An antibonding valence band maximum enables defect-tolerant and stable GeSe photovoltaics

Shun-Chang Liu1,2,6, Chen-Min Dai3,6, Yimeng Min4, Yi Hou4, Andrew H. Proppe4, Ying Zhou5, Chao Chen5, Shiyou Chen3, Jiang Tang5, Ding-Jiang Xue1,2✉, Edward H. Sargent4✉& Jin-Song Hu1,2✉

In lead–halide perovskites, antibonding states at the valence band maximum (VBM)—the result of Pb 6s–I 5p coupling—enable defect-tolerant properties; however, questions surrounding stability, and a reliance on lead, remain challenges for perovskite solar cells. Here, we report that binary GeSe has a perovskite-like antibonding VBM arising from Ge 4s-Se 4p coupling; and that it exhibits similarly shallow bulk defects combined with high stability. We find that the deep defect density in bulk GeSe is ~10^{12} cm^{-3}. We devise therefore a surface passivation strategy, and find that the resulting GeSe solar cells achieve a certified power conversion efficiency of 5.2%, 3.7 times higher than the best previously-reported GeSe photovoltaics. Unencapsulated devices show no efficiency loss after 12 months of storage in ambient conditions; 1100 hours under maximum power point tracking; a total ultraviolet irradiation dosage of 15 kWh m^{-2}; and 60 thermal cycles from −40 to 85 °C.

1 Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. 2 University of Chinese Academy of Sciences, Beijing 100049, China. 3 Key Laboratory of Polar Materials and Devices (MOE), East China Normal University, Shanghai 200241, China. 4 Department of Electrical and Computer Engineering, University of Toronto, Toronto Ontario M5S 1A4, Canada. 5 Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, Wuhan 430074, China. 6 These authors contributed equally: Shun-Chang Liu, Chen-Min Dai. ✉Email: djxue@iccas.ac.cn; ted.sargent@utoronto.ca; hujs@iccas.ac.cn
The macroscopic properties of a semiconductor depend on the chemical bonding between its constituent elements: electrostatics for ionic systems, and orbital hybridization for covalent systems. In an organic–inorganic hybrid perovskite solar cells (PSCs), power conversion efficiencies (PCEs) have increased from an initial 3.8% to a certified 25.2% in the last decade. The electronic structure of perovskites—Pb 6s–1 5p antibonding states at the valence band maximum (VBM), contrasting with semiconductors such as GaAs and GaN that have a bonding VBM—is a key to the extraordinary performance of perovskite-based optoelectronics. Because of this antibonding feature, defects in perovskites are confined to shallow states close to the band edges, instead of introducing states within the bandgap.

Another bonding feature in perovskites is high ionicity, which enables thin-film fabrication, wherein perovskites form highly crystalline materials when prepared even at room temperature. However, this high ionicity makes perovskites easily soluble in water and sensitive to moisture, inducing performance degradation. Ionic perovskites also exhibit ion migration, a reason for J–V hysteresis.

We reasoned that the combination of strong covalent bonding, coupled with high stability and a perovskite-like antibonding VBM electronic structure, could potentially add new defect-tolerant materials to photovoltaics.

We turned our attention to germanium monoselenide (GeSe), a material whose similar Pauling electronegativity of Ge (2.01) and Se (2.55) suggests a covalent semiconductor. GeSe has recently emerged as a promising absorber material for photovoltaics owing to its suitable bandgap (~1.14 eV), high carrier mobility (~128 cm² V⁻¹ s⁻¹), and its earth-abundant, and Pb-free composition. Whether or not GeSe can exhibit defect tolerance analogous to that of Pb-based perovskites, especially in light of its perovskite-like ns² electronic configuration, has so far remained unclear.

We began by investigating defects in GeSe. We found that GeSe, which has a 4s² electronic configuration, possesses a perovskite-like antibonding VBM arising from Ge 4s–Se 4p coupling; and that this leads to shallow bulk defects, and it also prevents GeSe oxidation. We then find that surface defects in GeSe photovoltaics have played a major role in device performance until now, and we, therefore, develop surface-passivated GeSe solar cells. These achieve a certified PCE of 5.2%, surpassing the best previously-reported GeSe results 3.7 fold. These devices exhibit excellent stability as required of thin-film photovoltaic modules (IEC 61646).

