

Design and Optimization of Self-Powered Photodetector Using Lead-Free Halide Perovskite Ba₃SbI₃: Insights from DFT and SCAPS-1D

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Table S1. Parameters employed in the simulation.

Structure	FTO [1]	In ₂ S ₃ [2]	Ba ₃ SbI ₃ [3]	Sb ₂ S ₃ [4, 5]
Thickness (μm)	0.05	0.1	0.8	0.2
Electron Affinity (eV)	4.5	4.4	4.25	3.8
Bandgap (eV)	3.6	2.35	1.384	1.7
Dielectric permittivity	10.0	13.5	6.02	7.08
Effective DOS at VB (cm ⁻³)	1.800 × 10 ¹⁹	1.800 × 10 ¹⁹	1.164 × 10 ¹⁸	1.0 × 10 ¹⁹
Effective DOS at CB (cm ⁻³)	2.0 × 10 ¹⁸	2.20 × 10 ¹⁷	9.613 × 10 ¹⁸	2.8 × 10 ¹⁹
Thermal velocity of holes (cm ⁻¹)	1.00 × 10 ⁷	1.00 × 10 ⁷	1.00 × 10 ⁷	1.00 × 10 ⁷
Thermal velocity of electron (cm ⁻¹)	1.00 × 10 ⁷	1.00 × 10 ⁷	1.00 × 10 ⁷	1.00 × 10 ⁷
Hole mobility (cm ² cm ⁻¹ s ⁻¹)	2.00 × 10 ¹	2.50 × 10 ¹	5.00 × 10 ¹	1.00 × 10 ¹
Electron mobility (cm ² cm ⁻¹ s ⁻¹)	1.00 × 10 ²	1.00 × 10 ²	5.00 × 10 ¹	9.80 × 10 ⁰
Bulk defect density (cm ⁻³)	1.00 × 10 ¹⁴	1.00 × 10 ¹⁴	1.00 × 10 ¹⁴	1.00 × 10 ¹⁴
Shallow uniform donor density N _D (cm ⁻³)	1.00 × 10 ¹⁸	1.00 × 10 ¹⁷		0
Shallow uniform acceptor density N _A (cm ⁻³)	0	0	1.00 × 10 ¹⁷	1.00 × 10 ¹⁹

Table S2. The interface defects parameters In₂S₃/Ba₃SbI₃ and Ba₃SbI₃/MoS₂.

Parameters (unit)	In ₂ S ₃ /Ba ₃ SbI ₃	Ba ₃ SbI ₃ /MoS ₂
Defect type	Neutral	Neutral
Capture cross section electrons (cm ²)	10 ⁻¹⁹	10 ⁻¹⁹
Capture cross section holes (cm ²)	10 ⁻¹⁹	10 ⁻¹⁹
Energy with respect to Reference (eV)	0.6	0.6
Total density (cm⁻²)	10 ¹⁰	10 ¹⁰

Table S3. The contacts parameters applied in the simulation.

Contacts	Unit	Back contact parameters	Front contact parameters
Metal work function	eV	5.35 [6]	4.2 [7]
Surface recombination velocity of electrons	cm/s	1.00×10^5	1.00×10^5
Surface recombination velocity of holes	cm/s	1.00×10^7	1.00×10^7

1. Band alignment analysis of FTO/In₂S₃/Ba₃SbI₃/Sb₂S₃/Ni structure

This section presents the band alignment analysis for in the FTO/In₂S₃/Ba₃SbI₃/Sb₂S₃/Ni interfaces-based photodetector. The conduction band offset (CBO) and valence band offset (VBO) values are calculated using Eq. (S1) and Eq. (S2), respectively [8] .

At the In₂S₃/Ba₃SbI₃ interface, the conduction band offset (CBO) is given by:

$$\text{CBO} = \chi_{\text{absorber}} - \chi_{\text{ETL}} = -0.15 \text{ eV} \quad (\text{S1})$$

Where the χ_{absorber} and χ_{ETL} are the electron for the absorber and ETL respectively. Since the ETL layer affinity is larger than the absorber layer affinity, a small cliff-like shape between the In₂S₃ and Ba₃SbI₃ layers is formed, which could suppress electron backflow.

The valence band offset (VBO) at the Ba₃SbI₃/Sb₂S₃ interface is determined using Eq. (S2), defined as:

$$\text{VBO} = (\chi_{\text{absorber}} - E_{\text{g,absorber}}) + (\chi_{\text{HTL}} + E_{\text{g,HTL}}) \quad (\text{S2})$$

$$\text{VBO} = (4.25 - 1.384) + (3.80 + 1.70) = 5.634 - 5.50 = + 0.134 \text{ eV}.$$

The Ba₃SbI₃/Sb₂S₃ interface exhibits a small positive valence band offset (VBO) of 0.134 eV, which help facilitating efficient hole transport from Ba₃SbI₃ into Sb₂S₃ while simultaneously suppressing interfacial recombination. Table S4 summarizes the bandgap alignment characteristics of the FTO/In₂S₃/Ba₃SbI₃/Sb₂S₃ heterojunction interfaces.

Table S4. Summary of the bandgap (E_g), electron affinity (χ), conduction band minimum (EC), valence band maximum (EV) for FTO, In₂S₃, Ba₃SbI₃, and Sb₂S₃ materials.

Material	E _g (eV)	χ (eV)	EC ≡ CBM (eV)	EV ≡ VBM (eV)
FTO	3.60	4.50	− 4.50	8.10
In ₂ S ₃	2.35	4.40	− 4.40	6.75
Ba ₃ SbI ₃	1.384	4.25	− 4.25	5.63
Sb ₂ S ₃	1.70	3.80	− 3.80	5.50

2. Lattice mismatch analysis of In₂S₃/Ba₃SbI₃/Sb₂S₃ and other ETL/HTL interfaces

The selection of In₂S₃ as the electron transport layer (ETL) and Sb₂S₃ as the hole transport layer (HTL) is primarily based on their superior lattice compatibility and favourable interface quality with the Ba₃SbI₃ absorber. A good lattice match minimizes interfacial strain and suppresses defect formation, which are key factors in enhancing charge carrier mobility and overall device stability. The lattice mismatch can be calculated using the formula (S3) [9]:

$$\delta = \frac{2|a_s - a_e|}{a_s + a_e} \times 100 \quad (\text{S3})$$

where a_e is the lattice constant of the epitaxial layer and a_s is the lattice constant of the substrate. The lattice parameters used for the layers are derived from previously reported structural data. The calculated δ values for both β -In₂S₃ (tetragonal) and TiO₂ and ZnO with respect to Ba₃SbI₃, are summarized in Table S5. It is determined that the δ value at the β -In₂S₃/Ba₃SbI₃ junction is considerably lower than that at the TiO₂ and ZnO/Ba₃SbI₃ interface. In order for TiO₂ and ZnO to work efficiently with the Ba₃SbI₃ absorber, they would require large supercell arrangements to reduce δ to a realistic level, making them less efficiency for experimental fabrication and long-term stability.

Table S5. The lattice mismatch analysis summarized below demonstrates why β -In₂S₃ is the most suitable ETL compared to TiO₂ and ZnO.

Layer	a (Å)	b (Å)	c (Å)	Lattice mismatch δ (%)	Reference
Ba ₃ SbI ₃ (absorber)	7.05	7.05	7.05		This work
In ₂ S ₃ (β)	7.62	7.62	32.36	7.8 %	[10]
TiO ₂	4.59	4.59	2.96	42.3 %	[9]
ZnO	3.242	3.242	5.188	74.0 %	[11]

Similarly, possible HTL (hole transport layer) materials were analysed to assess their structural compatibility with the Ba₃SbI₃ absorber. The calculated δ values for both Sb₂S and

MoS₂ with respect to Ba₃SbI₃ interfaces, are summarized in Table S6. The lattice mismatch results clearly indicate that Sb₂S₃ provides a much better interface match compared to MoS₂. Although Sb₂S₃ exhibits a noticeable lattice mismatch along one crystallographic axis (58.9%), it still offers a more stable and energetically favourable interface than MoS₂, which shows an extremely high mismatch of about 75.9%. Such a large mismatch in MoS₂ introduces significant lattice strain and misfit dislocations, which in turn increase nonradiative recombination and degrade interfacial charge extraction efficiency. Therefore, despite its partial mismatch, Sb₂S₃ remains the more favourable HTL candidate due to its better structural alignment, chemical stability, and compatibility with the Ba₃SbI₃ absorber. The superior structural coherence of tetragonal In₂S₃ with Ba₃SbI₃, combined with the acceptable interface quality of Sb₂S₃, contributes to enhanced charge transport, reduced recombination losses, and overall improved photodetector performance in the Al/FTO/In₂S₃/Ba₃SbI₃/Sb₂S₃/Ni device architecture.

