Above 600 mV Open-Circuit Voltage BiI\(_3\) Solar Cells

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Supporting Information

ABSTRACT: Phase-pure BiI\(_3\) films obtained by versatile gas-phase iodination of Bi\(_2\)S\(_3\) are investigated as an absorber in photovoltaic devices. This preparation method leads to highly crystalline BiI\(_3\) films featuring a rhombohedral phase and a high-degree of stacking order. The films are composed of micrometer-sized flat grains distributed homogeneously across the F-doped SnO\(_2\) (FTO) substrate, exhibiting an indirect band gap transition at 1.72 eV. High-level calculations based on G\(_0\)W\(_0\) approximation are used to rationalize the electronic structure of BiI\(_3\), confirming the band gap value estimated experimentally. The films show p-type conductivity with an acceptor density on the order of 10\(^{15}\) cm\(^{-3}\). Solar cells with the architecture glass/FTO/TiO\(_2\)/BiI\(_3\)/F\(_8\)/Au, where F\(_8\) is poly(9,9-di-octylfluorenyl-2,7-diyl), display a record open-circuit voltage above 600 mV and overall power conversion efficiency of 1.2% under AM 1.5G illumination. The large open-circuit potential is rationalized in terms of carrier lifetimes longer than 1 ns as probed by time-resolved photoluminescence spectroscopy.

Sustainable photovoltaic (PV) technologies beyond Si solar cells represent huge opportunities in key areas such as large-scale building integration and competitive tandem technologies close to 30%.\(^1\,\)\(^2\) This strategy requires new solar absorbers based on earth-abundant materials that can offer different alternatives to existing CdTe and CuInGa-S\(_2\)(S,Se\(_2\)) (CIGS) technologies.\(^3\,\)\(^–\)\(^6\) Hybrid perovskite solar cells have experienced an unprecedented rise from basic science to a technology close to commercialization, particularly in the context of Si-tandem solar cells, although significant challenges remain in terms of stability.\(^7\,\)\(^–\)\(^10\) Cu\(_2\)ZnSn(S,Se\(_4\)) has been the key target in the context of earth-abundant CIGS replacement; however, efficiency remains hindered by a loss mechanism yet to be fully elucidated.\(^8\),\(^11\)\(^–\)\(^14\) These developments have led to the establishment of guiding principles for the design of solar absorbers based on the concept of “defect-tolerant materials”, with Bi being one of the elements in these strategies.\(^5\),\(^6\) Indeed, Bi\(^{3+}\) and Pb\(^{2+}\) are heavy and highly polarizable cations associated with large spin–orbit coupling effects, dielectric constants, and band dispersion, resulting in low recombination probabilities and better charge separation.\(^5\),\(^6\),\(^11\) Bi compounds such as methylammonium bismuth iodide, bismuth chalcogenides, bismuth sulfide, silver bismuth sulfide, and bismuth iodide have been tested as solar absorbers with power conversion efficiencies up to 6.3%.\(^12\),\(^13\),\(^15\)–\(^19\) Previously, we reported on BiFeO\(_3\) all-oxide solar cells with a record power conversion efficiency of 4%.\(^18\) BiI\(_3\) is particularly attractive as a binary compound composed of low-cost elements and suitable optoelectronic properties.\(^20\) BiI\(_3\) fundamental optical transitions have been reported in the range of 1.67–1.90 eV, featuring capture sections larger than 10\(^3\) cm\(^{-1}\) for energies above 2 eV.\(^20\),\(^21\) Addition-ally, minority carrier lifetime (\(\tau_0\)) and electron mobilities (\(\mu_e\)) of 1.54 ns and 250 cm\(^2\) V\(^{-1}\) s\(^{-1}\) have been reported in BiI\(_3\) single crystals.\(^20\),\(^24\),\(^25\) The current record efficiency of BiI\(_3\) thin-film cells was reported by Hamdeh and co-workers, with a \(V_{OC}\) value below 400 mV and a power conversion efficiency of approximately 1%, although no statistical analysis of these performance indicators was reported.\(^17\) In contrast to single crystals, thin films deposited either by solution or physical vapor deposition are characterized by a shorter \(\tau_0\) (250 ps), which could be a limiting factor in PV performance.\(^20\) In this work, we develop a new methodology for preparing high-quality rhombohedral BiI\(_3\) thin films based on gas-phase iodination of Bi\(_2\)S\(_3\). The films exhibit a high degree stacking order with \(\tau_0\) values longer than 1 ns as estimated from time-resolved photoluminescence spectroscopy. PV devices with the architecture glass/FTO/TiO\(_2\)/BiI\(_3\)/F\(_8\)/Au, where F\(_8\) is poly(9,9-di-octylfluorenyl-2,7-diyl), display a record open-circuit voltage above 600 mV and overall efficiency of 1.2% under AM 1.5G.
1.5G illumination. Electronic and vibrational fingerprints of the phase-pure BiI₃ films are rationalized based on calculations employing G₀W₀ approximation and density functional perturbation theory (DFPT).