Results

Antibonding coupling for defect-tolerant GeSe. GeSe crystallizes in an orthorhombic layered structure with the Pnma 62 space group (Fig. 1a). Both Ge and Se atoms are three fold coordinated with each other. There is only one type of Ge and Se: GeSe is a binary chalcogenide both chemically and structurally. There are therefore only six possible point defects in GeSe: cation vacancy (V₆Ga), anion vacancy (V₆Se), cation interstitial (Ge₆), anion interstitial (Se₆), cation-replace-anion antisite (Ge₆Se), and anion-replace-cation antisite (Se₆Ga). This is simpler than in multicomponent semiconductors such as Cu(In,Ga)Se₂ (CIGS) and Cu₂ZnSn(S,Se)₄ (CZTSSe).

We first used density functional theory (DFT) to calculate the bandstructure, density of states (DOS), and partial DOS of GeSe, since the electronic properties of point defects depend sensitively on the structure. The conduction band minimum (CBM) of GeSe is dominated by the Ge 4p orbital, with significant coupling with the Se 4p orbital; and negligible coupling with the Se 4s orbital (Fig. 1b). This indicates the strong covalent character of GeSe, agreeing well with the above electronegativity analysis, and differing from perovskites with their high ionicity. As for the VBM, it is predominantly made up of the Se 4p orbital and the Ge 4p orbital due to p–p coupling, with a substantial contribution from the Ge 4s orbital. This is seen in the bandstructure of GeSe and the partial DOS of the Ge 4s orbital (Fig. 1b).

The reason that the inner-shell Ge 4s orbital is present in the VBM is illustrated through an atomic orbital picture (Fig. 1c): the Ge 4s and 4p orbitals are too far apart in energy to hybridize directly, and the Se 4p orbital is close to the Ge 4s orbital in energy, allowing these to couple and giving rise to a filled antibonding orbital at the VBM. The CBM also has an antibonding character originating from the Ge 4p–Se 4p coupling. In the lone pair model, the asymmetrical layered-crystal structure of GeSe arising from the stereochemically active lone pairs accounts for the contribution of the Ge 4s orbital to the VBM. This differs from other IV–VI materials such as PbS and SnTe, which have symmetric structures.

The partial oxidation of Ge to its Ge²⁺ oxidation state contributes an antibonding 4s character to the VBM, as in lead–halide perovskites.

We then calculated the formation energies and transition energy levels of the six possible point defects in GeSe mentioned above; we used the generalized gradient approximation (GGA) in these studies. The most striking observation is the high formation energies for all the defects, higher than 1.2 eV in their neutral charge states (Fig. 1e, f). This is in contrast with CH₃NH₃PbI₃, in which defects have low formation energies (close to zero). This is attributed to the stronger covalent Ge–Se bonds compared with the soft Pb–I bonds in perovskites.

The second notable feature is that V₆Ge, with the lowest formation energy, has a shallow level with (-/0) and (2-/-) transition energy levels only 0.05 and 0.15 eV above the VBM, whereas defects with deep levels such as Ge₆Ga and Ge₆Se have high formation energies (Supplementary Fig. 1). These are reconfirmed by Heyd-Scuseria-Ernzerhof (HSE) calculations (Supplementary Fig. 2).

The low formation energy of V₆Ge is attributed to energetically unfavorable Ge 4s–Se 4p antibonding coupling, with the fully occupied antibonding state having no electronic energy. The shallow nature of V₆Ge originates from the antibonding state at the VBM, a defect-tolerant electronic structure known to lead to shallow defects (Supplementary Fig. 3). This state pushes the VBM to a higher level such that the acceptor defect is shallower than the VBM by 1 eV, and not strong p–p coupling. The strongly covalent GeSe with an antibonding VBM, therefore, exhibits mostly shallow defects.

