conditions, as explained earlier in the paper.

Interestingly, the V_{oc} trend in this study is the reverse of the J_{sc} trend discussed above. BiOI cells display the lowest V_{oc} , whereas BiI₃ cells have a slightly better V_{oc} than the best BiI₃ devices in the literature (Table 2). As noted in the discussion of PL spectra, these V_{oc} differences are unlikely to arise from large differences in the bulk material quality between the three absorbers because their PL yields are within the same order of magnitude (Fig. 4(e)). Differences in the absorber/HTL band alignment are, on the other hand, likely to contribute to the V_{oc} trend. As the HTL material is the same (NiO) for all three absorbers, the absorber with the deepest valence band (BiOI) is the one where the largest V_{oc} losses are expected at the absorber/HTL interface.⁵¹ Photovoltaic parameters of the solar cells fabricated here with the two-step method are compared in Table 2 to the photovoltaic parameters of the highest efficiency cells reported for each absorber. The overarching trend is that V_{oc} values are generally comparable, but J_{sc} values are much lower with the two-step method, resulting in lower efficiencies. The positive V_{oc} results could be attributed to the anion-rich growth conditions and the relatively high purity of vacuum-processed metallic precursors. The negative J_{sc} results could be attributed to non-optimal texture control, absence of a mesoporous ETL (for ABI), and a possible barrier at the BiI₃/TiO₂ interface. As often reported in the literature^{23,32,49,55} the present ABI cells exhibit scan rate-dependent hysteresis (Fig. 6(b)). Considering the low activation energy for Ag ionic conduction in ABI,⁹ Ag⁺ migration within the absorber during voltage scanning is the most likely cause of the hysteresis effect. Hysteresis is also observed in tandem ABI/silicon cells fabricated using a recently proposed device structure (Fig. S9, Supplementary Information).⁵⁶ The performance of the tandem cells is not discussed further, as their negligible efficiency points to additional device-related issues that go beyond the ABI absorber quality.

Finally we note that, even though BiI₃ grown at temperatures above 100°C results in a lower photovoltaic efficiency, the dark ideality factors of BiI₃ cells grown at 180°C are consistently close to 1, as shown in Fig. 6(c) and confirmed in Figs. S6-S8, Supporting Information. While the physical origin of this surprising behavior is still under investigation, high-quality

diodes combined with a low synthesis temperature could open up future applications of BiI_3 within flexible electronics.

Conclusion and outlook

We synthesized thin films of BiI_3 , BiOI , and Ag_3BiI_6 by a two step method involving (oxy)iodization of metallic precursors. We performed basic characterization of the three materials and tested their performance as solar absorbers by producing single-junction photovoltaic devices. By growing and characterizing the three materials with the same methods, they could be compared as objectively as possible, with the caveat that the absorber thicknesses and device structures were not kept fixed but were inspired by previous literature results instead. This choice was made due to the differences in the absorption coefficient and band positions of the three absorbers.

The three bismuth-based (oxy)halides have some common features, such as low to moderate synthesis temperatures, layered crystal structures with large effective masses perpendicularly to the crystal layers, optimal band gaps for top absorbers in tandem solar cells, and relatively deep valence bands. Although Bi appears as a compelling replacement for Pb in perovskite-inspired materials, the "defect tolerance" of these Bi (oxy)iodides is questionable (at least for acceptor defects) because the energy alignment of I 5p states with Bi 6s states is poorer than their alignment with Pb 6s states.⁵⁸ Poor energy alignment between these orbitals limits their interaction and prevents the formation of a disperse, strongly antibonding valence band maximum. In fact, Table 1 shows that Bi 6s states only contribute minimally to the valence band maximum, hole effective masses are large in all directions, and deep acceptor defects are expected, at least for BiI_3 . As the conduction bands of these materials are, in general, more disperse and with stronger orbital mixing (Table 1) p-type background doping may be preferable in order to have the more mobile electrons as minority carriers. The room-temperature photoluminescence spectra of these compounds are

