

Antimony/Bismuth Chalcogenides

Subjects: Others
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Despite their comparable performance to commercial solar systems, lead-based perovskite (Pb-perovskite) solar cells exhibit limitations including Pb toxicity and instability for industrial applications. To address these issues, two types of Pb-free materials have been proposed as alternatives to Pb-perovskite: perovskite-based and non-perovskite-based materials. In this entry, we briefly introduce the crystal, energy band structures and theoretical insights of Sb/Bi chalcogenides as solar absorbers.

Keywords: antimony chalcogenides ; bismuth chalcogenides ; solar cells

1. Introduction

Since the Snaith group reported the 10.9% milestone power conversion efficiency (PCE) required for industrial applications for lead-based perovskite (Pb-perovskite) solar cells in 2012 ^[1], many types of Pb-perovskite solar cells have been fabricated, with performance significantly improving over the past few years ^{[2][3][4][5][6][7]}. At present, the certified PCE exceeds 25% ^[8], approaching the theoretical maximum efficiency for multi-junction Pb-perovskite solar cells ^[9]. This efficiency is also comparable to those of commercial solar systems based on Si, CdTe, and Cu(In,Ga)Se₂. Moreover, high-performance Pb-perovskite solar cells can be manufactured through solution processing at a low temperature of <150 °C, which can reduce costs. Therefore, these characteristics make them the most promising alternative to current photovoltaic systems. However, Pb-perovskite solar cells exhibit limitations for commercialization, with potential health problems and stability being the two main barriers ^{[6][7][10][11][12][13][14][15]}. In particular, Pb can be easily released from the Pb-perovskite because of its instability, which can cause major health problems ^{[10][11][12][13][14][15]}. Although techniques of material and interface engineering, surface passivation, and encapsulation can significantly improve the stability of Pb-perovskite ^{[7][15][16][17]}, thereby minimizing the Pb loss, the persistent toxicity problem requires attention to enhance commercialization.

To address these issues, many researchers have focused on finding Pb-free and stable materials with comparable optoelectronic properties. The Pb-free photovoltaic materials proposed as alternatives to date are presented in Table 1. Replacing Pb by tin (Sn) or germanium (Ge), with similar ionic radius and belonging to the same group of the periodic table, in Pb-perovskites is a simple method for fabricating Pb-free materials while maintaining the perovskite structure. These materials are known as Pb-free perovskites. In particular, Sn-based perovskites ASnX₃ (A = Cs⁺, organic cations; X = Cl, I, and Br) exhibit properties comparable to those of Pb-perovskites such as optimal band gaps (*E*_gs) of 1.1–1.4 eV, high carrier mobilities, long carrier lifetimes, and long diffusion lengths ^{[10][11]}. Thus, many researchers have devoted attention to developing Sn-based perovskite solar cells ^{[10][11]}. Consequently, a record PCE of 11.4% was achieved through the FASnI₃ (FA = CH₅N₂⁺) solar cell by introducing a phenylhydrazine hydrochloride ^[18]. However, Sn-perovskites still involve the serious disadvantage of rapid decomposition because Sn is readily oxidized from the +2 to +4 state on exposure to air ^{[10][11]}. Another approach for fabricating Pb-free perovskites involves replacing two Pb²⁺ ions with ions of two metals with oxidation states of +1 and +3 to form double perovskites represented as A₂M^IM^{III}X₆ ^{[12][19]}, with the Cs₂AgBiBr₆ as a typical example. Alternatively, the two Pb²⁺ ions are replaced by a tetravalent metal ion, such as Sn⁴⁺ or Ti⁴⁺, forming compounds with the general formula A₂M^{IV}X₆ ^{[12][20]}. Such compounds are termed vacancy-ordered double perovskites, with the Cs₂SnI₆ as a prime example. In addition, two-dimensional (2D) perovskites are produced by replacing the Pb²⁺ ions with trivalent metal ions such as Sb³⁺ or Bi³⁺ ^{[15][21]}. Although these Pb-free double and 2D perovskites display significant stability improvement over Pb- and Sn-perovskites, efficiency remains a limitation.

Table 1. Types of Pb-free photovoltaic materials and their best photovoltaic performance data.

