Sulfide Perovskites for Solar Energy Conversion Applications: Computational Screening and Synthesis of the Selected Compound LaYS₃

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One of the key challenges in photoelectrochemical water splitting is to identify efficient semiconductors with band gaps of the order of ~ 2 eV to operate as the large-band-gap component in water splitting tandem devices. Here, we address this challenge by extensive computational screening of ternary sulfides followed by synthesis and confirmation of the properties of one of the most promising materials. The screening focusses on materials with ABS₃ composition taking both perovskite and non-perovskite structures into consideration, and the material selection is based on descriptors for thermodynamic stability, light absorption, charge mobility, and defect tolerance. One of the most promising candidates identified is LaYS₃. This material was synthesized directly in thin-film form demonstrating its stability, crystal structure, light absorption, and strong photoluminescence. These data confirms its potential applicability in tandem photoelectrochemical devices for hydrogen production.

1 Introduction

Efficient harvesting of solar energy is urgently needed to tackle the growing energy demand and deleterious effects of the large scale consumption of fossil fuels. Different routes are actively being explored for the conversion of solar energy to other forms, for example electricity, or chemical or thermal fuels^{1–5}. This work focuses on photoelectrochemical production of fuels such as hydrogen through light-induced splitting of water.

In 1972 Fujishima and Honda demonstrated that direct light-driven water splitting was possible⁶, and since then a number of water splitting materials have been identified⁷. However, due to the large band gap required to split water with a single photon, the solar-to-hydrogen efficiency of such a device is currently below 1% and numerical modeling shows that the efficiency cannot exceed 11% even under optimistic assumptions⁸ and probably no more than 5–8% can be real-

ized in practice^{9–11}. These estimates can be easily verified using freely available numerical modeling tools^{12,13}.

A solution to this problem is to use two photons instead of one to obtain the required voltage. This requires a so-called tandem device with two semiconductors, one with a large band gap (LBG) to absorb the most energetic photons, and one with a small band gap (SBG) to absorb the photons of lower energy, operating in series to boost the voltage. Modeling shows that with an optimal combination of light absorbers such a device can, in principle, be as efficient as 25–29% depending on the estimates of catalytic efficiencies, Ohmic losses etc.^{9,10,14,15}, while efficiencies of up to about 21% should be realistic considering all real-world losses⁸. In the past two decades the record for highest solar-to-hydrogen efficiency for tandem devices has consistently been held by III–V (GaAs family) devices^{16–18} and recently, record efficiencies have risen above 16%¹⁹ for monolithic photoelectrochemical devices. These devices, however, are all prone to corrosion in electrolyte even in conjunction with protection layers²⁰ and contain the scarce elements Ga and In for which it is an open question whether supplies can scale to TW-level deployment²¹.

As an alternative to the III/V systems, modeling suggests that Si is an excellent choice as the SBG semiconductor with its 1.1 eV band gap. Many of the integration issues that previously plagued Si such as mitigating corrosion issues without affecting charge transport have now been resolved^{22–24}. One of the largest outstanding problems is to find an efficient LBG semiconductor with a band gap of 1.6–2.0 eV to match

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Si in a tandem device²⁵. Researchers have investigated several such materials including WO₃²⁶, BiVO₄²⁷, GaP²⁸, Fe₂O₃²⁹, Cu₂O³⁰, a-Si³¹, a-SiC³², CdSe³³, GaInP¹⁶, metal-organic perovskites^{34,35}, and most recently Cu₂BaSn(S,Se)₄³⁶, but, with the latter as a possible exception, they all have problems related to non-optimal band gaps, instability, poor charge transport, or they are made from non-abundant elements.

Significant computational screening investigations of water splitting materials have been performed for oxides, oxynitrides, and oxyfluorides in perovskite or perovskite-derived structures or based on the Inorganic Crystal Structure Database (ICSD)^{37–44}, but so far no break-through materials have resulted from these screenings. The oxides tend to have too large band gaps with very anodic valence band maxima (VBM) with respect to the water redox level resulting in large internal voltage loss in the device. However, both of the aforementioned issues can be resolved by substituting oxygen with sulfur, which reduces the band gap along with making the VBM more cathodic thus bringing it closer to the water redox level⁴⁵. The original motivation for the focus on oxides is their stability under the strongly oxidizing conditions of oxygen evolution, but the use of protection layers lends hope that less stable materials such as sulfides could work as photoabsorbers since they are protected from the electrolyte.

Here we investigate the possibility of ternary sulfides in the ABS₃ stoichiometry as LBG semiconductors. This class of materials has seen intense interest the last couple of years mostly in the context of PV solar cells. CuTaS₃ has been synthesized exhibiting good absorption properties⁴⁶. Perera et al.⁴⁷ have synthesized BaZrS₃, CaZrS₃, SrTiS₃, and SrZrS₃ using high temperature sulfurization of the corresponding oxides. Most recently Niu et al.⁴⁸ also synthesized and characterized BaZrS₃ and SrZrS₃, the latter one in two different phases. Furthermore, Meng et al.⁴⁹ have investigated the alloy system BaZr_{1-x}Ti_xS₃ suggesting tunability of the band gap. Two computational studies have suggested materials with appropriate band gaps for single-cell PV application: the study by Sun et al.⁵⁰ investigates nine sulfides and nine selenides and suggests that CaTiS₃ and BaZrS₃ (and the selenides CaZrSe₃ and CaHfSe₃) have relevant PV band gaps, while Ju et al.⁵¹ also investigate nine ABS₃ sulfides (and a similar number of selenides and oxides) and points to SrSnS₃ as a potential PV light absorber.