BiI₃ films are prepared by a sequential method starting from spin coating a Bi(NO₃)₃ and thiourea precursor solution onto FTO, followed by thermolysis at 200 °C to produce a homogeneous Bi₂S₃ film that is subsequently iodinated upon exposure to the I₂ gas. This methodology was inspired in our previous report on the fabrication of PbI₂ photocathodes, although in this case the Bi₂S₃ is placed above the I₂ granules, which are heated to 200 °C (see Supporting Information section S3 for further details). The reaction is governed by Pearson’s hard–soft acid–base principle in which the polarizable Bi³⁺ (soft-acid) spontaneously exchanges a hard S²⁻ base partner with a polarizable I⁻ (soft-base).

The structure, morphology, and phase purity of the as-grown BiI₃ films are investigated by X-ray diffraction (XRD) and
Raman spectroscopy (Figure 1). XRD of the film on the FTO substrate (Figure 1a) reveals crystallization of BiI₃ in its common rhombohedral structure (R₃̅m, space group: 148). No peaks due to sulfide, oxide, and oxyxide are detected. The high intensity of the (003) peak at ~12° suggests a high degree of orientation along the c-axis of the unit cell. The Bi atom is octahedrally coordinated to 1 atoms, forming hexagonally close-packed layers interacting by a weak Van der Waals force along the c-axis with the Bi atom, effectively occupying two-thirds of the octahedral sites. The SEM image in Figure 1b is characterized by flake-shaped grains with sizes in the range of 700–1200 nm homogeneously distributed across the substrate. This growth behavior is similar to that observed for Pbi₂ films.38

Figure 1c displays the Raman spectrum of BiI₃ showing three distinctive bands assigned to A g and E g modes. These assignments are supported by theoretically calculated spectra using DFPT, as shown in Figure 1d (the full spectrum is plotted in Figure s1). The measured and calculated spectra exhibit remarkable similarity in the range of 80–160 cm⁻¹. The spectral information below 83 cm⁻¹ cannot be accessed in our spectrometer. The modes at 98 and 114 cm⁻¹ are LO phonon modes at the Γ and Z special points, respectively. The nature of three vibrational modes at 98, 114, and 126 cm⁻¹ is captured in the movies provided in Supporting Information Movie S1 and Movie 2.

Figure 2a displays the optical transmittance and reflectance spectra of 230 nm thick BiI₃ films on the FTO-coated glass substrates, showing sharp absorption behavior between 650 and 700 nm. Considering an indirect band gap transition, a value of 1.72 eV can be estimated from the Tauc’s plot in Figure 2b. As mentioned previously, there is some debate in the literature concerning the value of the indirect band gap transition, which ranges between 1.65 and 1.90 eV, with reports of direct transitions between 1.8 and 2 eV.20−23 The dispersion in the reported experimental and computed value of E g has been found to depend on the experimental methodology and computational level.16,20,22,23,29−33 The most detailed optical study has been reported by Podraza et al., showing an indirect transition at 1.67 eV,22 which is close to our findings. On the other hand, the hybrid HSE functional DFT by Lehner et al. estimated a value of 1.93 eV.16