Metal (M) Ions	Chemical Compound	Record Device Performance		
		PCE	Material	Ref.

Perovskites	Sn ²⁺ , Ge ²⁺	Perovskite/AMX ₃	11.4%	FASnI ₃	[18]
	Ag ⁺ , Bi ³⁺	Double perovskite/A ₂ M ^I M ^{III} X ₆	2.84%	Cs ₂ AgBiBr ₆	[19]
	Sn ⁴⁺	Vacancy-ordered double perovskite/A ₂ M ^{IV} X ₆	3.28%	Cs ₂ TiBr ₆	[20]
	Sb ³⁺ , Bi ³⁺	2D perovskite/	3.34%	MA ₃ Sb ₂ I _{9-x} Cl _x	[21]
	Sb ³⁺	Sb chalcogenides/M ₂ Ch ₃ , CuMCh ₂	10.5%	Sb ₂ (S,Se) ₃	[22]
Sb/Bi-based non-perovskites	Sb ³⁺ , Bi ³⁺	Ternary chalcogenides/MChX, M ₁₃ Ch ₁₈ X ₂	4.07%	Sb _{0.67} Bi _{0.33} SI	[23]
	Sn ²⁺ , Pb ²⁺ , Sb ³⁺ , Bi ³⁺	Quaternary chalcogenides/	4.04%	Sn ₂ SbS ₂ I ₃	[24]

PCE— power conversion efficiency.

Apart from these Pb-free perovskites, antimony/bismuth (Sb/Bi)-based non-perovskites are another alternative to Pb-perovskites. Unlike perovskites, most of these non-perovskites crystallize in a layered structure, with the layers linked by weak van der Waals forces. This anisotropic crystal structure provides unique and interesting properties that can significantly affect photovoltaic performance [25][26][27]. To date, many Sb/Bi non-perovskites for solar cells have been reported, and these comprise two types, according to elemental composition. The first type is the Sb chalcogenides involving an orthorhombic structure, such as the Sb₂Ch₃ and CuSbCh₂ (Ch = S, Se). In fact, studies on these as photovoltaic materials predates those of Pb-perovskites because of their promising properties, such as the tunable *E_g* values of 1.0–1.8 eV, high visible light absorption coefficient, stability, low toxicity, and earth-abundant constituents [25][26]. Although varied engineering methods and device architectures have been employed to achieve high-efficiency for Sb chalcogenide solar cells, the performances of these cells remained below the 10% milestone until 2018 [26][27][28][29][30][31][32][33][34][35]. However, recently, a PCE of 9.2% was obtained from the [001]-oriented Sb₂Se₃ nanorod solar cells [36], and finally, a PCE of 10.5% was reported by Chen's group from the hydrothermally deposited Sb₂(S,Se)₃ thin film solar cells [22][37].

Sb/Bi chalcogenides represent the other type of Sb/Bi non-perovskites, comprising Sb/Bi-based semiconductors containing halides and chalcogenides. Following the initial application of Sb sulfide (SbS₂) in solar cells by the Seok group in 2018 [38], multiple Sb/Bi chalcogenide solar cells have been proposed. Thus far, the materials investigated for use in solar cells include ternary (MChX and M₁₃Ch₁₈X₂, where M = Sb, Bi) [23][38][39][40][41][42][43][44][45][46][47][48][49][50][51][52][53] and quaternary chalcogenides (, where M^I = Sn, Pb; M^{III} = Sb, Bi) [23][54]. These chalcogenides commonly exhibit advantageous properties that can be adjusted for use in solar cells. In particular, the electronic structure of the most studied MChX family is similar to that of Pb-perovskites, with beneficial properties for solar cells such as high dielectric constant, low effective mass, and tunable *E_g* [39][42][43][44][55]. Therefore, high-performance MChX solar cells comparable to Pb-perovskite cells are expected due to these properties. Recently, the Seok group reported a PCE of 4.07% for Sb_{0.67}Bi_{0.33}SI solar cells, highlighting the high-efficiency potential for the MChX family [23]. In addition, the MChX family is suitable for other applications including the fabrication of room-temperature radiation detectors and p-type transparent conductors [39]. This wide-ranging applicability facilitates designing multifunctional devices. In addition to the MChX family, PCEs of 0.85% and 4.04% have been reported for solar cells based on M₁₃Ch₁₈X₂ and , respectively. However, the highest PCE achieved for Sb/Bi chalcogenide solar cells remains at around 4%, although the performance has significantly improved over the past few years.