Table S6. The lattice mismatch analysis summarized below of Sb₂S₃ layer compared with other HTLs including TiO₂ and ZnO.

Layer	a (Å)	b (Å)	c (Å)	Lattice mismatch δ (%)	Reference
Ba ₃ SbI ₃ (absorber)	7.05	7.05	7.05		This work
Sb ₂ S ₃ (orthorhombic)	11.311	3.839	11.223	58.9 % (b-axis)	[12]
MoS ₂ (2H-phase)	3.190	3.190	14.879	75.9 %	[13]

3. Relaxing the B₃SbI₃ compound

The wavefunction cutoff energy and the Monkhorst–Pack k-point grid were independently optimized by testing multiple values to minimize the total energy difference between the initial and final volumes. The cutoff energy and the Monkhorst–Pack k-point that produced the smallest deviation were selected, yielding an optimal cutoff energy of 500 eV and a k-point mesh of $8 \times 8 \times 8$. The optimized cutoff energy and k-point mesh were subsequently employed to relax the Ba₃SbI₃ structure. This procedure enabled accurate minimization of the lattice constants, atomic positions, and total energy, ensuring that the equilibrium geometry was achieved. The resulting relaxed structure provided a reliable foundation for the subsequent electronic and optical property calculations.

As summarized in Table S7, the convergence criteria were successfully met once all the convergence criteria were satisfied. This occurs when the energy change per atom fell well

below the threshold of 1.0×10^{-6} eV, the maximum stress decreased to 8.44×10^{-4} GPa, and the maximum forces were reduced to 4.61×10^{-4} eV/Å, confirming robust relaxation. The only criterion that lagged was the maximum atomic displacement, which exceeded the target in the early steps (2.20×10^{-4} Å and 1.86×10^{-4} Å versus the 1.0×10^{-4} Å limit. This condition was eventually satisfied in the third relaxation step and fully minimized to zero in step four, which indicates a complete convergence was achieved and no further iterations were necessary.

Table S7. Summary of structural relaxation results for Ba₃SbI₃ perovskite obtained using the GGA/BPE functional

Metric	Tolerance	Step 1	Step 2	Step 3	Step 4	Convergence Status
ΔE (eV/atom)	$\leq 1.0 \times 10^{-6}$	9.32×10^{-8} ✓	9.39×10^{-8} ✓	9.48×10^{-8} ✓	9.44×10^{-8} ✓	Converged
Max force (eV/Å)	$\leq 2.5 \times 10^{-3}$	7.28×10^{-4} ✓	4.61×10^{-4} ✓	4.61×10^{-4} ✓	4.61×10^{-4} ✓	Converged
Max stress (GPa)	$\leq 5.0 \times 10^{-3}$	5.31×10^{-4} ✓	3.43×10^{-3} ✓	3.43×10^{-3} ✓	8.44×10^{-4} ✓	Converged
Max displacement (Å)	$\leq 1.0 \times 10^{-4}$	2.20×10^{-4} ✗	1.86×10^{-4} ✗	1.00×10^{-4} ✓	0.00 ✓	Converged

4. Influence of Sb₂S₃ (BSF) layer

This section scrutinizes the impact of surface field (BSF) layer width, doping level, and defect density on various device parameters, including photocurrent density, QE, responsivity, and specific detectivity. The BSF is critical for improving photodetector efficiency. This layer is formed by introducing a heavy-doping thin film between the active layer and the back contact (Ni). The doping disparity between the absorber and the BSF layer generates a high electric field that reflects minority carriers back to the absorber layer. As a result, this electric field reduces recombination and contributes to higher current generation [14].

4.1 The fluctuation of the photodetector performance with the change in the Sb₂S₃ layer width

Figure S1 investigates the influence of the Sb₂S₃ (BSF) layer width on the performance metrics of the photodetector, within the range of 0.1 μm to 0.35 μm. As illustrated in Figure S1(a), increasing the BSF layer width has no significant effect on the Voc and Jsc. Both values remain constant at 1.047 V and 31.65 mA/cm², respectively. This negligible impact on the photodetector functionality could be ascribed to the minimal absorption of photons in the Sb₂S₃

layer [15]. Similarly, the QE, as depicted in Figure S1(b), remains largely unaffected across BSF widths from 0.1 to 0.35 μm . It maintains nearly 100 % between 300 and 560 nm, after which it gradually decreases, reaching zero after 900 nm.

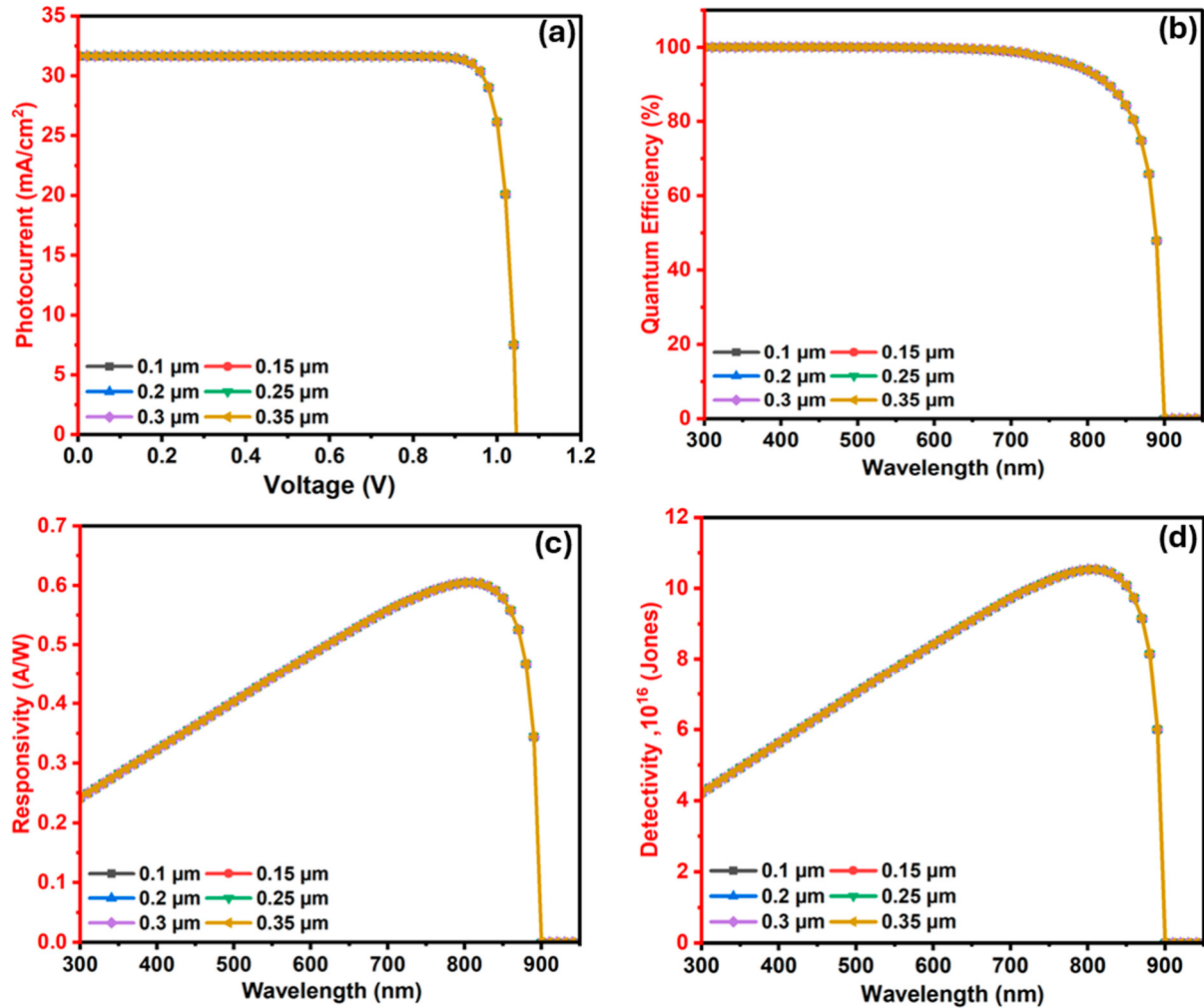


Figure S1. Effect of Sb_2S_3 -based BSF width (0.1–0.35 μm) on the Ba_3SbI_3 photodetector (a) the I–V characteristics (b) QE (c) responsivity (d) detectivity.