Figure 2c,d summarizes our estimations of the electronic structure of BiI₃ employing quasiparticle GₐW₀ approximation showing that the lowest-energy transition has an indirect nature with a value of 1.68 eV. Komatsu and Kaifu established that the temperature dependence of the BiI₃ band gap has a gradient of −3.7 × 10⁻⁴ eV/K between 286 and 77 K and −1.8 × 10⁻⁴ eV/K between 77 and 6 K.34 On the basis of these findings, the calculated band gap is expected to decrease to approximately 1.59 eV at room temperature. It is important to highlight that GₐW₀ calculations consistently underestimated experimental band gap values by 200 meV on average in over 200 materials.25,35 Consequently, the difference in our computed value and the experimental band gap on our thin films (Figure 2b) and on single crystals by Podraza et al.22 can be considered within the error of the method.

Although GₐW₀ calculations provide accurate accounts of spin−orbit coupling, band dispersions, and width, this comes at the expense of high computational costs, which limit calculating the projected density of states. However, this information is available with a good level of accuracy from the elegant work by Lehner et al. employing DFT with hybrid functionals.16 The conduction band is formed of highly covalent I 5p and Bi 6p hybridized states split due to spin−orbit coupling, while the valence band is primarily composed of an I 5p orbital with a minor contribution from Bi 6s electrons. Calculations also show that the conduction band is much more dispersed than the valence band as a result of spin−orbit coupling promoted by the Bi⁺⁺ ion. This results in a lighter effective mass of electrons in comparison to holes and thus higher electron mobility. This observation is also consistent with experimental studies on BiI₃ single crystals, showing effective electron mass 5 times lower than that of holes and electron mobility up to 250 cm² V⁻¹ s⁻¹.12,25 The high covariant interaction in the conduction band is also responsible for a substantial in-plane Born effective charge of 5.43. These optoelectronic features are very attractive in the context of thin-film PV devices.

Electrochemical impedance spectroscopy in nonaqueous electrolyte solutions was employed to estimate the doping density of the films. Analysis based on the Mott−Schottky plot in Figure s2 confirmed the p-type nature of BiI₃, with estimates of the majority carrier density in the range of 2.8 × 10¹⁵−1.4 × 10¹⁶ cm⁻³, considering the contrast in relative permittivity between in-plane (ε∥ = 8.6) and out-of-plane (ε⊥ = 54).37 These values should be considered as an upper limit as the effective roughness of the material is not considered in the calculations. PbI₂ films obtained by a similar route were also characterized by a low doping density.26 The analysis also shows that the flat band potential (E fb) is located at 1.53 V vs SHE, placing the valence band maxima (VBM) at approximately 5.97 eV with respect to the vacuum level, which is close to values obtained from photoemission spectroscopy.16 Considering E fb = 1.72 eV, the conduction band minima (CBM) is set close to 4.25 eV.

Current−voltage characteristics of 10 devices featuring an active area of 4 mm² under AM 1.5G (100 mW cm⁻²) illumination are shown in Figure 3a. Devices were designed with an architecture glass/FTO/TiO₂/PbI₂/F8/Al, with a BiI₃ film thickness of 230 nm. As described in Supporting Information section S3, electron (TiO₂) and hole (F8) transporting layers were processed by spin-coating. The best-performing device displayed a power conversion efficiency (η) of 1.21% with a short-circuit current (Isc) of 18.84 mA cm⁻² and an open-circuit voltage (Voc) of 4.28 V. Calculations also show that the conduction band minima close to values obtained from photoemission spectroscopy.16 Considering E fb = 1.72 eV, the conduction band minima (CBM) is set close to 4.25 eV.

The external quantum efficiency (EQE) for the champion cell shows a maximum value close to 35%, as displayed in Figure 3b. The variation of the key figure of merit was less than 10%, illustrating the reproducibility in the preparation method.