In the following we shall present a comprehensive screening of ABS₃ compounds where we initially consider all 2809 combinations of 53 A-metal atoms and 53 B-metal atoms. The screening funnel is illustrated in Figure 1. Based on valence considerations the initial number of compounds is reduced to 705 distinct ABS₃ combinations, which are investigated in a distorted perovskite structure to identify the ones which are semiconductors. The heats of formation of the compounds are investigated in an additional six crystal structures and the pos-

sibility of segregation is assessed by considering all reactions where the compounds disintegrate into one- or two-element constituents. The band gaps are calculated with the so-called GLLB-SC functional and only materials with visible-light absorption remain in the funnel. The electron and hole mobilities are considered through calculation of the effective band masses. In the case of a band conduction mechanism the mobility is simply proportional to the effective band mass, while the situation is more complex if polaron formation takes place. The polaron hopping mechanism is known to be of relevance for a number of oxides⁵², while much less is known for sulfide perovskites. The polaron formation involves electron localization which most easily occurs for narrow bands. Materials with low effective masses will therefore for a start be less likely to form polarons. In a recent DFT study by Bennett et al.⁵³, where BaZrS₃ is compared to BaZrO₃, it is shown that the bonding character in the sulfide is more covalent than in the oxide. The ionic contribution to the dielectric constant is also found to decrease from 48 to 36 when going from BaZrO₃ to BaZrS₃ while the high-frequency electronic dielectric constants increases from 4.9 to 9.6. Both of these changes point to a smaller Fröhlich electron-phonon coupling constant in the sulfide compared to the oxide, but we cannot exclude that polaron hopping could be of relevance for some of the compounds we identify.

Finally, the defect tolerance of the compounds are investigated by determining whether or not the introduction of vacancies gives rise to electronic states in the band gap.

We do not address the questions of level alignment of the valence band maxima and conduction band minima of the compounds relative to the water redox levels. The level determination requires consideration of interfaces in large supercells and is computationally more demanding than what is currently possible for large-scale screening. Furthermore, as already mentioned, the direct water-semiconductor contact is avoided due to the usage of protection layers. It has been shown with some of the best photocatalytic water splitting materials (Si and III-V semiconductors) that p-n junctions are the optimal approach to maximize performance. This approach mostly eliminates any band alignment issues caused by differences in the semiconductor band position versus the dominating redox couple in the electrolyte due to tunnel junctions at the interfaces.

Our screening study results in a short list of potential LBG photo-absorbers along with some potential PV materials. We synthesize and investigate one of the most promising LBG photo-absorbers, LaYS₃, and show that it does indeed have the predicted crystal structure and band gap. Photoluminescence experiments confirm that any potential defect state is not contributing to deep gap recombination sites.

Fig. 1 Sketch of the screening funnel. The different design criteria lead to a gradual reduction in the number of candidate materials.

2 Computational Details

The electronic structure calculations are performed using Density Functional Theory (DFT) in the Projector Augmented Wave (PAW) formalism⁵⁴ as implemented in the electronic structure code GPAW⁵⁵. The calculations are controlled using the Atomic Simulation Environment⁵⁶. The cell and atomic relaxations are performed using the PBEsol functional which gives better estimates of lattice constants compared to other semi-local functionals⁵⁷. The wavefunctions are expanded in a plane-wave basis with an energy cutoff of 800 eV. The sampling of the Brillouin zone is performed using the Monkhorst-Pack scheme⁵⁸. The k-point mesh is $7 \times 7 \times 7$ for the systems in the cubic, distorted cubic and orthorhombic (*Pna2*₁) structures, $6 \times 3 \times 6$ for the systems in the monoclinic structure, and $4 \times 3 \times 4$ for the orthorhombic *Pnma* structure. Finer k-point meshes are adopted for the calculation of band structures and effective masses. All the structures are optimized until the forces are converged to 0.05 eV/Å or below. The heat of formation together with the corresponding uncertainties have been calculated using the meta generalized gradient approximation functional mBEEF⁵⁹, which has been shown to give good predictions of the heat of formation in comparison with experiments⁶⁰. For the mBEEF calculations the wavefunctions are described on a real space grid. The band gaps and band structures are calculated using the more accurate semi-local GLLB-SC functional^{61,62}. The GLLB-SC functional with similar computational cost as the other semi-local functionals predicts band gaps which are quite close to the predictions of more computationally demanding many-body-perturbation-theory calculations (GW) and hybrid functionals⁴². In Ref. 42 it is shown that the mean absolute deviation between the band gaps calculated with GLLB-SC and with GW is 0.38 eV for a broad range of materials. To further examine the accuracy of the GLLB-SC band-gap calculations for the class of sulfur perovskites considered here, Table 1 includes a comparison of calculated and experimental gaps. The mean absolute error is ~ 0.30 eV.

Table 1 Comparison of the GLLB-SC calculated and the experimental band gaps (in eV) for sulfur perovskites, where experimental data are available. The mean absolute error of the calculated values from the experimental values is ~ 0.30 eV.

formula	$E_g^{\text{GLLB-SC}}$	E_g^{exp}
CuTaS ₃	0.98	1.00 ⁴⁶
BaZrS ₃	2.25	1.73-1.85 ^{47,48,63}
CaZrS ₃	2.48	1.90 ⁴⁷
SrZrS ₃ (NH ₄ CdCl ₃ /Sn ₂ S ₃)	1.46	1.53 ⁴⁷
SrZrS ₃ (GdFeO ₃)	2.50	2.13 ⁴⁷

Spin-orbit coupling was included in the calculations for materials containing elements with atomic number (Z) higher

than 56.

3 Experimental Details

LaYS₃ thin films are produced in two synthesis steps. The first is deposition of LaY thin-film precursors on a fused silica substrate by co-sputtering of La and Y metallic targets from magnetron sources with RF and DC power respectively. The power densities on each target are tuned to obtain a La/Y atomic ratio close to 1 in the precursors, as measured by energy dispersive x-ray spectroscopy (EDX) after deposition. The second step is sulfurization of the LaY precursors in a quartz tube furnace with a 70 sccm flow of 5% H₂S in Ar at atmospheric pressure. The precursors are sulfurized for 10 hours at 1000°C, with ramp rates of 10°C/min (up) and 5°C/min (down).