We used deep-level transient spectroscopy (DLTS) to investigate the defect energy levels, concentrations, and types in semiconductor devices. The DLTS spectrum of GeSe photovoltaic devices fabricated using the previously-reported rapid thermal sublimation approach is shown in Supplementary Fig. 4. Two positive peaks denoted as H1 and H2 are observed at 285 K and 310 K, indicating two types of hole trap defects in the GeSe film. The activation energy (Eₐ) and capture cross-section (σ) values determined from the Arrhenius plots are 0.35 eV and 4.3 × 10⁻¹⁶ cm² in H1, and 0.51 eV and 7.6 × 10⁻²¹ cm² in H2, respectively (Fig. 1d). The concentration of defects (Nₐ) calculated from the equation of Nₐ = 2ΔCΔN/Vₐ (Nₐ is the net acceptor concentration in GeSe film) are 1.3 × 10¹² cm⁻³ for H1 and 3.0 × 10¹² cm⁻³ for H2, lower.
than state-of-art chalcogenides such as CIGS (~4.2 × 10¹³ cm⁻³) and CZTS (~3.7 × 10¹⁴ cm⁻³)³⁵,³⁶.

There are only two deep acceptor defects, SeGe and GeSe. We associate the H₁ and H₂ defects observed in the DLTS fitting results at 0.35 eV and 0.51 eV with SeGe and GeSe, respectively. No V₆Ge is observed in the DLTS measurement since V₆Ge is too shallow to produce a response in the DLTS signal. Note that the densities of deep defects in GeSe including SeGe and GeSe are at a magnitude of 10¹² cm⁻³, well below the bulk density of GeSe (~10¹⁵ cm⁻³)²⁴,³⁰. Admittance spectroscopy (AS) measurements further confirmed the low densities of deep-level defects in GeSe. The Eₐ values deduced from the Arrhenius plots are 0.29 eV and 0.45 eV, while the integrated defect densities of these two defects are 1.6 × 10¹³ cm⁻³ and 3.5 × 10¹² cm⁻³ (Supplementary Fig. 5), respectively. In sum, defects with low formation energies generate only shallow levels, whereas deep-level defects have high formation energies and their density is low.

Photovoltaic device performance. When we fabricated devices using an architecture of ITO/Cds/GeSe/Au, we obtained a low PCE of 1.4%, with a V₆oc of 0.23 V, a J₆sc of 15.7 mA cm⁻², and a FF of 40% (Fig. 2a). We reasoned that this inferior performance could arise from surface states. We then characterized the density of interfacial defects at the CdS/GeSe heterojunction through a combination of capacitance-voltage (C-V) profiling and drive-level capacitance profiling (DLCP) measurements. C-V measurements are sensitive to free carriers as well as bulk and interfacial defects, while DLCP measurements are responsive to free carriers and bulk defects³⁷,³⁸. Thus, the density of interfacial defects at the heterojunction is estimated by subtracting N₆DLCP (defect density calculated from DLCP) from N₆C-V (defect density calculated from C-V). We calculated an interfacial defect density of 2 × 10¹² cm⁻² at the GeSe/CdS interface (Fig. 2b), which can lead to severe recombination losses.

We focused therefore on surface passivation of GeSe films. We posited that Sb₂Se₃ would act as a bridge between CdS and GeSe. Recently, a buried CdS/Sb₂Se₃ homojunction has been reported to arise due to the interfacial diffusion of cadmium, forming a good interface between CdS and Sb₂Se₃ layers³⁹. We applied DFT to investigate the interface formation energy between GeSe and Sb₂Se₃ with a preferred orientation of [111] for GeSe and [221] for Sb₂Se₃. The formation energy is −0.12 eV, indicating that the growth of GeSe on Sb₂Se₃ is feasible. X-ray diffraction (XRD) was then used to characterize the orientation of both GeSe and Sb₂Se₃ layers. When we deposited a GeSe film onto a [211]-oriented Sb₂Se₃ layer (Supplementary Fig. 6), we found that the modified GeSe has a preferred [111] orientation, whereas the peaks of (200) and (400) with the lowest surface energies for GeSe disappear completely (Supplementary Fig. 7). This confirms the strong interaction between [211]-oriented Sb₂Se₃ and [111]-oriented GeSe, in agreement with theoretical calculations.