The improved device performance with respect to previous reports can be linked to the device architecture and the quality of the BiI₃ film. Conducting polymers such as polytiaryliumine (PTA; IP = 5.1 eV) and polyindacenodithiophene-difluorobenzothiadiazole (PIDT-DDBT; IP = 5.5 eV) have been employed as hole transport layers (HTLs) by Lehner et al.16 The HTL with a higher IP resulted in an improvement of Voc from 220 to 420 mV but at the cost of the short-circuit current (Jsc), leading to only an incremental change in the overall efficiency (η) from 0.3 to 0.32%.16 Hamdeh et al. used a thin layer of V₂O₅, which resulted in Jsc of up to 8 mA cm⁻² and η of 1.06%, however, the Voc remained limited to 365 mV.17 The use of F₈ in our devices was inspired by Ganose et al.’s theoretical
studies on BiSI, suggesting that the high IP value (5.8 eV) of this polymer offers a better match to the VBM. This point partially accounts for the record V_{OC} values measured in our devices. Indeed, we have investigated cells employing F8 as the HTL but following previous protocols in which commercially available BiI\textsubscript{3} powders were spin-coated to the TiO\textsubscript{2} surface (so-called “direct” method).\textsuperscript{20} The corresponding J−V curves (Figure s3a) exhibited J_{SC} and FF values that were 10−15% lower, while the V_{OC} dropped by 56% in comparison to the devices prepared by our gas-phase iodination method. The EQE spectra also show significantly lower values at wavelengths close to the band edge for the devices prepared via the direct method (Figure s3b). These results strongly suggest that the minority carrier lifetime is significantly different in these two films.

Finally, Figure 3c shows a characteristic time-resolved photoluminescence measurement of BiI\textsubscript{3} prepared by gas-phase iodination. The data were fitted to a biexponential function, yielding two lifetime values of around 460 ps and 1.4 ns. These values are comparable to the lifetimes measured on BiI\textsubscript{3} single crystals and significantly longer than those in thin films reported in previous studies.\textsuperscript{17,20} It is rather difficult to quantitatively rationalize the increase in V_{OC} with carrier lifetime as there is no theoretical framework directly combining these two parameters. Repins and co-workers provided an empirical correlation after analyzing a large number of CIGS devices, showing that V_{OC} is strongly dependent on carrier lifetime in the range below 10 ns.\textsuperscript{39} Consequently, the high quality of the BiI\textsubscript{3} thin films generated by our method is key for achieving record V_{OC} and PCE values. There is significant room for improvement in device architecture, not only in terms of better alignment of ETL and HTL layers to the absorber layer but also in the carrier collection efficiencies. Indeed, it is anticipated that interfacial recombination at the boundaries with carrier extracting layers is the main performance limiting factor in these devices.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b01182.

BiI\textsubscript{3} thin film deposition and cell fabrication, film characterization and device measurements, computational details, BiI\textsubscript{3} Raman spectrum calculated by DFPT, Mott–Schottky plot of the BiI\textsubscript{3} film in dichloromethane, and device performance of cells fabricated by direct spin-coating of BiI\textsubscript{3} particles (PDF)

Movie illustrating the Raman A\textsubscript{g} vibrational mode of BiI\textsubscript{3} (AVI)

Movie illustrating the Raman E\textsubscript{g} vibrational mode of BiI\textsubscript{3} (AVI)

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Notes
The authors declare no competing financial interest. All data presented in this Letter can be freely accessed from the Bristol’s Research Data Repository (https://doi.org/10.5523/bris.2b4tiz6awpgy29o33jdjfxzk0).

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Figure 3. PV performance of glass/FTO/TiO\textsubscript{2}/BiI\textsubscript{3}/F8/Au devices: J−V characteristics of 10 cells under AM 1.5G (100 mW/cm\textsuperscript{2}) illumination (a) and characteristic EQE spectrum (b). Time-resolved photoluminescence spectrum of the BiI\textsubscript{3} films (c). The purple trace corresponds to the instrument response function (IRF).
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