Similarly, Figure S1(c) shows that responsivity remains stable as the BSF width varies in range from 0.1 to 0.35 μm . It starts at $0.22 \text{ A}\cdot\text{W}^{-1}$ at 300 nm. It displays its peak magnitude of $0.605 \text{ A}\cdot\text{W}^{-1}$ at a BSF width of 0.2 μm at 810 nm. After this value, it decays and drops to zero beyond 900 nm. As shown in Figure S1(d), the detectivity follows the same trend as the responsivity, remaining flat across all BSF widths. The diffusion length and lifetime of carriers greatly exceed the thickness of the Sb_2S_3 layer. Thus, variations in its thickness have only a minor influence on device performance [16]. The optimal value of the detectivity is observed at 0.2 μm , with 1.05×10^{17} Jones at 810 nm. However, beyond 900 nm, the detectivity decreases sharply, indicating reduced photoresponse in the longer-wavelength region

4.2 The Sb₂S₃ layer doping on the photodetector characteristics

This section thoroughly probes the effect of dopant level (N_A) variation in the Sb₂S₃ on photodetector functionality, with N_A swept from 1×10^{17} to $1 \times 10^{21} \text{ cm}^{-3}$. As shown in Figure S2(a), both V_{oc} and J_{sc} persevere roughly stable values at almost 1.047 V and 31.65 mA/cm², respectively, across all doping levels. The QE does not show any fluctuation by the surges of the dopant level, as indicated in Figure S2 (b), sustaining nearly 100 % from 300 nm to 560 nm, before sharply falling to zero beyond 900 nm.

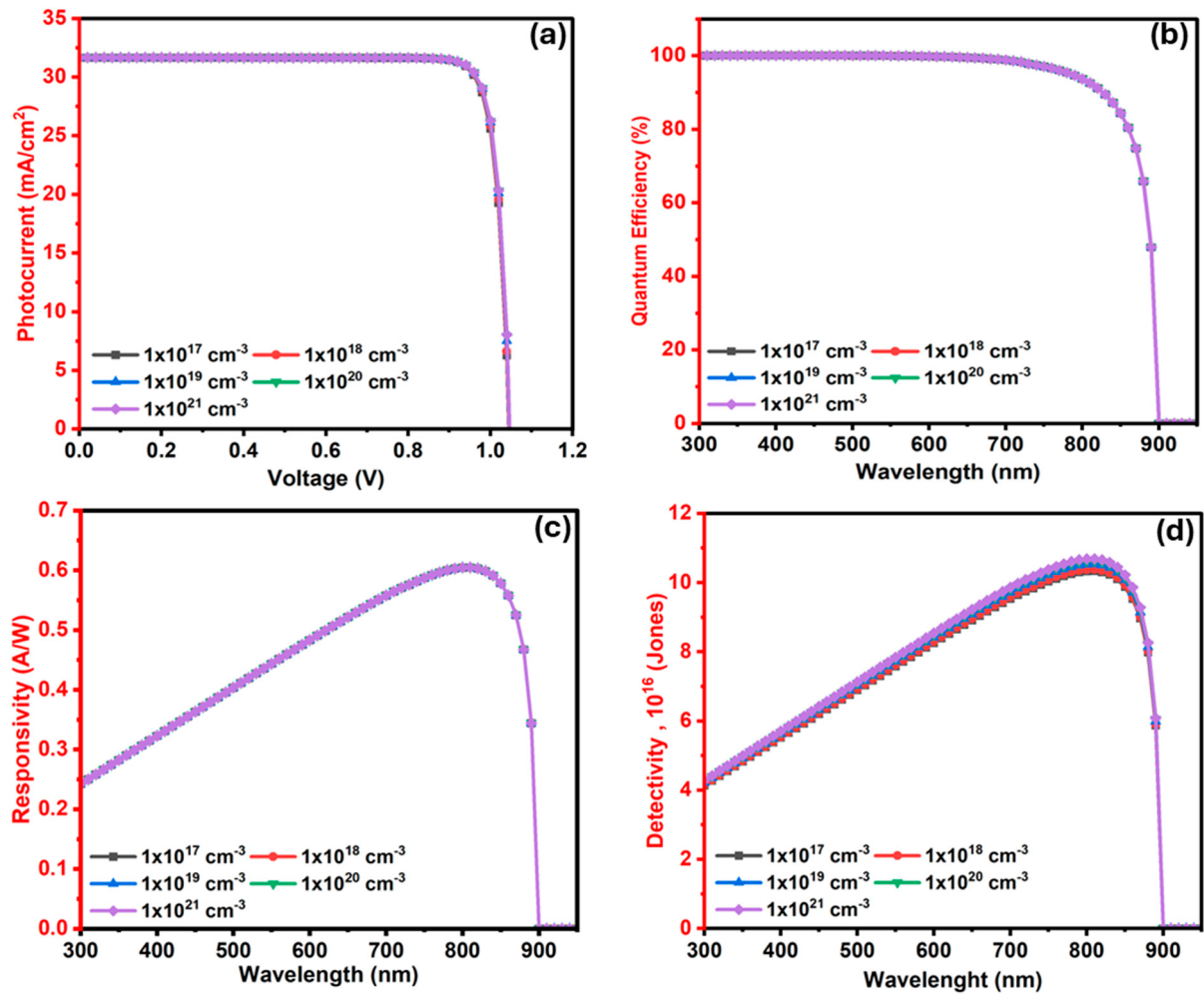


Figure S2. The effect of dopant level (N_A) in the Sb₂S₃-based BSF layer (ranging from 1×10^{17} - $1 \times 10^{21} \text{ cm}^{-3}$) on device performance (a) I-V characteristics (b) QE (c) responsiveness (d) detectivity.

In Figure S2(c), the responsivity mirrors the QE, exhibiting a consistent trend across all dopant levels, start at $0.24 \text{ A} \cdot \text{W}^{-1}$ at 300 nm and reaching its maximum value of $0.605 \text{ A} \cdot \text{W}^{-1}$

at 810 nm. The dependence of detectivity on the dopant level (N_A) in the Sb_2S_3 photodetector was examined across the range from 1×10^{17} to $1 \times 10^{21} \text{ cm}^{-3}$. For doping in the 1×10^{17} – $1 \times 10^{18} \text{ cm}^{-3}$ range, the detectivity lies between 4.1×10^{16} and 7.0×10^{16} Jones at wavelengths of 300–500 nm. Increasing the acceptor level further, from 1×10^{19} to $1 \times 10^{21} \text{ cm}^{-3}$, leads to a climb in detectivity from 9.5×10^{16} Jones at 700 nm to nearly 1.07×10^{17} Jones at 810 nm. Beyond 900 nm, it falls rapidly, and the device becomes ineffective. The observed enhancement in device detectivity with increasing doping level is primarily ascribed to the suppression of dark current at higher dopant levels [6].

4.3 The Sb_2S_3 layer defects on the photodetector characteristics

In this section, the impact of varying the defect density in the Sb_2S_3 layer on overall device performance is comprehensively analysed. The defect density (N_t) is swapped systematically from 1×10^{12} to $1 \times 10^{17} \text{ cm}^{-3}$ to assess its influence on key performance parameters. This investigation aims to evaluate the device's tolerance to intrinsic material imperfections within the Sb_2S_3 layer and understand their implications for photodetection applications.