Photovoltaic devices that use the modified GeSe films are improved with a V₆oc of 0.36 V, a J₆sc of 26.9 mA cm⁻², a FF of 54%, and a PCE of 5.2% (Fig. 2a). This efficiency is 3.7× higher than that of control devices. DFT calculations were used to study further the role of Sb₂Se₃: dangling bonds on the surface of [111]-oriented GeSe film lead to localized states inside the bandgap, causing recombination losses (Fig. 2c), whereas the electron distribution becomes delocalized following modification with Sb₂Se₃ (Fig. 2d). C-V profiling and DLCP measurements reveal an order of magnitude lower interfacial defect density (2 × 10¹¹ cm⁻²) than...
Achieving high-performance GeSe solar cells will require further work on the passivation of surface defects rather than bulk defects. We fabricated over 100 GeSe solar cells (device architecture in Fig. 3a). Figure 3b shows a cross-sectional scanning electron microscope (SEM) image of a device; mapping with false coloring delineates the layers. The thickness of the GeSe layer is 500 nm, and the thickness of the passivation layer is 10 nm (Supplementary Fig. 8). The average grain size of the GeSe film is 250 nm (Supplementary Fig. 9). There is a narrow distribution of PCE values (Fig. 3c), with an average efficiency of 5.2% and a standard deviation of 0.14%. The best-performing device reaches a laboratory PCE of 5.5% ($V_{oc} = 0.36 \text{ V}, J_{sc} = 26.6 \text{ mA cm}^{-2}$, and FF = 56%) (Supplementary Fig. 10). No hysteresis is observed between forward and reverse scans.

We shipped an unencapsulated device to an accredited independent photovoltaic testing laboratory (Newport Corporation PV Lab, USA). This device displays a certified PCE of 5.2% ($V_{oc} = 0.38 \text{ V}, J_{sc} = 24.6 \text{ mA cm}^{-2}$, and FF = 56%) (accreditation certificate in Supplementary Fig. 11). This is the highest PCE reported so far for GeSe solar cells.

The control devices ($2 \times 10^{12} \text{ cm}^{-2}$) (Fig. 2b). Achieving high-performance GeSe solar cells will require further work on the passivation of surface defects rather than bulk defects.
under the standard AM 1.5 G solar spectrum yields a current density of 23.8 mA cm
-2 (Fig. 3e), in good agreement with the J
sc value measured from J-V characterization (within 5% deviation) and also consistent with the absorption edge of GeSe (Supplementary Fig. 12). When we measured device performance at low-light intensities (Fig. 3f), we found that devices exhibit PCE values of 5.3%, 6.3%, and 8.6% (Supplementary Table 1) as we progress down to 0.01 sun. The corresponding light intensity-dependent V
oc measurement is 1.36(kBT/q), larger than kBT/q for trap-assisted recombination, indicating that trap-assisted recombination is still present in these GeSe devices.

**Device and materials stability.** Stability of the GeSe devices was monitored by storing unencapsulated devices in an ambient atmosphere at room temperature and a relative humidity of 50–85%. Devices retain 100% of their initial PCE after storage for 12 months (Fig. 4a). They also show negligible efficiency loss after continuous operation close to the maximum power point (MPP) under 1-sun illumination for 1100 h (Fig. 4b). We then investigated the ultraviolet photostability of unencapsulated devices under ultraviolet irradiation (200–400 nm). They retain their efficiency after exposure to an ultraviolet irradiation dosage of 15.5 kWh m
-2 (Fig. 4c). The thermal stability was investigated by cycling the temperature from -40 to 85 °C for a total of 60 cycles. They show no loss of efficiency after 60 thermal cycles (Fig. 4d).