2. Crystal and Energy Band Structures of Sb/Bi Chalcogenides

In this section, the crystal and energy band structures of Sb/Bi chalcogenides used to date for solar cells are briefly presented. Depending on the number of elements and composition, Sb/Bi chalcogenides with different structures can be created, as shown in Table 2. The ternary chalcogenides employed for solar cells are the MChX and $M_{13}Ch_{18}X_2$ types. The MChX type, such as SbSI and BiSI, involves the orthorhombic structure with the $Pnma$ space group, crystallizing into an $[(MChX)_2]_n$ double-chained structure, with the adjacent chains joined by van der Waals forces [57][58]. Conversely, the $M_{13}Ch_{18}X_2$ type such as the $Bi_{13}S_{18}I_2$ possesses a hexagonal structure with a ribbon-shaped $(M_4Ch_6)_\infty$ subunit. The M_4Ch_6 subunits form six spokes around the central hexagonal channel at the corners of the unit cell, with iodine in between [53][58]. For the quaternary chalcogenides ($M_2^{II}M^{III}Ch_2X_3$), such as $Pb_2SbS_2I_3$ and $Sn_2SbS_2I_3$, crystallization produces the orthorhombic structure with the $Cmcm$ space group [24][54][59].

Table 2. Summarized data for the structural properties of Sb/Bi chalcogenides used for solar cells.

	Chemical Formula	Structure/Space Group	Typical Materials	Ref.
Ternary chalcogenides	MChX	Orthorhombic/ $Pnma$	SbSI, BiSI	[23][38][39][40][41][42][43][44][45][46][47][49][58]
	$M_{13}Ch_{18}X_2$	Hexagonal/ $P6_3$	$Bi_{13}S_{18}I_2$	[53][58]
Quaternary chalcogenide	$M_2^{II}M^{III}Ch_2X_3$	Orthorhombic/ $Cmcm$	$Pb_2SbS_2I_3$, $Sn_2SbS_2I_3$	[24][54][59]

To employ Sb/Bi chalcogenides in solar cells, the energy band structure deserves priority because of its importance in light harvesting and conversion. Specifically, the E_g should be checked because it determines the maximum PCE achievable for each material according to the Shockley–Queisser limit [60][61]. Thus, materials with an E_g value between 1.10 and 1.55 eV are preferred for solar cells. Figure 1 displays the energy band diagram of typical Sb/Bi chalcogenides reported to date. The positions of the conduction band minimum and valence band maximum as well as the E_g value vary depending on the elemental composition and number of elements. Along with the chalcogenides shown in Figure 1, Sb/Bi chalcogenides exhibit E_g values varying from 0.75 eV for $Bi_{13}S_{18}I_2$ [53] to 2.31 eV for SbSBr [42]. These results indicate that their band structures can be tuned via chemical substitution, and that the electron transporting layer (ETL) and hole transporting layer (HTL) applications necessitate selectivity for each solar cell depending on the chalcogenide used. In addition to the band structures, other factors such as the optical absorption strength, charge effective mass, dielectric constant, and defects require consideration [44][61]. However, research on these remains insufficient, and this highlights the need for further studies.

Figure 1. Energy band diagram of typical Sb/Bi chalcogenides. The SbSI, $Sb_{0.67}Bi_{0.33}SI$, BiSI, $Pb_2SbS_2I_3$, and $Sn_2SbS_2I_3$ energy levels were obtained from [23][38][47][54] and [24], respectively. For comparison, the energy levels for typical conducting oxides (F-doped SnO_2 (FTO) and In-doped SnO_2 (ITO)), the electron transporting layer (ETL), and hole transporting layer (HTL) are included. P3HT, PCPDTBT, and F8 denote poly(3-hexylthiophene), poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)], and poly(9,9-di-n-octylfluorenyl-2,7-diyl), respectively.