The elemental composition of both the thin film precursors and the sulfurized thin film is characterized in a FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with an EDX detector (X-Max^N 50, Oxford Instruments). A beam voltage of 8 kV is sufficient to reliably determine the intensity of the *L* x-ray lines of La and Y without penetrating into the fused silica substrate. Complementary characterization of composition is performed by x-ray photoemission spectroscopy (XPS) using a Thermo Scientific K-Alpha instrument with monochromatized Al *K*_α x-ray source at 1486.68 eV. Before acquiring the XPS spectrum, the sample surface is cleaned of its native oxide by in-situ ion beam etching. Elemental composition is determined using the following lines: La 3d, Y 3p, S 2s, and O 1s. Identification of the crystal structure of the sulfurized film is done through analysis of x-ray diffraction patterns (XRD) obtained with a PANalytical Empyrean diffractometer in the Bragg-Brentano measurement configuration using Cu *K*_α radiation. As a reference for XRD phase analysis, the unit cell details of each possible LaYS₃ structural prototype calculated in this work are entered as input in the program GDIS⁶⁴. The program simulates the powder XRD patterns of the different prototypes, which are used as a reference to assign experimental XRD peaks to a certain prototype.

The band gap of the sulfurized film is estimated based on its absorption coefficient, which is in turn extracted by spectroscopic ellipsometry in the visible-UV range using a J.A. Woollam M-2000 rotating compensator ellipsometer. The (unknown) optical functions of the LaYS₃ compound are fitted to a Kramers-Kronig consistent b-spline function with 3 nodes/eV. Thickness and roughness of the LaYS₃ film are also fitted, whereas the optical functions of the fused silica substrate are obtained from a separate ellipsometry measurement on the bare substrate. This method has been described in detail before for films of other sulfide materials on glass^{65,66}. Steady-state photoluminescence (PL) spectra are measured at

room temperature with an Accent RPM2000 system at an excitation wavelength of 405 nm and power density 1 W/mm².

4 Results and Discussion

4.1 Computational Screening

In order for a material to possess a band gap it has to obey the valence rule which requires that the valences (with sign) of the cations and anions add up to zero. A few exceptions to the valence rule exists under extreme conditions of temperature and/or pressure but violation of the rule under normal physical conditions is very unlikely⁶⁷. Therefore, as a starting point we impose the valence rule on the selection of cations A and B so that the sum of oxidation states of the cations should be 6 corresponding to the value of -6 from the three sulfur anions. As a result, the selection of A and B cations (lanthanides except lanthanum and actinides excluded) gives 705 distinct AB_3S_3 combinations. However, imposing the valence rule is not sufficient for a compound to be stable and have a non-zero band gap and we therefore proceed as follows: we first carry out the structural relaxation of the AB_3S_3 compounds in a perfectly symmetric five atom cubic unit cell retaining the unit cell symmetry during relaxation. Thereafter, the same set of compounds are relaxed by breaking the cubic symmetry of the unit cell in order to see the effect of symmetry breaking on the energies and band gaps. Interestingly, only 15 out of the 705 combinations in the perfectly cubic structure have non-zero band gaps. However, breaking the symmetry has a significant effect on the band gaps and results in the identification of 56 compounds where both the AB_3S_3 and BAS_3 distorted structures exhibit a gap and 73 compounds where only one of the two distorted structures show a gap. In 8 cases the two-component systems A_2S_3 exhibit a gap, but we shall not investigate these further here. An overview of the band gap values for the compounds in the distorted structure is shown in Figure 2.

The set of $56 + 73 = 129$ compounds provides a good starting point for identifying compounds which might be semiconducting in other non-cubic structures; however, finding global energy minimum structures of 129 compounds is a challenging task. Therefore, we decided to rely on the frequency of the crystal structures of compounds of AB_3S_3 stoichiometry occurring in the experimental data reported in ICSD^{68,69}. Selecting the database entries of AB_3S_3 stoichiometry (ignoring the lanthanides and actinides in the entry) shows that most of the compounds crystallize in only a few prototypes. The six most frequently occurring prototypes are (see Figure 3): (1) Hexagonal $P6_3/mmc$ structure of $BaNiO_3$. This is a perovskite with face sharing octahedra. (2) Orthorhombic $Pna2_1$ structure of $YScS_3$. A perovskite with corner sharing octahedra. (3) Orthorhombic $Pnma$ structure of $GdFeO_3$ (similar to the

the black structure of $CsSnI_3$). This is a perovskite with corner sharing octahedra. (4) another orthorhombic $Pnma$ structure of NH_4CdCl_3/Sn_2S_3 or the so-called “needle-like” structure (similar to the yellow structure of $CsSnI_3$). In this perovskite the octahedra share edges. (5) monoclinic $C12/m1$ structure of $FePS_3$. This is a layered perovskite with edge sharing octahedra. (6) monoclinic $P1c1$ structure of $PbPS_3$. It is worth mentioning that we are not limiting ourselves to explore only perovskite structures, which are recognized by having octahedra containing B cations in their centers and non-metal atoms in their corners, but we also consider the structure $PbPS_3$ which is not a perovskite. This non-perovskite structure is chosen due to the high frequency of occurrence in the ICSD. For convenience we hereafter refer to all the structures as perovskites.