Figure S3 (a) shows the photocurrent density versus voltage characteristics. The device performance is flat and unaffected by the presence of defect states up to 10^{17} cm^{-3} level. For instance, the J_{sc} remains consistently around 31.65 mA/cm^2 , and the V_{oc} stays fixed at 1.047 V across all defect densities. Figure S3 (b) illustrates the QE dependent spectral wavelength for various defect levels. The QE remains impressively flat and close to 100 % in the spectrum extending from 300 nm to around 560 nm before dropping sharply beyond 900 nm. The responsivity, as shown in Figure S3(c), exhibits a similar trend to QE. It increases with wavelength and reaches a peak value of 0.605 A/W at 810 nm. The curves for all defect concentrations are nearly identical.

Figure S3 (d) presents the detectivity response over the wavelength range. The maximum detectivity is observed to be around 1.05×10^{17} Jones, corresponding to a defect level of $1 \times 10^{17} \text{ cm}^{-3}$ at 810 nm. Notably, this parameter remains nearly unchanged across all examined defect densities. This behaviour agrees well with previous work on photodetectors [15]. For the BSF layer, a thickness of $0.2 \text{ }\mu\text{m}$, a dopant level of $1 \times 10^{19} \text{ cm}^{-3}$, and a defect density of $1 \times 10^{14} \text{ cm}^{-3}$ are considered optimal conditions for further optimization.

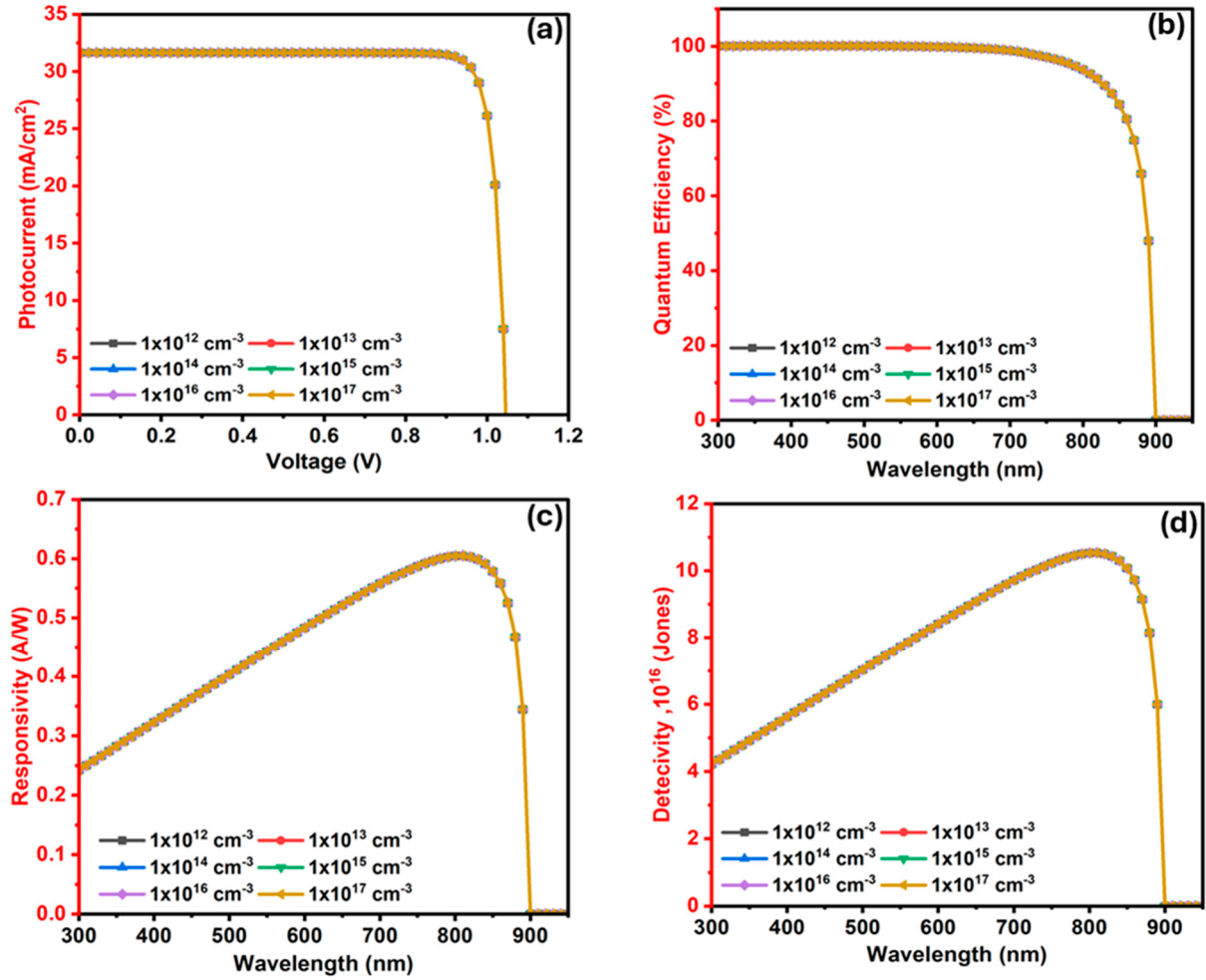


Figure S3. The effect of flaw level (N_t) in the Sb_2S_3 -based in level ranging from 1×10^{12} – $1 \times 10^{17} \text{ cm}^{-2}$ on device performance (a) I–V characteristics (b) QE (c) responsivity (d) detectivity.

5. Influence of $\text{In}_2\text{S}_3/\text{Ba}_3\text{SbI}_3$ junction interface defect on the Ba_3SbI_3 photodetector

To optimize photodetector performance, we investigate the defect density (N_t) at the $\text{In}_2\text{S}_3/\text{Ba}_3\text{SbI}_3$ interface, systematically varying it from 1×10^8 to $1 \times 10^{15} \text{ cm}^{-2}$. Figure S4 shows the influence of interface defect density on the characteristics of the $\text{In}_2\text{S}_3/\text{Ba}_3\text{SbI}_3$ junction. In Figure S4 (a), it is noted that as the interface defect density increases from 1×10^8 to $1 \times 10^{15} \text{ cm}^{-2}$, the J_{sc} remains nearly constant at 31.655 mA/cm^2 . This signifies that the carrier generation and extraction under short-circuit conditions are largely unaffected by interface recombination. Conversely, the V_{oc} exhibits a noteworthy sensitivity to defect density. It remains fixed at 1.047 V for defect concentrations up to $1 \times 10^{11} \text{ cm}^{-2}$. However, a further increase in defect density from 1×10^{12} to $1 \times 10^{15} \text{ cm}^{-2}$ resulted in a gradual decline in V_{oc} from 1.044 V to 0.844 V. This decrease is ascribed to improved Shockley–Read–Hall recombination at the interface, which diminishes the built-in potential across the junction [17].