3. Theoretical Insights on Sb/Bi Chalcogenides as Solar Absorbers

Theoretical calculations, such as first-principle methods, provide further insight into the potential of specific materials (e.g., as solar absorbers) and clues for designing device structures. However, the research on such theoretical investigations is very limited because Sb/Bi chalcogenide solar cells are still in their early stages of development compared to the Pb-perovskite cells. Thus, in this section, theoretical insights into only the most studied MChX family are briefly introduced.

Based on the first-principle calculations, Brandt et al. identified the MChX family as promising solar absorbers due to its low effective masses, large dielectric constants, and strong absorption, as shown in Table 3 [62]. They further found that BiSI and BiSeI are most suitable for achieving high-performance solar cells because of their much stronger spin-orbit coupling. The suitability of these Bi compounds for solar cells was also confirmed by other groups [39][43][44][63]. Ganose et al. suggested that the conducting oxide and HTL should be selected for efficient charge transfers by considering the electron affinity (EA = 4.9–5.0 eV) and ionized potential (IP = 6.2–6.4 eV) of these Bi chalcogenides, respectively [43]. They also concluded from the defect analysis that these Bi compounds represent intrinsic semiconductors regardless of fabrication conditions, making them best suited for application in *p-i-n* device architecture [44].

Table 3. Summary of effective masses of hole (m_h^*) and electron (m_e^*), static dielectric constant, and absorption coefficient of MChX family, calculated by different methods.

MChX Compounds	m_h^*	m_e^*	Static Dielectric Constant	Absorption Coefficient ¹	References
Pb-perovskite ²	0.10	0.16	20.07	$>1 \times 10^5 \text{ cm}^{-1}$	[61][62]
BiSI	0.61–4.79	0.53–2.33	14.26–71.32	$>1 \times 10^5 \text{ cm}^{-1}$	[39][44][62][63]
BiSeI	0.81–5.89	0.25–1.61	14.78–62.82	$>1 \times 10^5 \text{ cm}^{-1}$	[39][44][62][63]
SbSI	0.27–2.06	0.21–1.25	10.56–69.38	-	[42][55][62][63][64]
SbSeI	0.57–4.37	0.35–1.83	14.70–57.18	-	[42][55][62][63][64]
SbSBr	0.24–3.55	0.51, 0.52	13.81–105.15	-	[42][55][62][63][64]

¹ Absorption coefficient values at visible region are presented. ² Data of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ are shown as typical of Pb-perovskites for comparison.

Butler et al. analyzed the band structures of SbChX (SbSI, SbSeI, and SbSBr) by different calculation methods [42][55]. The effective masses were calculated to be below 0.65, indicating that SbChX have high charge carrier mobilities suitable for solar cells. They also found that the SbSBr have deeper IP energy (5.8 eV) than that of I-containing SbChX (5.3 eV for SbSeI and 5.4 eV for SbSI). This different IP energy suggests that contacting layers such as ETL and HTL should be selected depending on the halide ion of SbChX for optimal device performance [42]. For example, the contacting layers used in $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) can be applied to SbSBr solar cells due to their similar IP value with that of CZTS. In addition, a heterojunction structure composed of SbSI/SbSBr with SbSBr epitaxially grown on SbSI was proposed for efficient charge separation based on their closely matched lattice parameters and band offsets [55].

References

1. Lee, M.M.; Teuscher, J.; Miyasaka, T.; Murakami, T.N.; Snaith, H.J. Efficient Hybrid Solar Cells Based on Meso-Structured Organometal Halide Perovskites. *Science* 2012, 338, 643–647.