Temperature-dependent XRD under an ambient atmosphere was applied to explore the origin of air and thermal stability. The film keeps its orthorhombic GeSe (JCPDS 48-1226) phase with no impurity peaks observed (such as GeO2) even up to 400 °C for 30 min (Fig. 4e). Since XRD is unable to detect amorphous components, we performed X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) on the same GeSe film after temperature-dependent XRD measurements. Oxygen and carbon are not detected in GeSe films (see magnified XPS spectrum at 520–550 eV and 281–295 eV) (Fig. 4f), consistent with the EDS results (Supplementary Fig. 14). The Ge 3d
3/2 and Ge 3d
5/2 peaks in the Ge 3d spectrum are observed at 29.85 eV and 30.43 eV (Fig. 4g), corresponding to Ge in the +2 oxidation state. Gaussian-Lorentzian fitting confirms that no peak corresponding to +4 or 0 state of Ge is observed within the detection limit of the XPS instrument. The Se 3d spectrum also reveals that Se is in the expected oxidation state of Se
2-, corresponding to GeSe (Fig. 4f). The above results, therefore, demonstrate the high air and thermal stability of GeSe. In addition, GeSe also exhibits excellent humidity and light stability (Supplementary Fig. 15). The 4s
2 electrons on the Ge cation in ionic perovskites are exposed, making them vulnerable to oxidation; while the lone-pair electrons on the Ge atoms in covalent GeSe participate in Ge 4s–Se 4p coupling, leading to chemical inactivity.

**Discussion**

In summary, we report a binary and non-toxic photovoltaic absorber material, GeSe, with benign defect properties and high stability arising from its antibonding VBM from Ge 4s–Se 4p coupling. We found photovoltaic devices to be limited by surface defects rather than by bulk defects. By passivating these interfacial defects, we achieved a certified record PCE of 5.2%. Unencapsulated GeSe devices exhibited no performance degradation under long-term ambient air, operating, ultraviolet soaking, and thermal cycling conditions. This work provides a deep understanding of the relationship between chemical bonding and macroscopic, device-relevant properties including the nature of defects and material's stability.

**Methods**

**Solar cell fabrication.** All devices were deposited on ITO (Sn-doped In
2O
3) conductive glass, which was cleaned using detergent, deionized water, acetone, and isopropanol in sequence. GeSe thin-film solar cells were fabricated with a structure...
consisting of CdS, passivated layer, GeSe, and Au. First, a CdS buffer layer was deposited by chemical bath deposition (CBD) on ITO conductive glass according to a previous report. Then, the passivation layer (SBSe) was deposited on a modified rapid thermal evaporation (RTE) method, and then a tube furnace was set at 300 °C for 15 min to warm up the substrate, before raising the temperature to 550 °C in 30 s to start the evaporation. We then kept this temperature and carried out a 2 s deposition of the 10 nm thick SBSe layer, then the power is turned off to stop the evaporation, and finally, the film was removed when it was cooled to 180 °C. We then transferred this SBSe-modified substrate to another tube furnace in ambient air without protection; this next step was to enable the deposition of GeSe film. GeSe films were fabricated by rapid thermal sublimation method as in a previous report. We preheated the GeSe powder and substrate at 350 °C for 20 min, before quickly increasing the source temperature to 400 °C within 2 s, maintaining this temperature for 5 s, before finally turning off the heating. Finally, Au back contacts (80 nm) were deposited using a thermal evaporation system (Beijing Technol Science) through a shadow mask (0.09 cm²).

**Materials characterization.** Powder XRD patterns were recorded using a Rigaku D/MAX-2500 diffractometer with a Cu target (Kα radiation, λ=1.54056 Å). High-resolution XPS measurements were performed on an ESCALab220i-XL electron spectrometer (VG Scientific) using 300 W Al Kα radiation. The optical transmission was measured using a UV–vis near IR spectrophotometer (UH4150, HITACHI). Scanning electron microscopy (SEM) cross-sectional images were obtained by Hitachi S-4800 microscope. Atomic force microscopy (AFM) data were collected on a Bruker Dimension Icon microscope.