The prototypes introduced above represent the initial structures for the sulfide perovskites. Using the crystal structure of the prototypes as templates the atomic sites are substituted with A's and B's from our previously determined compounds. In the 56 cases where both the AB_3S_3 and BAS_3 exhibit gaps in the distorted structure, we investigate both AB permutations, while in the 73 cases with only one of the AB combinations showing a gap in the distorted structure we only investigate the relevant permutation. The number of atoms in the unit cell of the $BaNiO_3$ type structure is 10 whereas the other prototypes have 20 atoms in the unit cell. The structures are subsequently completely relaxed with respect to the unit cell and the atomic positions. The initial structures contain small symmetry-breaking displacements, which mean that in some cases the structures change considerably during relaxation. In order to obtain a correct classification of the final structures, we monitor potential changes of the space groups using the spglib-library⁷⁰. Within a reasonable tolerance most of the lowest-energy structures have unchanged symmetry. Some exceptions are systems initially in the distorted $P1$ structure, which often during relaxation obtain a higher, but still mostly quite low, degree of symmetry. In one case, the $MnTaS_3$ compound, the symmetry of the distorted perovskite increases to the $R3$ space group. About one third of the compounds initially in the $YScS_3$ structure ($Pna2_1$) increase their symmetry to $Pnma$. The character of this structure is further investigated using feature vectors and a metric which describe local atomic structures in crystals⁷¹. It turns out that the $YScS_3$ structure in these cases has relaxed into the $GdFeO_3$ structure. Among the lowest energy structures this transformation happens for $BaHfS_3$ and $BaZrS_3$. Two compounds, $CdHfS_3$ and $TeHfS_3$, obtain the lowest energy by distorting the $BaNiO_3$ prototype so that the symmetry is reduced from $P6_3/mmc$ to $P2_1m$.

The structural optimizations result in total energies of all the compounds in the different structures, which can be compared to find the most stable structure with the lowest energy per atom. In order to get not only an estimate of the energy differences but also their uncertainties we employ the technique

Fig. 2 Calculated band gap values using the GLLB-SC functional for the distorted 5-atom unit cell. Most of the materials do not have a band gap because the valences do not add up to zero. 129 compounds exhibit a band gap in the distorted 5-atom unit cell.

Fig. 3 The most common prototypes in the ICSD^{68,69} for ABS₃ materials. We investigate all compounds in these six structures plus the cubic and the distorted cubic structures.

of Bayesian error estimation in the mBEEF functional⁷². The reference energy for a given compound is taken as the energy of the lowest-energy structure from the set of the obtained ABS_3 and BAS_3 structures. Thereafter, the energy differences and uncertainties are calculated with respect to this reference energy. Additionally, the stability of compounds is also calculated with respect to competing phases consisting of elemental, binary, and ternary phases, where the elemental phases are the standard states of the elements, and the binary and ternary phases are the sulfides of one ($\text{A}_\alpha\text{S}_\beta$, $\text{B}_\gamma\text{S}_\delta$ type) and two ($\text{A}_\mu\text{B}_\nu\text{S}_\epsilon$ type) elements, respectively. The pool of competing phases is taken as the stable compounds in the Open Quantum Materials Database (OQMD)⁷³. The pool consists of the elementary phases of the elements and 208 compounds. Their structures are re-optimized with the PBEsol functional and their energies calculated with mBEEF.

The stability versus segregation of a given ABS_3 compound is determined by constructing the convex energy hull in the A-B-S space. The elemental phases are placed in the corners of a triangle defining a plane (with, say, $z = 0$) and the z -coordinate of the remaining phases are their standard heats of formation. The in-plane positions of the compounds with respect to the elemental phases are given by their stoichiometry. By considering all triangles obtained by connecting three of the points the so-called convex hull, which includes all triangles with maximal stability, can be constructed.

In constructing the hull, the compounds with the ABS_3 compositions are not included and we refer to the energy of the hull at this composition as simply the hull energy. The phase ABS_3 is unstable if the hull energy (E_{hull}) is lower than the energy of ABS_3 (E_{ABS_3}). Additionally, the Bayesian error estimates of the hull energy (ΔE_{hull}) is calculated in the same manner as described before. The comparison of E_{hull} and E_{ABS_3} (along with the uncertainties) gives a robust criterion to assess the low-temperature stability of ABS_3 .

Besides comparing the energies of different structures of ABS_3 with the convex hull we also compare their relative energies in order to address potential (meta-)stability. The $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure turns out to be the most common lowest energy structure whereas the cubic and BaNiO_3 structures are rarely the most stable one. The remaining structures have roughly equal frequency of appearance as the lowest energy structure.

With respect to stability of the different phases, three different situations can be identified. They are illustrated for some selected compounds in Figure 4. 1) The convex hull has the lowest energy even when the uncertainty is taken into account. If this is the situation the ABS_3 compound cannot be expected to be stable in any of the suggested structures and should therefore be discarded. This is for example the case with HfTeS_3 as seen in Figure 4. 2) Several structures and/or the convex hull are within the uncertainties of the lowest energy structure

or have an energy of less than 25 meV above the lowest energy structure. In this case it is unclear whether the compound in the lowest energy structure is stable and/or metastable even at low temperatures. The perovskites often exhibit symmetry breaking phase transitions at moderate temperatures, but the prediction of the complete phase diagram would require a detailed study of the entropic contributions to the free energy. Such studies have been carried out for for example BaTiO_3 ⁷⁴ and to some extent for CsSnI_3 ⁷⁵. An extensive study of perovskite phase stability in sulfides including some discussion of thermal effects due to phonons can be found in Ref. 76. By choosing an appropriate synthesis route the phase formation can to some extent be controlled, and it might be possible to form non-equilibrium phases which for all practical purposes are stable. We therefore keep the compounds in this class for further studies. An example is ZrMgS_3 , as shown in Figure 4. 3) A single structure has a significantly lower energy compared to all the other structures and the convex hull. We take a compound to be in this class if the energy of the most stable structure is lower than the competing energies minus the error bar and if there are no other structures within 25 meV. The 25 meV leaves some space for entropic effects at room temperature. The compounds in this class are the potentially most promising ones since the room temperature phase can be predicted with considerable certainty. The compound LaRhS_3 illustrates this case in Figure 4. Overall, we find 75 different ABS_3 compositions in 155 structures to be further investigated.