2. Choi, Y.C.; Lee, S.W.; Jo, H.J.; Kim, D.-H.; Sung, S.-J. Controlled growth of organic-inorganic hybrid CH₃NH₃PbI₃ perovskite thin films from phase-controlled crystalline powders. *RSC Adv.* 2016, 6, 104359–104365.
3. Choi, Y.C.; Lee, S.W.; Kim, D.-H. Antisolvent-assisted powder engineering for controlled growth of hybrid CH₃NH₃PbI₃ perovskite thin films. *APL Mater.* 2017, 5, 026101.
4. 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.
5. Seok, S.I.; Grätzel, M.; Park, N.G. Methodologies toward Highly Efficient Perovskite Solar Cells. *Small* 2018, 14, 1704177.
6. Jena, A.K.; Kulkarni, A.; Miyasaka, T. Halide perovskite photovoltaics: Background, status, and future prospects. *Rev.* 2019, 119, 3036–3103.
7. Kim, B.; Seok, S.I. Molecular aspects of organic cations affecting the humidity stability of perovskites. *Energy Environ. Sci.* 2020, 13, 805–820.
8. Green, M.A.; Dunlop, E.D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Hao, X. Solar cell efficiency tables (version 56). *Photovolt.* 2020, 28, 629–638.
9. Granas, O.; Vinichenko, D.; Kaxiras, E. Establishing the limits of efficiency of perovskite solar cells from first principles modeling. *Rep.* 2016, 6, 36108.
10. Nasti, G.; Abate, A. Tin Halide Perovskite (ASnX₃) Solar Cells: A Comprehensive Guide toward the Highest Power Conversion Efficiency. *Energy Mater.* 2020, 10, 1902467.
11. Hasan, S.A.U.; Lee, D.S.; Im, S.H.; Hong, K.-H. Present Status and Research Prospects of Tin-based Perovskite Solar Cells. *Solar RRL* 2019, 4, 1900310.
12. Kung, P.-K.; Li, M.-H.; Lin, P.-Y.; Jhang, J.-Y.; Pantaler, M.; Lupascu, D.C.; Grancini, G.; Chen, P. Lead-Free Double Perovskites for Perovskite Solar Cells. *Solar RRL* 2019, 4, 1900306.
13. 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? *Energy Mater.* 2020, 10, 1902500.
14. Nie, R.; Sumukam, R.R.; Reddy, S.H.; Banavoth, M.; Seok, S.I. Lead-free perovskite solar cells enabled by hetero-valent substitutes. *Energy Environ. Sci.* 2020, 13, 2363–2385.
15. Jin, Z.; Zhang, Z.; Xiu, J.; Song, H.; Gatti, T.; He, Z. A critical review on bismuth and antimony halide based perovskites and their derivatives for photovoltaic applications: Recent advances and challenges. *Mater. Chem. A* 2020, 8, 16166–16188.
16. Uddin, A.; Upama, M.; Yi, H.; Duan, L. Encapsulation of Organic and Perovskite Solar Cells: A Review. *Coatings* 2019, 9, 65.
17. Wang, R.; Mujahid, M.; Duan, Y.; Wang, Z.K.; Xue, J.; Yang, Y. A Review of Perovskites Solar Cell Stability. *Funct. Mater.* 2019, 29, 1808843.
18. Wang, C.; Gu, F.; Zhao, Z.; Rao, H.; Qiu, Y.; Cai, Z.; Zhan, G.; Li, X.; Sun, B.; Yu, X.; et al. Self-Repairing Tin-Based Perovskite Solar Cells with a Breakthrough Efficiency Over 11%. *Mater.* 2020, 32, 1907623.
19. Yang, X.; Chen, Y.; Liu, P.; Xiang, H.; Wang, W.; Ran, R.; Zhou, W.; Shao, Z. Simultaneous Power Conversion Efficiency and Stability Enhancement of Cs₂AgBiBr₆ Lead-Free Inorganic Perovskite Solar Cell through Adopting a Multifunctional Dye Interlayer. *Funct. Mater.* 2020, 30, 2001557.
20. Chen, M.; Ju, M.-G.; Carl, A.D.; Zong, Y.; Grimm, R.L.; Gu, J.; Zeng, X.C.; Zhou, Y.; Padture, N.P. Cesium Titanium(IV) Bromide Thin Films Based Stable Lead-free Perovskite Solar Cells. *Joule* 2018, 2, 558–570.
21. Yang, Y.; Liu, C.; Cai, M.; Liao, Y.; Ding, Y.; Ma, S.; Liu, X.; Guli, M.; Dai, S.; Nazeeruddin, M.K. Dimension-Controlled Growth of Antimony-Based Perovskite-like Halides for Lead-Free and Semitransparent Photovoltaics. *ACS Appl. Mater. Interfaces* 2020, 12, 17062–17069.
22. Wang, X.; Tang, R.; Jiang, C.; Lian, W.; Ju, H.; Jiang, G.; Li, Z.; Zhu, C.; Chen, T. Manipulating the Electrical Properties of Sb₂(S,Se)₃ Film for High-Efficiency Solar Cell. *Energy Mater.* 2020, 10, 2002341.
23. Nie, R.; Im, J.; Seok, S.I. Efficient Solar Cells Employing Light-Harvesting Sb₆Bi_{0.33}SI. *Adv. Mater.* 2019, 31, 1808344.
24. Nie, R.; Lee, K.S.; Hu, M.; Paik, M.J.; Seok, S.I. Heteroleptic Tin-Antimony Sulfoiodide for Stable and Lead-free Solar Cells. *Matter* 2020, 3, 1701–1713.
25. Chen, C.; Tang, J. Open-Circuit Voltage Loss of Antimony Chalcogenide Solar Cells: Status, Origin, and Possible Solutions. *ACS Energy Lett.* 2020, 5, 2294–2304.