**Device performance characterization.** J-V curves of the solar cells were obtained using an AM 1.5 G solar simulator (Newport, USA) equipped with a Keithley 2420 source meter and 450 W xenon lamp (OSRAM) in the air at room temperature. Light intensity was adjusted using an NREL-certified Si solar cell with a KG-2 filter for approximating AM 1.5 G light (100 mW cm⁻²). The device was covered with a metal mask with an aperture area of 0.09 cm² during efficiency measurement. The J-V curves were measured with a scanning rate of 100 mV s⁻¹ (voltage step of 20 mV and delay time of 200 ms). Both forward (−1 to 1 V) and backward (1 to −1 V) scans were recorded.

**Electrical characterization.** DLTS measurements were performed using an FT-1030 HERA DLTS system equipped with a JANIS VPF-800 cryostat controller on the high-performance device. The temperature was scanned between 140 and 380 K. The reverse bias voltage was set to −0.5 V. The filling pulse voltage and width were 0.4 V and 20 ms, respectively. The C-V curves and DLCP spectra were obtained using a Keithley 4200. C-V measurements were performed at room temperature in an electromagnetic shielding box at a frequency of 10 kHz and an A.C. amplitude of 30 mV. The D.C. bias voltage was scanned from −1.0 V to 0.5 V with a step size of 0.01 V. DLCP measurements were performed with an A.C. amplitude ranging from 14 mV to 140 V and D.C. bias voltage from −0.2 V to 0.2 V.

**Light-soaking test.** Devices were illuminated using a Xe light source (PLS-SXE300, 1.35 sun intensity) with an AM 1.5 light filter. A 160 Ω resistor was connected and the load was measured to be 175 Ω due to the contribution from the additional connection circuit. The device was continuously operated near the MPP, and the load was measured to be 175 Ω due to the contribution from the additional connection circuit. The device was continuously operated near the MPP, and the load was measured to be 175 Ω due to the contribution from the additional connection circuit.

**Ultraviolet stability tests.** Devices were exposed to UV light with wavelength range from 200 to 400 nm (Xe light source, PLS-SXE300) for 62 h and the power was kept at 25 mW cm⁻². The devices were put on a hot plate maintaining the temperature at 60 °C. After illumination, we took out the device and measured the J-V curves under AM 1.5 G illumination. The device was illuminated with a 100 mW cm⁻² light source for 2 h. The measurement results showed that the device showed no degradation under AM 1.5 G illumination.

**Thermal cycling test.** Devices were placed inside a high-low temperature test chamber under the atmosphere. Chamber temperature was periodically changed from 40 to 85 °C for 60 cycles. Every cycle, the total time is 70 min and the device temperature remained stable at each extreme for 10 min. After each cycle, the device temperature was adjusted to 298 K and device performance was measured.

**Density functional theory.** The crystal structure, total energy, and bandstructure were calculated using DFT methods as implemented in the Vienna ab initio simulation package (VASP) code. Frozen-core projector augmented-wave (PAW) pseudopotentials and a plane wave basis set with an energy cutoff of 520 eV were employed, with a 8 × 8 × 4 Monkhorst-Pack k-point mesh included in the Brillouin zone integration for the 16-atom primitive cell and a 3 × 3 × 3 mesh for the 64-atom supercell, which was used for the calculation of defect properties. Test calculations were performed with a higher energy cutoff, denser k-point mesh, and larger supercell size, and we found the same trends. The GGA to the exchange-correlation functional was used in all the calculations, which predicted a bandgap around 0.9 eV for GeSe, slightly lower than the experimental value at 1.1 eV. To estimate the influence of GGA on the calculated results, the non-local hybrid functional was also used which predicted the bandgap more accurately, showing that the conclusions were not influenced by the specific functionals.

**Reporting Summary.** Further information on research design is available in the Nature Research Reporting Summary linked to this article.

**Data availability.** The data that support the findings of this study are available on reasonable request from the corresponding author.