At this stage of the screening we check if any of these compounds have been experimentally synthesized according to ICSD, and in which structures. For example, BaZrS_3 (ICSD 23288), PbZrS_3 (ICSD 2439) and SrZrS_3 (ICSD 23287) appear in ICSD in the structures the calculations show to have the lowest energy. LaScS_3 (ICSD 641844) and YScS_3 (ICSD 23422) appear experimentally in the YScS_3 prototype with $Pna2_1$ symmetry. This structure is already included in our investigations, but the calculations find LaScS_3 to be slightly more stable in the GdFeO_3 structure and YScS_3 to be slightly more stable in the PbPS_3 structure. We observe a similar situation with CaZrS_3 and CaHfS_3 , both reported in the ICSD in the GdFeO_3 structure, but the calculations show PbPS_3 structure to be the most stable one. However, in all four cases the energy differences are smaller than the calculated error bars on the energy differences. SnSrS_3 (ICSD 651032) is reported in the ICSD in the $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure, but the structure was synthesized under high pressure. The calculations on the other hand, predict GdFeO_3 to be the lowest energy structure.

Four compounds appear in entirely new structures in ICSD: LaYS_3 , AgTaS_3 , BiInS_3 and CuTaS_3 . The BiInS_3 -structure (ICSD 290195) is not the result of an experimental structure determination but comes from a computational study. However, we confirm that it has a low energy and include it in the

Fig. 4 Comparison of formation energies, E , and band gaps, E_g , of different phases for a selection of compounds. The energy error bars are calculated relative to the most stable $AB\text{S}_3$ structure. For some compounds, like LaRhS_3 (top panel) there is a single structure significantly more stable than the other structures and the convex hull. In other cases, like ZrMgS_3 (middle panel), several structures have energies within the uncertainties of the calculations and might be (meta-)stable. In such cases it is useful to check the corresponding band gaps for all the (meta-)stable structures. Finally, in cases, like TeHfS_3 (bottom panel), all the investigated phases are unstable relative to the convex hull and the compounds do therefore not need to be considered further.

Fig. 5 All the stable compounds, according to the procedure described in the caption of Fig. 4, with the corresponding band gaps in the region relevant for solar cells (0.5-1.5 eV) and water splitting (1.5-2.5 eV) application. All the band gap values were calculated using the GLLB-SC functional. Markers with crosses on top indicate that the chemical formula should be read in reverse, instead of AB (written on the x-label), it is BA. The cases where one structure is considered significantly more stable than the competing phases are indicated with a circle around the symbol, whereas compositions where all stable structures have a band gap size relevant for either PV or PEC are written in bold.

further studies. CuTaS_3 appears in a genuinely new prototype (ICSD 43272), which is a 'needle-like' perovskite and different from the $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure we identify. Calculations on the CuTaS_3 structure confirm that it is more stable than the $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure. CuTaS_3 was recently synthesized⁴⁶, and the band gap measured to around 1 eV in good agreement with our calculated value for this structure of 0.98 eV.

The ICSD reports the LaYS_3 in the CeTmS_3 prototype. Calculating the energy of this structure, we find that it is the most stable one, while we also find the $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure within the calculational uncertainty. In the CeTmS_3 we calculate a direct band gap of 1.79 eV close to the direct band gap of 1.87 eV calculated in the $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure.

Our main focus is on identifying LBG materials for water splitting. However, the screening approach is also of relevance for identification of PV materials. The known successful solar cell materials have band gaps around 1 eV as a balance between the number of photons absorbed and the energy gain per photon. Considering the approximate nature of the band gap calculations, we therefore focus on materials with band gaps in the range 0.5-1.5 eV as candidates for solar cell absorbers. The semiconductors in the water splitting devices and tandem solar cells are required to have a wider band gap, around 2 eV, if incorporated as a LBG component in a tandem device, so here we choose a range of 1.5-2.5 eV as the target for our candidates. The selection is performed based on the calculated GLLB-SC gaps. In most cases the gaps are indirect, but for some systems the gaps are direct. The latter ones are particularly relevant for thin photo-absorbers because of the higher absorbance.

The result of the selection based on band gap is shown in Fig. 5. Overall 90 compounds with 57 different ABS_3 compositions fall within the relevant gap ranges and will proceed to the next step in the selection procedure. Compounds in the $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$ structure are the most common ones while there are no cubic compounds and only two compounds in the BaNiO_3 structure. Three different cases can be identified.

1) A given compound has one structure which is significantly more stable than the competing phases and which has a band gap in the relevant range. A compound where this is the case is indicated in the figure with a circle around the symbol and the name of the compound is written in bold. An example is LaYS_3 .

2) A compound has several structures at low energies, but they all have gaps in the interesting ranges. In this case several symbols for the gaps will appear in the figure and the name of the compound is written in bold. This is, for example, the case for BaZrS_3 , where the GdFeO_3 structure has the lowest energy with a band gap of 2.3 eV, and the distorted structure has also a low energy and a band gap of 1.6 eV.

3) Finally, a compound might have one or more low-energy

structures with relevant band gaps, but it also has low-energy structures with gaps outside the range (for example metallic). These cases show up in Fig. 5 with their names written in ordinary non-bold font. A complete overview of the energies and band gaps for all the different compounds and structures can be found in the supplementary material. The data are furthermore available at the Computational Materials Repository (CMR)^{77,78} and at the NoMaD repository⁷⁹.

Appropriate photoabsorption alone is not sufficient for a material to perform well in a PV or PEC device, so it is important to address the issues occurring after the photon has been absorbed and the carriers have been generated. Ideally, the carriers (electrons and holes) would separate and generate current, but if a large part of carriers recombine almost immediately all the energy is lost. The recombination probability is smaller for carriers with higher mobilities, and it can be used as a targeted property in the screening procedure. Carrier mobility is difficult to calculate, but effective mass, which is in relation with the mobility as $\propto 1/\mu$, can easily be obtained from a DFT calculation. Carrier effective masses were obtained by fitting a parabola to the top of the valence band and bottom of the conduction band of the material. Band structures are calculated along the high-symmetry points as suggested by Setyawan and Curtarolo⁸⁰. We further consider candidates with the absolute values of the effective masses of both carriers smaller than 1 electron mass (because of the orientation of the fitted parabola we use negative signs for hole masses and positive signs for electron masses). This criterion leads to a further reduction in the number of candidate materials to 36 different ABS_3 compositions in 42 structures.