26. Lei, H.; Chen, J.; Tan, Z.; Fang, G. Review of Recent Progress in Antimony Chalcogenide-Based Solar Cells: Materials and Devices. *Solar RRL* 2019, 3, 1900026.
27. Zhou, Y.; Wang, L.; Chen, S.; Qin, S.; Liu, X.; Chen, J.; Xue, D.-J.; Luo, M.; Cao, Y.; Cheng, Y.; et al. Thin-film Sb₂Se₃ photovoltaics with oriented one-dimensional ribbons and benign grain boundaries. *Photonics* 2015, 9, 409–415.
28. Choi, Y.C.; Lee, D.U.; Noh, J.H.; Kim, E.K.; Seok, S.I. Highly Improved Sb₂S₃ Sensitized-Inorganic-Organic Heterojunction Solar Cells and Quantification of Traps by Deep-Level Transient Spectroscopy. *Funct. Mater.* 2014, 24, 3587–3592.
29. Choi, Y.C.; Mandal, T.N.; Yang, W.S.; Lee, Y.H.; Im, S.H.; Noh, J.H.; Seok, S.I. Sb₂Se₃-Sensitized Inorganic-Organic Heterojunction Solar Cells Fabricated Using a Single-Source Precursor. *Chem. Int. Ed.* 2014, 53, 1329–1333.
30. Choi, Y.C.; Lee, Y.H.; Im, S.H.; Noh, J.H.; Mandal, T.N.; Yang, W.S.; Seok, S.I. Efficient Inorganic-Organic Heterojunction Solar Cells Employing Sb₂(S_x/Se_{1-x})₃ Graded-Composition Sensitizers. *Energy Mater.* 2014, 4, 1301680.
31. Choi, Y.C.; Seok, S.I. Efficient Sb₂S₃-Sensitized Solar Cells Via Single-Step Deposition of Sb₂S₃ Using S/Sb-Ratio-Controlled SbCl₃-Thiourea Complex Solution. *Funct. Mater.* 2015, 25, 2892–2898.
32. Choi, Y.C.; Yeom, E.J.; Ahn, T.K.; Seok, S.I. CuSbS₂-Sensitized Inorganic-Organic Heterojunction Solar Cells Fabricated Using a Metal-Thiourea Complex Solution. *Chem. Int. Ed.* 2015, 54, 4005–4009.
33. Chen, C.; Li, K.; Chen, S.; Wang, L.; Lu, S.; Liu, Y.; Li, D.; Song, H.; Tang, J. Efficiency Improvement of Sb₂Se₃ Solar Cells via Grain Boundary Inversion. *ACS Energy Lett.* 2018, 3, 2335–2341.
34. Wu, C.; Zhang, L.; Ding, H.; Ju, H.; Jin, X.; Wang, X.; Zhu, C.; Chen, T. Direct solution deposition of device quality Sb₂S₃-xSex films for high efficiency solar cells. *Energy Mater. Sol. Cells* 2018, 183, 52–58.
35. Tang, R.; Wang, X.; Jiang, C.; Li, S.; Jiang, G.; Yang, S.; Zhu, C.; Chen, T. Vacuum assisted solution processing for highly efficient Sb₂S₃ solar cells. *Mater. Chem. A* 2018, 6, 16322–16327.
36. Li, Z.; Liang, X.; Li, G.; Liu, H.; Zhang, H.; Guo, J.; Chen, J.; Shen, K.; San, X.; Yu, W.; et al. 9.2%-efficient core-shell structured antimony selenide nanorod array solar cells. *Commun.* 2019, 10, 125.