**References.**
1. Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. J. Am. Chem. Soc. 131, 6050–6051 (2009).
2. National Renewable Energy Laboratory. Best Research-Cell Efficiencies https://www.nrel.gov/pv/assets/pdf/best-research-cell-efficiencies-20200406.pdf.
3. Walsh, A. & Zunger, A. Instilling defect tolerance in new compounds. Nat. Mater. 16, 964–967 (2017).
4. Walsh, A., Payne, D. J., Egdell, R. G. & Watson, G. W. Stereochemistry of post-transition metal oxides: revision of the classical lone pair model. Chem. Soc. Rev. 40, 4455–4463 (2011).
5. Kurchin, R. C., Gorai, P., Buonassisi, T. & Stevanovic, V. Structural and chemical features giving rise to defect tolerance of binary semiconductors. Chem. Mater. 30, 5583–5592 (2018).
6. Brandt, R. E., Stevanovic, V., Ginley, D. S. & Buonassisi, T. Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites. MRS Commun. 5, 265–275 (2015).
7. Ganose, A. M., Savory, C. N. & Scanlon, D. O. Beyond methylammonium lead iodide: prospects for the emergent field of ns² containing solar absorbers. Chem. Commun. 53, 20–44 (2017).
8. Xiao, Z., Meng, W., Wang, J., Mitzi, D. B. & Yan, Y. Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality. Mater. Horiz. 4, 206–216 (2017).
9. Zakutayev, A. et al. Defect tolerant semiconductors for solar energy conversion. J. Phys. Chem. Lett. 5, 1117–1125 (2014).
10. Pandey, M. et al. Defect-tolerant monolayer transition metal dichalcogenides. Nano Lett. 16, 2234–2239 (2016).
11. Maughan, A. E. et al. Defect tolerance in intercalation the vacancy-ordered double perovskite semiconductors CsSnI₃ and Cs₂SnI₆. J. Phys. Chem. Lett. 5, 1117–1125 (2014).
12. Hall, J. M. & Petrozza, A. Defects in perovskite-halides and their effects in solar cells. Nat. Energy 1, 16149 (2016).
13. Huang, J., Yuan, Y., Shao, Y. & Yan, Y. Understanding the physical properties of hybrid perovskites for photovoltaic applications. Nat. Rev. Mater. 2, 17042 (2017).
14. Yin, W.-J., Shi, T. & Yan, Y. Unusual defect physics in CH₃NH₃PbI₃ perovskite solar cell absorber. Appl. Phys. Lett. 104, 063903 (2014).
15. Xiao, Z., Song, Z. & Yan, Y. From lead halide perovskites to lead-free metal halide perovskites and perovskite derivatives. Adv. Mater. 31, 1803792 (2019).
16. Steiger, K. X. et al. Defect tolerance in methylammonium lead iodide perovskite. ACS Energy Lett. 1, 360–366 (2016).
17. Xue, D.-J. et al. Regulating strain in perovskite thin films through charge-transport layers. Nat. Commun. 11, 1514 (2020).
18. Liu, D. & Kelly, T. L. Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. Nat. Photonics 8, 133 (2013).
19. Boyd, C. C., Cheacharoen, R., Leijtens, T. & McGehee, M. D. Understanding degradation mechanisms and improving stability of perovskite photovoltaics. Chem. Rev. 119, 3418–3451 (2019).
20. Jiang, Q. et al. Surface passivation of perovskite film for efficient solar cells. Nat. Photonics 13, 460–466 (2019).
21. Earnes, C. et al. Ionic transport in hybrid lead iodide perovskite solar cells. Nat. Commun. 6, 7497 (2015).
22. Hoke, E. T. et al. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. Chem. Sci. 6, 613–617 (2015).
23. Zhao, Y.-C. et al. Quantification of light-enhanced ionic transport in lead iodide perovskite thin films and its solar cell applications. Light Sci. Appl. 6, e16243–e16243 (2017).

24. Xue, D.-J. et al. GeSe thin-film solar cells fabricated by self-regulated rapid thermal sublimation. J. Am. Chem. Soc. 139, 985–986 (2017).

25. Wang, X. et al. Short-wave near-infrared linear dichroism of two-dimensional germanium semilens. J. Am. Chem. Soc. 139, 14976–14982 (2017).

26. Liu, S.-C. et al. Investigation of physical and electronic properties of GeSe for photovoltaic applications. Adv. Electron. Mater. 3, 1700141 (2017).