In Table 2 we report the calculated effective masses of the 42 selected candidates together with the calculated band gaps and the type of band gap. We find 18 compounds and structures with a direct band gap, and they are mostly in one of the orthorhombic structures $\text{NH}_4\text{CdCl}_3/\text{Sn}_2\text{S}_3$, GdFeO_3 and YScS_3 . The 42 compounds (composition+structure) with desirable electronic properties are now passed on to the next step in the screening procedure which considers defects.

Defects in a material are often limiting its optoelectronic performance because point defects in crystals may introduce additional states inside the band gap. These additional gap states may act as recombination centers and reduce the charge separation efficiency. Whether the formation of point defects will be detrimental for the photovoltaic performance of a material, depends on the position of the additional states: materials with defect states deep inside the band gap are called defect sensitive, while the ones with defect states inside the bands or close to the band edges are called defect tolerant.

We explore the defect tolerance of the selected candidates by performing defect calculations on the supercells for three types of atomic vacancies: A atom, B atom and S vacancy. Defects were created in a $2 \times 2 \times 2$ ($3 \times 3 \times 3$ for the distorted and

Fig. 6 Projected and total densities of states for BaZrS₃ (GdFeO₃ structure)(left) and SnCaS₃ (NH₄CdCl₃/Sn₂S₃ structure)(right) with and without a neutral sulfur vacancy. The zero of the energy is set at the Fermi level. In the case of BaZrS₃ the introduction of a vacancy does not give rise additional states inside the band gap, while in the case of SnCaS₃, deep states are found within the band gap.

Table 2 Candidates selected based on stability, band gaps in the range 0.5-2.5 eV, and carrier effective masses smaller than 1 electron mass. Compounds, where all low-energy structures exhibit band gaps in the range 0.5-2.5 eV, are indicated in bold. The formulas of the materials with direct band gaps are underlined. Band gaps are given in eV and effective masses in units of the electron mass.

	formula	E_g^{LLB-SC}	E_g^{LLB-SC} $E_g^{(direct)}$	m_h^*	m_e^*	prototype
Ag - Ta	TaAgS ₃	0.90	0.97	-0.27	0.61	FePS ₃
Ba - Hf	BaHfS₃	1.31	1.31	-0.35	0.94	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ba - Te	BaTeS₃	1.40	1.40	-0.21	0.32	YScS ₃
	<u>BaTeS₃</u>	0.95	1.21	-0.48	0.34	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ba - Zr	BaZrS ₃	2.25	2.25	-0.75	0.43	GdFeO ₃
Bi - Ga	BiGaS ₃	2.05	2.47	-0.83	0.45	FePS ₃
	BiGaS ₃	2.45	2.76	-0.68	0.20	distorted
Bi - Sc	BiScS₃	2.45	2.72	-0.47	0.80	PbPS ₃
Bi - Ti	BiTiS₃	1.36	1.98	-0.64	0.31	FePS ₃
Ca - Hf	CaHfS ₃	0.99	0.99	-0.34	0.76	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ca - Sn	CaSnS ₃	1.58	1.93	-0.61	0.94	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ca - Zr	CaZrS ₃	2.48	2.48	-0.22	0.41	GdFeO ₃
	CaZrS ₃	1.36	1.36	-0.37	0.80	NH ₄ CdCl ₃ /Sn ₂ S ₃
Cd - Ge	CdGeS ₃	1.77	1.77	-0.61	0.23	distorted
Cd - Sn	SnCdS₃	1.58	1.58	-0.58	0.15	FePS ₃
Cd - Ti	TiCdS₃	1.26	1.39	-0.35	0.55	FePS ₃
Cd - Zr	ZrCdS₃	2.27	2.39	-0.42	0.45	FePS ₃
Ga - Sb	SbGaS ₃	2.26	2.29	-0.59	0.90	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ga - Sc	GaScS ₃	2.15	2.15	-0.32	0.32	NH ₄ CdCl ₃ /Sn ₂ S ₃
	ScGaS ₃	2.29	2.40	-0.71	0.55	FePS ₃
Ga - Y	GaYS ₃	2.39	2.39	-0.54	0.90	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ge - Ti	GeTiS₃	0.54	0.61	-0.25	0.68	NH ₄ CdCl ₃ /Sn ₂ S ₃
Hf - Pb	HfPbS ₃	1.12	1.63	-0.27	0.23	BaNiO ₃
Hf - Sr	SrHfS₃	1.12	1.12	-0.33	0.81	NH ₄ CdCl ₃ /Sn ₂ S ₃
In - La	LaInS ₃	1.42	2.30	-0.57	0.83	NH ₄ CdCl ₃ /Sn ₂ S ₃
In - Sb	InSbS₃	2.16	2.16	-0.43	0.17	NH ₄ CdCl ₃ /Sn ₂ S ₃
In - Ti	InTiS ₃	0.87	0.87	-0.61	0.14	FePS ₃
La - Sc	LaScS ₃	0.78	0.78	-0.41	0.46	NH ₄ CdCl ₃ /Sn ₂ S ₃
La - Y	LaYS₃	1.79	1.79	-0.67	0.49	CeTmS ₃
Li - Ta	TaLiS₃	1.98	2.00	-0.75	0.98	FePS ₃
Mg - Zr	MgZrS ₃	2.21	2.32	-0.72	0.78	distorted
Na - Ta	TaNas₃	2.37	2.39	-0.40	0.49	FePS ₃
Sb - Sc	ScSbS₃	2.42	2.57	-0.39	0.35	NH ₄ CdCl ₃ /Sn ₂ S ₃
Sb - Y	SbYS ₃	2.03	2.09	-0.37	0.48	NH ₄ CdCl ₃ /Sn ₂ S ₃
Sc - Ti	ScTiS₃	1.48	1.65	-0.80	0.40	FePS ₃
Sr - Te	SrTeS ₃	0.79	0.79	-0.26	0.29	YScS ₃
	SrTeS ₃	0.82	1.01	-0.40	0.20	NH ₄ CdCl ₃ /Sn ₂ S ₃
Sr - Zr	SrZrS₃	1.46	1.46	-0.34	0.79	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ta - Ti	TaTiS₃	1.15	1.15	-0.30	0.24	distorted
	TaTiS ₃	1.47	1.15	-0.87	0.61	FePS ₃
Ti - Zn	TiZnS₃	0.95	1.03	-0.24	0.44	FePS ₃
Zn - Zr	ZrZnS₃	1.91	1.97	-0.62	0.42	FePS ₃