37. Tang, R.; Wang, X.; Lian, W.; Huang, J.; Wei, Q.; Huang, M.; Yin, Y.; Jiang, C.; Yang, S.; Xing, G.; et al. Hydrothermal deposition of antimony selenosulfide thin films enables solar cells with 10% efficiency. *Energy* 2020, 5, 587–595.
38. Nie, R.; Yun, H.-S.; Paik, M.-J.; Mehta, A.; Park, B.-W.; Choi, Y.C.; Seok, S.I. Efficient Solar Cells Based on Light-Harvesting Antimony Sulfoiodide. *Energy Mater.* 2017, 8, 1701901.
39. Shi, H.; Ming, W.; Du, M.-H. Bismuth chalcogenides and oxyhalides as optoelectronic materials. *Rev. B* 2016, 93, 104108.
40. Hahn, N.T.; Rettie, A.J.E.; Beal, S.K.; Fullon, R.R.; Mullins, C.B. n-BiSI Thin Films: Selenium Doping and Solar Cell Behavior. *Phys. Chem. C* 2012, 116, 24878–24886.
41. Kunioku, H.; Higashi, M.; Abe, R. Low-Temperature Synthesis of Bismuth Chalcogenides: Candidate Photovoltaic Materials with Easily, Continuously Controllable Band gap. *Rep.* 2016, 6, 32664.
42. Butler, K.T.; McKechnie, S.; Azarhoosh, P.; van Schilfgaarde, M.; Scanlon, D.O.; Walsh, A. Quasi-particle electronic band structure and alignment of the V-VI-VII semiconductors SbSI, SbSBr, and SbSeI for solar cells. *Phys. Lett.* 2016, 108, 112103.
43. Ganose, A.M.; Butler, K.T.; Walsh, A.; Scanlon, D.O. Relativistic electronic structure and band alignment of BiSI and BiSeI: Candidate photovoltaic materials. *Mater. Chem. A* 2016, 4, 2060–2068.
44. Ganose, A.M.; Matsumoto, S.; Buckeridge, J.; Scanlon, D.O. Defect Engineering of Earth-Abundant Solar Absorbers BiSI and BiSeI. *Mater.* 2018, 30, 3827–3835.
45. Choi, Y.C.; Hwang, E.; Kim, D.-H. Controlled growth of SbSI thin films from amorphous Sb₂S₃ for low-temperature solution processed chalcogenide solar cells. *APL Mater.* 2018, 6, 121108.
46. Tiwari, D.; Cardoso-Delgado, F.; Alibhai, D.; Mombrú, M.; Fermín, D.J. Photovoltaic Performance of Phase-Pure Orthorhombic BiSI Thin-Films. *ACS Appl. Energy Mater.* 2019, 2, 3878–3885.
47. Choi, Y.C.; Hwang, E. Controlled Growth of BiSI Nanorod-Based Films Through a Two-Step Solution Process for Solar Cell Applications. *Nanomaterials* 2019, 9, 1650.
48. Pathak, A.K.; Prasad, M.D.; Batabyal, S.K. One-dimensional SbSI crystals from Sb, S, and I mixtures in ethylene glycol for solar energy harvesting. *Phys. A* 2019, 125, 213.
49. Xiong, J.; You, Z.; Lei, S.; Zhao, K.; Bian, Q.; Xiao, Y.; Cheng, B. Solution Growth of BiSI Nanorod Arrays on a Tungsten Substrate for Solar Cell Application. *ACS Sustainable Chem. Eng.* 2020, 8, 13488–13496.