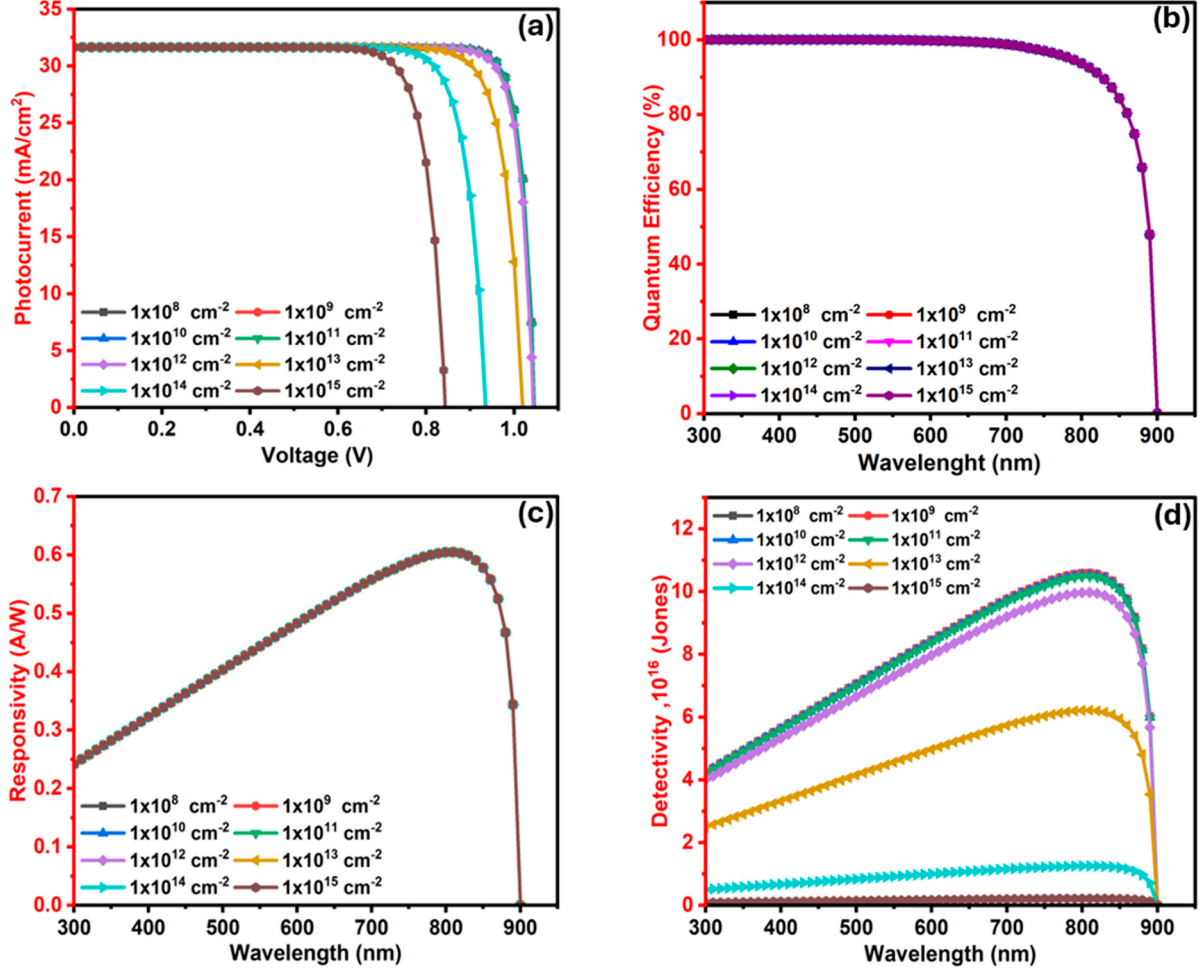


Figure S4. The characteristics of the Ba₃SbI₃ photodetector with respect to the change in the interface flaw at the In₂S₃/Ba₃SbI₃ junction (a) I–V characteristics (b) QE (c) responsivity, and (d) detectivity.

In Figure S4(b), the QE remains stable across the visible range for all defect densities, with a maximum of 100 % in the 300–560 nm range. Beyond 560 nm, QE gradually decreases, reaching ~ 94 % at 800 nm and ~ 80 % at 860 nm, and finally dropping to zero near 900 nm, which corresponds to the band edge of Ba₃SbI₃. Figure S4(c) presents the responsivity characteristics dependent on the wavelength and interface defects. It exhibits the same spectral profile for all defect densities, rising from 0.24 A/W at 300 nm to a peak of 0.605 A/W near 810 nm, before falling sharply at the band edge of 900 nm. This stability confirms that interface defects have minimal influence on the photocurrent generation under same illumination condition discussed in Figure S4(a).

In contrast, detectivity is significantly impacted by interface quality, as indicated in Figure S4(d). For low- interfacial defect densities less than $1 \times 10^{11} \text{ cm}^{-2}$, D* reaches its peak

magnitude of 1.05×10^{17} Jones at 810 nm, while higher defect concentrations result in a marked reduction, falling to 2×10^{15} Jones for $1 \times 10^{15} \text{ cm}^{-2}$ at the same wavelength. This decline in D^* might be linked to the increased dark current originating from defect-assisted recombination [18]. These results indicate that while the $\text{In}_2\text{S}_3/\text{Ba}_3\text{SbI}_3$ photodetector maintains stable J_{sc} , QE, and R across a wide range of interface defect densities, V_{oc} and D^* degrade significantly beyond $1 \times 10^{11} \text{ cm}^{-2}$. An optimal performance is observed at around $1 \times 10^{10} \text{ cm}^{-2}$, and this value is therefore selected for the subsequent calculations.

5. Influence of $\text{Ba}_3\text{SbI}_3/\text{Sb}_2\text{S}_3$ junction interface defect on the Ba_3SbI_3 photodetector

Figure S5(a) illustrates the influence of interface-defect density on J_{sc} and V_{oc} for the $\text{Ba}_3\text{SbI}_3/\text{Sb}_2\text{S}_3$ heterojunction. From 10^8 to 10^{13} cm^{-2} , both parameters remain nearly constant, with J_{sc} at $31.655 \text{ mA cm}^{-2}$ and V_{oc} at 1.047 V , as low trap density minimizes Shockley–Read–Hall recombination and ensures efficient carrier collection [17]. A slight V_{oc} drop from 1.0465 to 1.0426 V when the interface defects are between 10^{12} and 10^{13} cm^{-2} marks the onset of recombination losses, while J_{sc} is unaffected. Once the interface defects increase to 10^{14} – 10^{15} cm^{-2} , both parameters deteriorate more noticeably, with V_{oc} decreasing from 1.0197 to 0.971 V and J_{sc} declining from 31.617 to $31.300 \text{ mA.cm}^{-2}$. The higher interface defect density introduces mid-gap recombination centres, reduces quasi-Fermi level splitting and built-in potential, and enables trap-assisted tunnelling that weakens the voltage and photocurrent [19].

Figure S5(b) presents the QE spectra dependent wavelength and $\text{Ba}_3\text{SbI}_3/\text{Sb}_2\text{S}_3$ interface defects. At low and moderate defect densities spanning from 10^8 – 10^{13} cm^{-2} , QE is $\sim 100 \%$ from 300 to 550 nm. The gradual decrease beyond 550 nm reflects the reduced absorption coefficient as the photon energy approaches the bandgap, not interface losses. At 10^{14} – 10^{15} cm^{-2} , the QE curve shows a slight uniform downward shift, with $\sim 1.7 \%$ loss at 800 nm from $\sim 93.7 \%$ to $\sim 92.0 \%$. The abrupt cut-off near 900 nm corresponds to the absorber band edge, where photons lack sufficient energy to generate electron–hole pairs.

Figure S5(c) shows the responsivity spectra, which mirrors the QE trends. For defect densities less than 10^{13} cm^{-2} , R rises with wavelength due to the increasing fraction of photons absorbed closer to the depletion region. It reaches its summit magnitude of about 0.605 A W^{-1} at 810 nm. Unlike the $\text{In}_2\text{S}_3/\text{Ba}_3\text{SbI}_3$ interface, responsivity is slightly reduced at $\text{Ba}_3\text{SbI}_3/\text{Sb}_2\text{S}_3$ interfaces as interfacial defect level ascends to 10^{15} cm^{-2} . Its peak value drops slightly to around 0.594 A W^{-1} at 810 nm, consistent with the QE reduction.