cubic prototypes) supercells. The calculations for both the pristine and defect structures were carried out using the PBE exchange correlation functional and the wavefunctions were expanded in an LCAO (dzp) basis set. The k-point mesh was chosen to scale with the system size: pristine structures were calculated with a dense 14x14x14 mesh, while the mesh for the supercells was reduced to 7x7x7. In the cases of the supercells of the distorted and cubic structures (3x3x3 supercells), the k-point mesh was further decreased to 5x5x5. Due to limitations of computer time, relaxations were not performed, and the spectral analysis was carried out based on the PBE band

structure. Only neutral defects were considered. It should be stressed that the defect states cannot be expected to be treated accurately at the level of a semi-local exchange-correlation functional as applied here due to the underestimation of the band gap and the delocalization error. A more accurate but also more computationally demanding approach would be to use total energy calculations based on hybrid functionals or GW. However, the aim here is not to study the defect level positions or the character of the defect states in detail, but only to qualitatively determine whether or not defect states are present within the band gap.

We identify the defect sensitive materials by calculating the band structure and the electronic density of states (DOS). The presence of a deep lying state in the gap shows up as a contribution to the DOS in the region of the band gap. Fig. 6 illustrates this for a sulfur vacancy in the two cases BaZrS₃, where there are no gap states, and SnCaS₃, where states in the gap are present. In the cases where deep gap states appear they are always caused by sulfur vacancies while the cation vacancies do not seem to introduce deep gap states.

We identify 15 out of the 42 candidate materials to be tolerant to vacancies. This set of 15 materials, summarized in Table: 3, is the final output of the screening and we suggest them as a potential materials for solar energy conversion application. Some of the materials mentioned in Table: 3 have also been studied in previous experimental and theoretical works. For example, band gap tuning and the defect properties of BaZrS₃ have been explored by Meng *et. al* and Sun *et. al*^{50,63}. The band gap reported for BaZr₃ in different studies varies in range from 1.7-1.9 eV which agrees reasonably well with our calculated value^{47,48}. Interestingly, our defect analysis based on the band structure identifies BaZrS₃ as tolerant towards vacancy defects and the total energy based defect calculations by Meng *et. al* also predicts only shallow level defects in the material. Similarly, our calculated value of the band gap of SrZrS₃ agree well with the reported experimental value of 1.53 eV by Niu *et. al*⁴⁸. However, there are also some differences in our predicted set of candidates as compared to the predictions by Ju *et. al* and Sun *et. al*. For example, SrSnS₃ and CaTiS₃ are discarded from our proposed list of materials. According to our calculations the most stable structure of SrSnS₃, and the only one in our stability threshold, is GdFeO₃ with a gap of only 0.1 eV. However, Ju *et. al* did not explore GdFeO₃ as a possible prototype which explains the difference in our results. Similarly, we find that the lowest energy structure of CaTiS₃ is the needle-like with a band gap of 0.2 eV which is too small as per our criteria. On the other hand, some of the compounds we find are not reported in other studies because we do not impose the constraint of Goldschmidt tolerance factor in the selection of elements, because Goldschmidt's criterion is after all only an empirical rule and developed mainly for oxides. CuTaS₃, which was recently studied by Heo *et. al*⁴⁶, is removed from

our final list because of too large effective masses.

Table 3 List of selected candidates based on stability, band gaps, carrier effective masses, and defect tolerance. Compounds where all low-energy structures exhibit band gaps in the range of solar light absorption are indicated in bold. Band gaps are in units of eV and the effective masses are in units of the electron mass.

	formula	$E_g^{GLLB-SC}$	$E_g^{GLLB-SC(direct)}$	m_h^*	m_e^*	prototype
Ba-Hf	BaHfS ₃	1.31	1.31	-0.35	0.94	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ba-Zr	BaZrS ₃	2.25	2.25	-0.75	0.43	GdFeO ₃
Bi-Tl	BiTlS ₃	1.36	1.98	-0.64	0.31	FePS ₃
Ca-Hf	CaHfS ₃	0.99	0.99	-0.34	0.76	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ca-Sn	CaSnS ₃	1.58	1.93	-0.61	0.94	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ca-Zr	CaZrS ₃	1.36	1.36	-0.76	0.88	NH ₄ CdCl ₃ /Sn ₂ S ₃
Hf-Sr	SrHfS ₃	1.12	1.12	-0.33	0.81	NH ₄ CdCl ₃ /Sn ₂ S ₃
Hf-Pb	HfPbS ₃	1.12	1.63	-0.27	0.23	BaNiO ₃
La-Y	LaYS ₃	1.79	1.79	-0.67	0.49	CeTmS ₃
Li-Ta	TaLiS ₃	1.98	2.00	-0.75	0.98	FePS ₃
Mg-Zr	MgZrS ₃	2.21	2.32	-0.72	0.78	distorted
Sb-Y	SbYS ₃	2.03	2.09	-0.37	0.48	NH ₄ CdCl ₃ /Sn ₂ S ₃
Sr-Zr	SrZrS ₃	1.46	1.46	-0.64	3.11	NH ₄ CdCl ₃ /Sn ₂ S ₃
Ta-Tl	TaTlS ₃	1.15	1.15	-0.30	0.24	distorted
Zn-Zr	ZrZnS ₃	1.91	1.97	-0.62	0.42	FePS ₃