27. Zhou, X. et al. Highly anisotropic GeSe nanosheets for phototransistors with ultrahigh photoreponsivity. Adv. Sci. 5, 1800478 (2018).

28. Yang, Y. et al. In-plane optical anisotropy of low-symmetry 2D GeSe. Adv. Opt. Mater. 7, 1801311 (2019).

29. Yang, Z. et al. WSe2/GeSe heterojunction photodiode with giant gate tunability. Nano Energy 49, 103–108 (2018).

30. Liu, S.-C., Yang, Y., Li, Z., Xue, D.-J. & Hu, J.-S. GeSe thin-film solar cells. Mater. Chem. Front. 4, 775–787 (2020).

31. Murgatroyd, P. A. E. et al. GeSe: optical spectroscopy and theoretical study of a van der Waals solar absorber. Chem. Mater. 32, 3245–3253 (2020).

32. Walsh, A., Chen, S., Wei, S.-H. & Gong, X.-G. Kesterite thin-film solar cells: advances in materials modelling of Cu2ZnSnS4, Adv. Energy Mater. 2, 400–409 (2012).

33. Chen, S., Walsh, A., Gong, X.-G. & Chen, S.-H. Classification of lattice defects in the kesterite Cu2ZnSnSe4 and Cu2ZnSnS4 earth-abundant solar cell absorbers. Adv. Mater. 25, 1522–1539 (2013).

34. Waghmare, U. V., Spaldin, N. A., Kandpal, H. C. & Seshadri, R. First-principles indicators of metallicity and cation off-centricity in the IV–VI rocksalt chalcogenides of divalent Ge, Sn, and Pb. Phys. Rev. B 67, 125111 (2003).

35. Qi, Y.-F. et al. Engineering of interface band bending and defects elimination via a Ag-graded active layer for efficient (Cu1/2Ag1/2)2ZnSn(S,Se)4 solar cells. Energy Environ. Sci. 10, 2401–2410 (2017).

36. Repins, I. L. et al. Comparison of device performance and measured transport parameters in widely-varying Cu(In,Ga) (Se,S) solar cells. Prog. Photovolt. 14, 25–43 (2006).

37. Wang, W. et al. Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. Adv. Energy Mater. 4, 1301465 (2014).

38. Duan, H.-S. et al. The role of sulfur in solution-processed Cu2ZnSn(Se,S)4 and its effect on defect properties. Adv. Funct. Mater. 23, 1466–1471 (2013).

39. Zhou, Y. et al. Buried homojunction in CdS/Se thin films photovoltaics generated by interfacial diffusion. Appl. Phys. Lett. 111, 013901 (2017).

40. Zhou, Y. et al. Thin-film SeBr-Se photovoltaics with oriented one-dimensional ribbons and benign grain boundaries. Nat. Photonics 9, 409–415 (2015).

41. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

42. Heyd, J. & Scuseria, G. E. Efficient hybrid density functional calculations in solids: assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional. J. Chem. Phys. 121, 1187–1192 (2004).

Acknowledgements
This work is supported by the National Natural Science Foundation of China (21922512, 21873264, 61725201), the Youth Innovation Promotion Association CAS (2017050). The work of Y.M., Y.H., A.P., and E.H.S. is supported by the US Department of the Navy, Office of Naval Research (Grant Award NO. N00014-17-1-2524).

Author contributions
D.-J.X. conceived the idea and designed the experiments. S.-C.L. prepared films, fabricated devices, and characterized them. C.-M.D., Y.M., and S.C. performed the DFT calculations and analyzed the results. Y.Z. and C.C. assisted in the device characterization. Y.H. and A.P. helped with the manuscript preparation. J.T. discussed the results and commented on the paper. D.-J.X., S.-C.L., and E.H.S. wrote the paper. E.H.S. supervised the manuscript preparation. D.-J.X. and J.-S.H. supervised the project. All authors read and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information

Supplementary information
The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-20955-5.

Correspondence and requests for materials should be addressed to D.-J.X., E.H.S. or J.-S.H.

Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2021