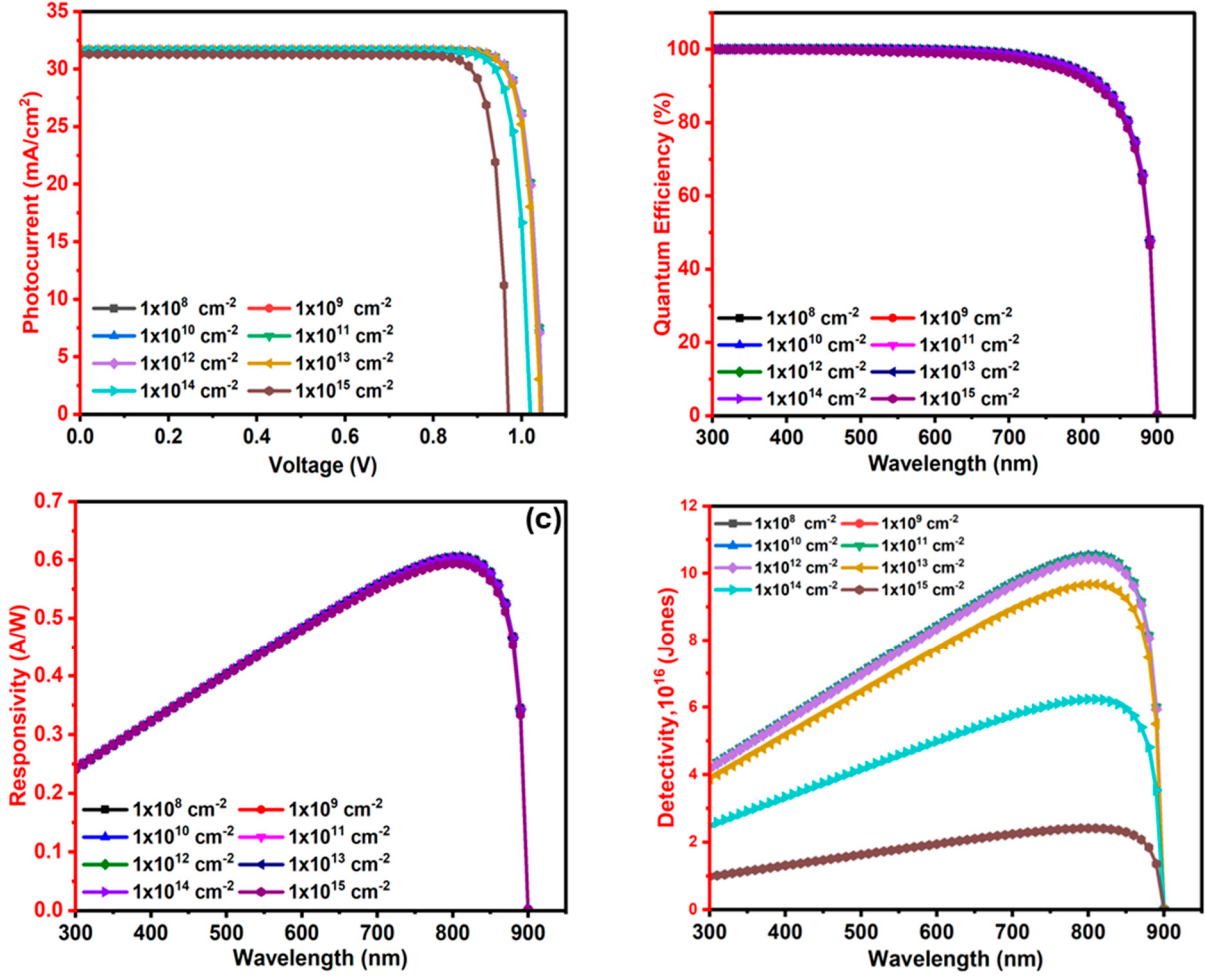


Figure S5. The characteristics of the Ba₃SbI₃ photodetector with the change I the interface defect concentration at the Ba₃SbI₃/Sb₂S₃ interface (a) I–V characteristics (b) QE (c) responsivity, (d) detectivity.

Figure S5(d) illustrates the dependence of detectivity on wavelength and interface defect density in the Ba₃SbI₃/Sb₂S₃ heterojunction photodetector. It appears that detectivity is the parameter most sensitive to interface defects. At 10^8 – 10^{11} cm⁻², D^* hikes from 1.03×10^{17} Jones to its peaks of 1.05×10^{17} Jones at 810 nm. As the interface defect density increases, D^* declines sharply to 1.04×10^{17} Jones at 10^{12} cm⁻², 9.65×10^{16} Jones at 10^{13} cm⁻², 6.21×10^{16} Jones at 10^{14} cm⁻², and 2.41×10^{16} Jones at 10^{15} cm⁻². Such pronounced deterioration is caused by the exponential sensitivity of dark current to recombination-active traps [18]. To balance the interface effects across all parameters, the Ba₃SbI₃/Sb₂S₃ interface defect density should be maintained at a moderate level to preserve overall device performance. This condition is achieved when the defect density does not exceed 10^{11} cm⁻², while a value of 10^{10} cm⁻² is considered optimal for subsequent calculations.

6. The total recombination for the structure with and without Sb_2S_3

Recombination in photodetectors occurs when electrons and holes recombine, resulting in the loss of photogenerated charge carriers. In highly optimized photodetectors, the overall device performance is strongly influenced by the carrier density and lifetime, which together govern the recombination rate.

Figure S6 presents the total recombination profile of the Ba_3SbI_9 -based photodetector with and without the incorporation of the Sb_2S_3 interfacial layer. The results reveal that introducing Sb_2S_3 significantly suppresses recombination, particularly near the front junction region, where interfacial defects typically dominate carrier loss. The total recombination rate in the Sb_2S_3 -modified device decreases by several orders of magnitude compared to the reference sample, clearly indicating the reduction of interface-related recombination pathways. This behaviour confirms that the Sb_2S_3 layer acts as an effective surface passivation material, reducing defect-assisted non-radiative recombination and enhancing charge carrier lifetime. Consequently, carrier transport across the heterojunction is improved, leading to superior photoresponse and enhanced overall device efficiency.

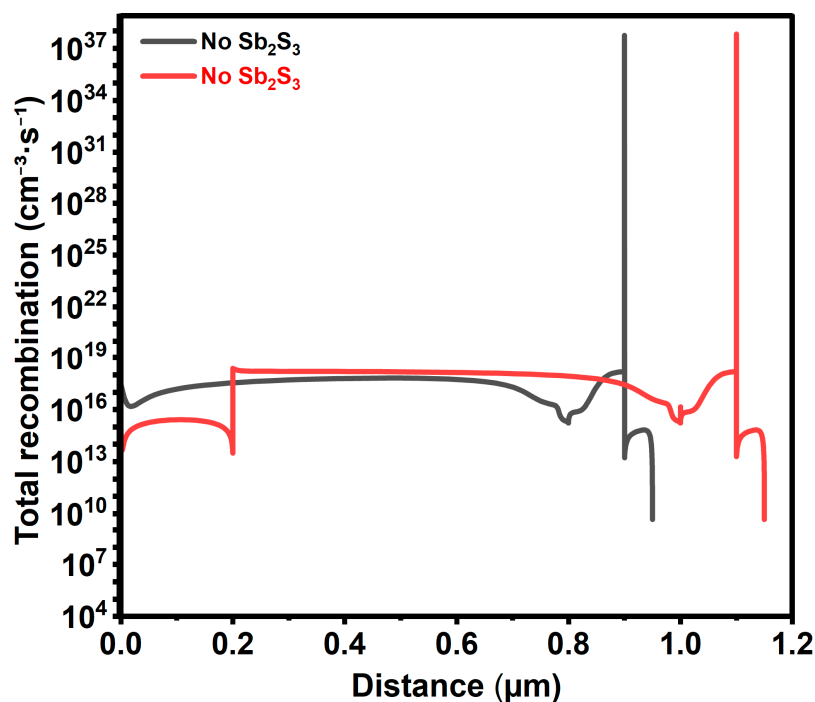


Figure S6. spatial distribution of total recombination rate across the device structure for photodetectors with and without the Sb_2S_3 layer.

7. The series, and shunt resistance impact on the Ba_3SbI_3 photodetector

Figure S6 depicts the influence of series resistance (R_s) and shunt resistance (R_{sh}) on photodetector efficiency. Ideally, the value of the series resistance is zero, while the shunt resistance is infinite. Practically, R_s originates from contact resistance and interfacial barriers between device layers, whereas R_{sh} arises from defect-related recombination and lateral leakage paths [6]. This section examines how sweeping the R_s from 0 to $20 \Omega\cdot\text{cm}^2$ and R_{sh} from 0 to $5 \times 10^4 \Omega\cdot\text{cm}^2$ affects the J–V characteristics of the photodetector.

Figure S7 (a) reveals that R_s has a slight impact on both J_{sc} and V_{oc} as its value increases. At $R_s = 0 \Omega\cdot\text{cm}^2$, the photodetector displays a J_{sc} of $1.655 \text{ mA}/\text{cm}^2$, while the V_{oc} reaches 1.044 V at the same R_s value. As R_s gradually increases from 0 to $20 \Omega\cdot\text{cm}^2$, both parameters experience a slight reduction, with J_{sc} and V_{oc} lessening to $1.655 \text{ mA}/\text{cm}^2$ and 1.044 V , individually. This finding indicates that an elevated R_s introduces ohmic losses, which limit the flow of photogenerated carriers and thereby reduce device sensitivity and efficiency. This behaviour is consistent with reported work on photodetectors [20].