50. Mistewicz, K.; Matysiak, W.; Jesionek, M.; Jarka, P.; Kępińska, M.; Nowak, M.; Tański, T.; Stróż, D.; Szade, J.; Balin, K.; et al. A simple route for manufacture of photovoltaic devices based on chalcohalide nanowires. *Surf. Sci.* 2020, 517, 146138.
51. Nishikubo, R.; Kanda, H.; García-Benito, I.; Molina-Ontoria, A.; Pozzi, G.; Asiri, A.M.; Nazeeruddin, M.K.; Saeki, A. Optoelectronic and Energy Level Exploration of Bismuth and Antimony-Based Materials for Lead-Free Solar Cells. *Mater.* 2020, 32, 6416–6424.
52. Murtaza, S.Z.M.; Vaqueiro, P. Rapid synthesis of chalcohalides by ball milling: Preparation and characterisation of BiSI and BiSeI. *Solid State Chem.* 2020, 291, 121625.
53. Li, S.; Xu, L.; Kong, X.; Kusunose, T.; Tsurumachi, N.; Feng, Q. Bismuth chalcogenide iodides Bi₁₃S₁₈I₂ and BiSI: Solvothermal synthesis, photoelectric behavior, and photovoltaic performance. *Mater. Chem. C* 2020, 8, 3821–3829.
54. Nie, R.; Kim, B.; Hong, S.-T.; Seok, S.I. Nanostructured Heterojunction Solar Cells Based on Pb₂SbS₂I₃: Linking Lead Halide Perovskites and Metal Chalcogenides. *ACS Energy Lett.* 2018, 3, 2376–2382.
55. Butler, K.T.; Frost, J.M.; Walsh, A. Ferroelectric materials for solar energy conversion: Photoferroics revisited. *Energy Environ. Sci.* 2015, 8, 838–848.
56. Nie, R.; Mehta, A.; Park, B.W.; Kwon, H.W.; Im, J.; Seok, S.I. Mixed Sulfur and Iodide-Based Lead-Free Perovskite Solar Cells. *J. Am. Chem. Soc.* 2018, 140, 872–875.
57. Savytskii, D.; Sanders, M.; Golovchak, R.; Knorr, B.; Dierolf, V.; Jain, H.; Heo, J. Crystallization of Stoichiometric SbSI Glass. *J. Am. Ceram. Soc.* 2014, 97, 198–205.
58. Groom, R.; Jacobs, A.; Cepeda, M.; Drummey, R.; Lattner, S.E. Bi₁₃S₁₈I₂: (Re)discovery of a Subvalent Bismuth Compound Featuring [Bi₂]⁴⁺ Dimers Grown in Sulfur/Iodine Flux Mixtures. *Chem. Mater.* 2017, 29, 3314–3323.
59. Doussier, C.; Moëlo, Y.; Léone, P.; Meerschaut, A.; Evain, M. Crystal structure of Pb₂SbS₂I₃, and re-examination of the crystal chemistry within the group of (Pb/Sn/Sb) chalcogeno-iodides. *Solid State Sci.* 2007, 9, 792–803.
60. Shockley, W.; Queisser, H.J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* 1961, 32, 510–519.
61. Ganose, A.M.; Savory, C.N.; Scanlon, D.O. Beyond methylammonium lead iodide: Prospects for the emergent field of ns(2) containing solar absorbers. *Chem. Commun.* 2016, 53, 20–44.
62. Brandt, R.E.; Stevanović, V.; Ginley, D.S.; Buonassisi, T. Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: Beyond hybrid lead halide perovskites. *MRS Commun.* 2015, 5, 265–275.
63. Ran, Z.; Wang, X.; Li, Y.; Yang, D.; Zhao, X.-G.; Biswas, K.; Singh, D.J.; Zhang, L. Bismuth and antimony-based oxyhalides and chalcohalides as potential optoelectronic materials. *NPJ Comput. Mater.* 2018, 4, 14.
64. Peng, B.; Xu, K.; Zhang, H.; Ning, Z.; Shao, H.; Ni, G.; Li, J.; Zhu, Y.; Zhu, H.; Soukoulis, C.M. 1D SbSeI, SbSI, and SbSBr With High Stability and Novel Properties for Microelectronic, Optoelectronic, and Thermoelectric Applications. *Adv. Theory Simul.* 2018, 1, 1700005.

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