	Material: BiI ₃	Material: BiOI	Material: Ag _x BiI _{x+3}	Method: (oxy)iodization of metallic precursors
Advantages	Strong absorption, low growth temperature.	Stable, good texture control, moderate growth temperature.	Strong absorption, low growth temperature.	High V _{oc} (BiI ₃), anion-rich growth, high-quality vacuum-processed metals.
Disadvantages	Soft and potentially unstable, poor texture control, deep VBM, high exciton binding energy.	Weak absorption, very deep VBM, poor adhesion to substrate.	Soft and potentially unstable, poor texture control, deep VBM, hysteresis.	Generally low J _{sc} , incomplete texture control, limited growth T window (BiOI).
Potential areas for investigation	Improved texture control at higher growth T, experimental defect characterization, new HTL, p-type doping.	Illuminating from electron contact side, experimental defect characterization, new HTL, p-type doping.	Extra electronic structure calculations, experimental defect characterization, role of ion migration, new HTL, p-type doping.	Using seed layers to promote texturing, including a p-type dopant in the precursors, growing BiOI directly from Bi without the BiI ₃ intermediate

Table 3: Summary of advantages and disadvantages of Bi₃, BiOI, and Ag₃BiI₆ absorbers in general, as well as of the two-step process used to grow them in this work. Suggestions for future work are also given.

generally rather weak and broad, so potential limitations due to native defects should be further investigated experimentally. Partially compensating other unfavorable features, BiI_3 and BiOI have very large static relative permittivities (although probably only along the **ab** planes), which may help screen charged defects and decrease their capture cross section. Unfortunately, the relative permittivity, the defect landscape, and even accurate effective masses and band edge orbital character are not available for the family of ABI absorbers.¹⁷ More detailed calculations are thus called for.

While the three absorbers considered in this study certainly have some common features, they also have substantial differences in their absorption coefficient, ease of texture control, growth temperature, and stability. Advantages and disadvantages of the individual absorbers are summarized in Table 3. The results of this work and a review of the existing literature suggest that the photovoltaic performance of all three materials would strongly benefit if their texture could be controlled so to obtain **ab** planes oriented perpendicularly to the substrate plane. Texture control was a key step in unlocking the photovoltaic potential of other layered compounds (Sb_2Se_3 and 2D perovskites) enabling efficiencies above 10%.³⁵ In the present work, texture control was only achieved partially for BiOI and BiI_3 , and not at all for Ag_3BiI_6 . In previous studies using different deposition techniques, the growth of textured films was rarely mentioned as a priority and not achieved in practice, with possibly only one exception.¹⁹ Therefore, the best BiI_3 and Ag_3BiI_6 solar cells still need either a very thin absorber or a mesoporous architecture to mitigate the poor collection efficiency related to carrier transport perpendicularly to the crystal layers.^{14,30} Future work on these compounds should focus on growth techniques that are likely to enable texture control, such as vapor transport and closed-space sublimation. There is also no guarantee that the absorber thicknesses and device structures employed so far in the literature are optimal.

BiI_3 , BiOI , and ABI solar cells produced by (oxy)iodization of metallic precursors had similar open circuit voltages (V_{oc}) to the best devices reported for each absorber (except for BiOI), but significantly lower short circuit currents. The particularly low J_{sc} of Ag_3BiI_6

cells was attributed to a combination of poor texture control combined with the absence of a mesoporous TiO_2 layer aiding carrier collection. Beyond the original goal of evaluating the photovoltaic performance of these materials, the low ideality factors of BiI_3 diodes in the dark (< 1.1), combined with a low synthesis temperature ($< 200^\circ\text{C}$) could make BiI_3 an attractive material for flexible electronics. Furthermore, the combined electronic and ionic conductivity of ABI could be used to create light-controlled memristors and synaptic devices as already demonstrated for halide perovskites.^{57,59}

Supporting Information

Further experimental details, photographs of growth setups, EDX spectra, additional XRD patterns and SEM images, determination of the ideality factor of BiI_3 diodes, device structure and JV characteristics of an ABI/silicon tandem cell.

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