Figure S7 (b) shows the impact of varying R_{sh} from 0 to $5 \times 10^4 \Omega\cdot\text{cm}^2$ on the photodetector's behaviour. The results indicate that changes in R_{sh} have a negligible effect on J_{sc} and V_{oc} , which remain constant at 1.047 V and $31.655 \text{ mA}/\text{cm}^2$, respectively. Further increases in R_{sh} do not exert any noticeable improvement. These findings suggest that, to achieve higher performance, R_s should remain at its ideal boundary value of $0 \Omega\cdot\text{cm}^2$, while R_{sh} must exceed $5 \times 10^4 \Omega\cdot\text{cm}^2$ [21].

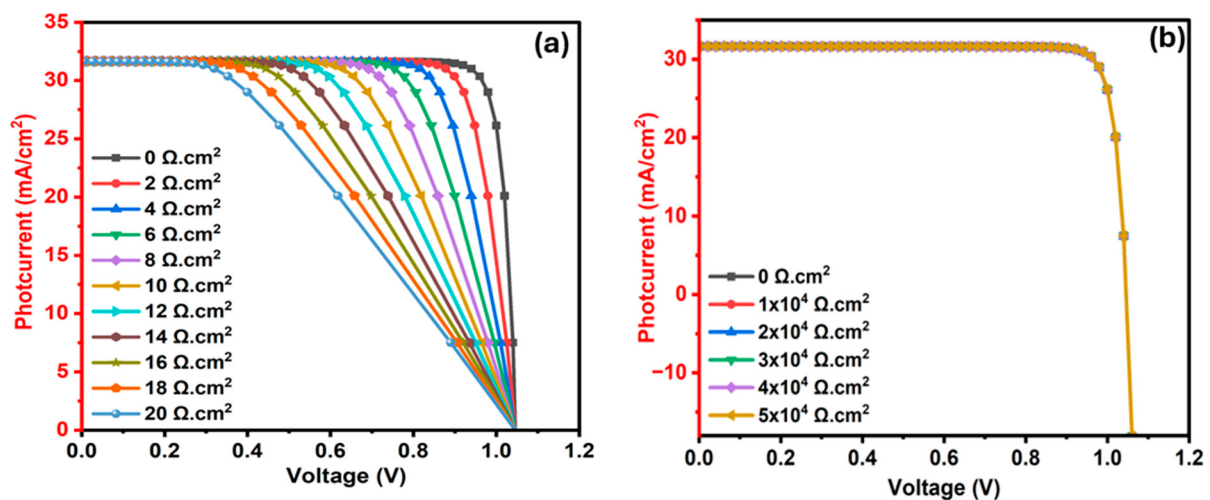


Figure S7. (a) Influence of series resistance on Voc I-V characteristics (b) impact of shunt resistance on I-V curve.

8. Analysis the noise-equivalent power (NEP) of optimized photodetector

The noise-equivalent power (NEP) represents the minimum detectable optical power corresponding to a signal-to-noise ratio of unity. For a shot-noise-limited photodetector, NEP can be expressed as [22]:

$$\text{NEP} = \frac{\sqrt{2qI_d}}{R} \quad (\text{S4})$$

where q is the elementary charge, I_d is the dark current density (mA/cm²), and R is the responsivity (A/W). Using the equation (S4), the calculated NEP is $7.6 \times 10^{-18} \text{ W Hz}^{1/2}$.

This remarkably low NEP value confirms the high sensitivity and low-noise characteristics of the proposed photodetector, demonstrating its potential for weak-light detection applications. The obtained NEP is comparable to or even lower than those reported for state-of-the-art photodetectors based on two-dimensional materials and perovskite heterostructures, highlighting the superior performance of the present device [23, 24].

Table S8. Performance comparison of proposed photodetector at different visible and NIR wavelengths.

Parameter	Symbol	Value	Unit
Dark current density	I_d	1.03×10^{-16}	Ma/cm ²
Responsivity	R	0.605	A/W
Elementary charge	q	1.602×10^{-19}	C
Equation		$\text{NEP} = \frac{\sqrt{2qI_d}}{R}$	—

9. The responsivity and the detectivity at different wavelengths in the visible and NIR regions for the optimized photodetector

Table S8 presents the optimized photodetector's photoresponse under visible and near-infrared (NIR) light at various wavelengths, under a constant incident power of 100 mW/cm². The device exhibits the highest responsivity and specific detectivity at 810 nm, outperforming its response at other wavelengths. This enhanced performance is primarily attributed to efficient photon absorption near the absorber's band edge, where the photon energy closely matches the material's bandgap. As a result, carrier generation is improved, leading to a stronger photocurrent response [7].

Table S9. Performance comparison of proposed photodetector at different visible and NIR wavelengths.

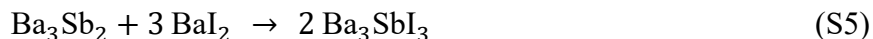
Spectral Wavelength (nm)	Responsivity (A/W)	Detectivity (Jones)
400	0.323	6.62×10^{16}
500	0.403	7.03×10^{16}
600	0.483	8.41×10^{16}
700	0.558	9.72×10^{16}
810	0.605	1.05×10^{17}
890	0.344	5.99×10^{16}

10. The proposed synthesis routes for the Ba₃SbI₃ compound

The synthesis of Ba₃SbI₃ has not yet been achieved and remains experimentally unexplored. Nevertheless, DFT calculations indicate that this compound is thermodynamically stable and could be realized under appropriate synthesis conditions. Building on these theoretical predictions, we propose a feasible solid-state reaction route for the preparation of Ba₃SbI₃, analogous to those reported for related halide systems. Notably, several ternary halide compounds with similar chemical frameworks have already been synthesized via solid-state reactions between binary precursors of comparable composition [25]. For instance, Ca₃AsI₃ has been reported to form when Ca₃As₂ reacts with CaI₂ in a 1:3 molar ratio under annealing at 800 °C [26]. Increasing the reaction temperature to 900 °C, Ca₃AsBr₃ was obtained by combining Ca₃As₂ with CaBr₂ in the same stoichiometric proportion [27]. Likewise, Ca₃PCl₃ was produced from Ca₃P₂ and CaCl₂ in a 1:3 molar ratio at 1000 °C [28]. Beyond compounds containing heavier elements, this synthetic strategy has also been extended to lighter systems. For example, Mg₃NF₃ was prepared through the reaction between Mg₃N₂ and MgF₂, employing the same 1:3 stoichiometric ratio and a higher annealing temperature of 1050 °C [29]. These examples collectively demonstrate feasibility of similar synthesis pattern among A₃BX₃-type halide materials, in which a binary compound (A₃B₂ or A₃N₂) reacts with the corresponding halide (AX₂) in a 1:3 molar ratio to yield the desired ternary phase.

A feasible route involves reacting Ba₃Sb₂ with BaI₂ in a 1:3 molar ratio under an inert argon atmosphere or within vacuum-sealed quartz ampoules to prevent oxidation and moisture degradation. The mixture can be homogenized thoroughly, pelletized, and annealed at 750–900 °C for 2–24 hours, followed by slow cooling to promote crystallinity. To synthesize Ba₃SbI₃ via a solid-state reaction, the most suitable precursors are Ba₃Sb₂ and BaI₂ in a (1:3) molar

ratio, following the general scheme observed for analogous compounds. The overall reaction can be represented as:



All procedures involving barium, antimony, and iodine compounds should follow appropriate safety measures. Barium compounds are toxic and must be handled in a fume hood with proper PPE (gloves, lab coat, and goggles). Antimony may cause irritation, especially as fine powders, so dust exposure should be minimized. Iodine compounds such as BaI_2 are hygroscopic and corrosive, requiring storage and handling under dry, inert conditions (e.g., argon glovebox).

11. Supplementary References

- [1] A. Ghosh *et al.*, "Innovative double absorber solar cell design combining Ca_3AsI_3 and Ca_3PI_3 perovskites for achieving over 29% efficiency," *Optics & Laser Technology*, vol. 183, p. 112399, 2025.
- [2] M. A. H. Pappu, M. I. R. Ebon, and J. Hossain, "Design and simulation of BeSiP_2 -based high-performance solar cell and photosensor," *Solar Energy*, vol. 279, p. 112837, 2024.
- [3] M. M. Islam, M. F. Rahman, M. H. Rahman, M. Z. Bani-Fwaz, R. Pandey, and M. Harun-Or-Rashid, "Unlocking the lead-free new all inorganic cubic halide perovskites of Ba_3MI_3 (M= P, As, Sb) with efficiency above 29%," *Journal of Materials Science*, vol. 59, no. 48, pp. 22109-22131, 2024.
- [4] M. N. H. Riyad, A. Sunny, M. M. Khatun, S. Rahman, and S. R. A. Ahmed, "Performance evaluation of WS_2 as buffer and Sb_2S_3 as hole transport layer in CZTS solar cell by numerical simulation," *Engineering Reports*, vol. 5, no. 5, p. e12600, 2023.
- [5] A. Kumar *et al.*, "Boosting the efficiency up to 33% for chalcogenide tin mono-sulfide-based heterojunction solar cell using SCAPS simulation technique," *Renewable Energy*, vol. 226, p. 120462, 2024.
- [6] M. C. Islam, B. K. Mondal, M. A. H. Pappu, and J. Hossain, "Numerical evaluation and optimization of high sensitivity $\text{Cu}_2\text{CdSnSe}_4$ photodetector," *Heliyon*, vol. 10, no. 17, 2024.
- [7] M. I. R. Ebon, M. A. H. Pappu, S. N. Shiddique, and J. Hossain, "Unveiling the potentiality of a self-powered CGT chalcopyrite-based photodetector: theoretical insights," *Optical Materials Express*, vol. 14, no. 4, pp. 907-921, 2024.
- [8] M. A. Nalianya *et al.*, "Numerical study of lead free $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ perovskite solar cell by SCAPS-1D," *Optik*, vol. 248, p. 168060, 2021.
- [9] S. R. A. Ahmed, "Investigation on the performance enhancement of heterojunction SnS thin-film solar cell with a Zn_3P_2 hole transport layer and a TiO_2 electron transport layer," *Energy & Fuels*, vol. 38, no. 2, pp. 1462-1476, 2023.
- [10] F. Horani and E. Lifshitz, "Deciphering the Structural Evolution and Growth Mechanism of 3D $\beta\text{-In}_2\text{S}_3$ Nanostructures," *The Journal of Physical Chemistry C*, vol. 123, no. 50, pp. 30723-30731, 2019.

- [11] X. Ma, Y. Wu, Y. Lv, and Y. Zhu, "Correlation effects on lattice relaxation and electronic structure of ZnO within the GGA+ U formalism," *The Journal of Physical Chemistry C*, vol. 117, no. 49, pp. 26029-26039, 2013.
- [12] A. Radzwan, R. Ahmed, A. Shaari, A. Lawal, and Y. X. Ng, "First-principles calculations of antimony sulphide Sb₂S₃," *Malays. J. Fundam. Appl. Sci.*, vol. 13, no. 3, pp. 285-289, 2017.
- [13] M. H. Jameel *et al.*, "A comparative DFT study of bandgap engineering and tuning of structural, electronic, and optical properties of 2D WS₂, PtS₂, and MoS₂ between WSe₂, PtSe₂, and MoSe₂ materials for photocatalytic and solar cell applications," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 34, no. 1, pp. 322-335, 2024.
- [14] S. Abdo *et al.*, "Unveiling the Potential of Novel Ternary Chalcogenide SrHfSe₃ for Eco-Friendly, Self-Powered, Near-Infrared Photodetectors: A SCAPS-1D Simulation Study," *Sci*, vol. 7, no. 3, p. 113, 2025.
- [15] S. N. Shiddique, A. T. Abir, S. S. Nushin, B. K. Mondal, and J. Hossain, "Numerical probing into the role of experimentally developed ZnTe window layer in high-performance Ag₃AuSe₂ photodetector," *Results in Materials*, vol. 25, p. 100651, 2025.
- [16] M. R. Miah, M. I. R. Ebon, A. T. Abir, and J. Hossain, "Discovering the inherent properties of CdS/TiTe₂/Cu₂Te near infrared photodetector: A computational analysis," *Next Research*, vol. 2, no. 2, p. 100262, 2025.
- [17] P. Jadeja, S. Yadav, A. Ravalia, and S. Katba, "Investigating the impact of various Electron Transport Layers on the performance of Sn-based Perovskite Solar Cells: A Device Simulation using SCAPS-1D," *Journal of Physics and Chemistry of Solids*, p. 113088, 2025.
- [18] M. S. Mollah, M. A. H. Pappu, and J. Hossain, "Theoretical design and insight of Fe₂GeS₄-based optoelectronic devices," *Next Research*, p. 100575, 2025.
- [19] M. N. Hasan, M. I. R. Ebon, and J. Hossain, "Numerical Simulation to Achieve High Efficiency in CuTiSe₂-Based Photosensor and Solar Cell," *International Journal of Energy Research*, vol. 2025, no. 1, p. 4967875, 2025.
- [20] M. I. R. Ebon, A. T. Abir, D. Pathak, and J. Hossain, "Theoretical insights toward a highly responsive AgInSe₂ photodetector," *Applied Research*, vol. 3, no. 6, p. e202400038, 2024.
- [21] S. Singh, S. Kumar, M. Deo, and R. Chauhan, "Unveiling the potential of organometal halide perovskite materials in enhancing photodetector performance," *Optical and Quantum Electronics*, vol. 55, no. 10, p. 846, 2023.
- [22] S. Masanta, C. Nayak, P. Agarwal, K. Das, and A. Singha, "Monolayer Graphene-MoSSe van der Waals Heterostructure for Highly Responsive Gate-Tunable Near-Infrared-Sensitive Broadband Fast Photodetector," *ACS Applied Materials & Interfaces*, vol. 15, no. 11, pp. 14523-14531, 2023.
- [23] J. Wang *et al.*, "Self-driven perovskite narrowband photodetectors with tunable spectral responses," *Advanced Materials*, vol. 33, no. 3, p. 2005557, 2021.
- [24] H. Arora *et al.*, "Demonstration of a broadband photodetector based on a two-dimensional metal-organic framework," *Advanced Materials*, vol. 32, no. 9, p. 1907063, 2020.
- [25] H.-J. Feng and Q. Zhang, "Predicting efficiencies > 25% A₃MX₃ photovoltaic materials and Cu ion implantation modification," *Applied Physics Letters*, vol. 118, no. 11, 2021.

- [26] C. Hadenfeldt and W. Fester, "Reindarstellung und thermische Stabilität von Calcium-phosphid-und-arsenidiodiden: Ca_3PI_3 , Ca_3AsI_3 , Ca_2PI und Ca_2AsI ," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 490, no. 1, pp. 25-30, 1982.
- [27] C. Hadenfeldt and P. Schulz, "Darstellung, Struktur und Temperaturabhängigkeit der Phasenbreite der Phase $\text{Ca}_{2-x}\text{As}_{1-x}\text{Br}_{1+x}$ und thermisches Verhalten der Verbindung Ca_3AsBr_3 ," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 518, no. 11, pp. 77-86, 1984.
- [28] C. Hadenfeldt and H. Herdejürgen, "Darstellung, kristallstruktur und thermisches verhalten der calciumphosphidchloride $\text{Ca}_{2-x}\text{P}_{1-x}\text{Cl}_{1+x}$ ($0 \leq x \leq 0,18$) und Ca_3PCl_3 ," *Journal of the Less Common Metals*, vol. 124, no. 1-2, pp. 93-103, 1986.
- [29] M. A. Brogan, R. W. Hughes, R. I. Smith, and D. H. Gregory, "Structural studies of magnesium nitride fluorides by powder neutron diffraction," *Journal of Solid State Chemistry*, vol. 185, pp. 213-218, 2012.