Finally, the set of suggested candidates consists of eight direct band gap materials, BaZrS₃ in the GdFeO₃ structure, BaHfS₃, CaHfS₃, CaZrS₃, SrZrS₃ and SrHfS₃ in the NH₄CdCl₃/Sn₂S₃ structure, TaTlS₃ in distorted structure and LaYS₃ in CeTmS₃ structure. All but TaTlS₃ happen to be in one of the three orthorhombic structures. Furthermore, in cases where the material can be found in more than one stable phase, there is a risk that some of the other phases are metallic. Since the energy differences are small, there is a concern that during material synthesis, one will obtain (partially or fully) the metallic structure of the compound, which would be fatal for the material's PV performance. Out of our candidates, the metallic competing structures only appear in the case of Ba-Zr (BaZrS₃ and ZrBaS₃), where two metallic ZrBaS₃ structures, YScS₃ and PbPS₃ have energies within the calculational uncertainty. In the next section we proceed through synthesis of LaYS₃, one of the most promising candidates in Table 3.

4.2 Synthesis of LaYS₃

According to our results, the structure with the lowest energy of LaYS₃ is the CeTmS₃ structure. We attempt to synthesize LaYS₃ in thin film form, which is more relevant for actual devices than the powder form. The La/Y atomic ratio is checked after sputter deposition of the LaY precursor films. Averaging EDX measurements from three random spots yields La/Y = 1.01 ± 0.01 as desired. After sulfurization, the (La+Y)/S ratio is 0.70 according to EDX and 0.66 according to XPS, which is consistent with the ratio of 0.67 expected for a stoichiometric LaYS₃ film. Residual oxygen is quantified by EDX and XPS as 7% and 9% of the total atomic concentration, re-

spectively. The thickness of the sulfurized film is 550 nm according to ellipsometry.

As discussed in the Experimental Details, theoretical XRD patterns based on the relaxed structure of each LaYS₃/YLaS₃ prototype are employed to index experimental peaks. The only existing experimental XRD reference among those compounds is a powder sample studied in the 1970s, which was identified as LaYS₃ in the CeTmS₃ prototype (ICSD 641874)⁸². The main peaks of this previous experimental pattern are very close (within 0.2°) to those of our theoretical XRD pattern for the same prototype (Figure S3, supplementary material). The measured XRD pattern of our sulfurized film is shown in Figure 7, together with the simulated pattern of LaYS₃ (CeTmS₃ structure). Among the 35 peaks identified in the XRD pattern, 32 are within a distance of 0.2°2θ from a major peak expected by theory, and the remaining 3 are within 0.3°2θ. By visualizing the XRD pattern over a broader 2θ range, a few other low-intensity peaks can be identified (Figure S3, supplementary material). They can all be indexed to the CeTmS₃ structure. It must be noted that some major peaks expected for a randomly oriented LaYS₃ powder with the CeTmS₃ structure are absent in the measured XRD pattern of our thin film. This can tentatively be explained by texturing of the film, i.e., the tendency of some crystal planes of LaYS₃ to grow parallel to the substrate plane.

Further confirmation that the LaYS₃ structure with the CeTmS₃ prototype is the main constituent of the film is given by analysis of its absorption coefficient α , shown in Figure 8. All the lowest-energy structures of LaYS₃ and YLaS₃ are predicted to have direct band gaps (Fig. S1, supplementary material). For a direct band gap material, linear extrapolation of $(\alpha hv n)^2$ against $h\nu$ is expected to yield the band gap⁸¹. In the above expressions $h\nu$ is the photon energy and n is the refractive index, which is simply derived from α through the Kramers-Kronig relationship. This procedure yields a band gap of 2.0 eV, as shown in the inset of Figure 8. The value is within the calculation error for both the CeTmS₃ structure of LaYS₃ (calculated band gap: 1.79 eV) and the NH₄CdCl₃/Sn₂S₃ structure of both LaYS₃ and YLaS₃ (calculated band gap: 1.87 eV). However, the two NH₄CdCl₃/Sn₂S₃ structures can be excluded due to their incompatibility with the measured XRD pattern (Figure S3, supplementary material). The band gaps of all other possible structures of LaYS₃ and YLaS₃ are incompatible with the experimental band gap.

To give a preliminary assessment on whether LaYS₃ can be potentially used as a photoabsorber, a steady-state PL spectrum is measured (Figure 9). Considering the value of the absorption coefficient of LaYS₃ at the PL excitation wavelength (Figure 8), a PL analysis depth of 250 nm is derived. Therefore, the PL measurement probes recombination properties in the bulk of the film. In an ideal semiconductor the PL peak position should be centered on the band gap, as elec-

Fig. 7 Top plot (red): experimental XRD pattern of the synthesized film. Bottom plot (blue): theoretical XRD pattern of LaYS_3 in the CeTmS_3 prototype, assuming random orientation and $0.2^\circ 2\theta$ broadening. Vertical lines (black): theoretical XRD peak positions and relative intensities of LaYS_3 in the CeTmS_3 prototype assuming random orientation. Due to the very large number of low-intensity peaks predicted for this structure, theoretical peaks having intensity less than 1/25 the most intense peak at 24.3° are not visualized in the figure and are disregarded in the analysis. The * and x symbols indicate experimental peaks located within $0.2^\circ 2\theta$ and $0.3^\circ 2\theta$ of a theoretical peak, respectively.

Fig. 8 Main plot: absorption coefficient of LaYS_3 according to spectroscopic ellipsometry. Inset: Determination of the value of the direct band gap from absorption coefficient and refractive index⁸¹, both extracted by spectroscopic ellipsometry.

Fig. 9 Photoluminescence spectra of LaYS_3 (red) and $\text{Cu}_2\text{ZnSnS}_4$ (blue) thin films. The scale is the same for both spectra. The solid (dashed) vertical lines indicate the PL peak position and band gap of LaYS_3 ($\text{Cu}_2\text{ZnSnS}_4$).

trons from the conduction band minimum recombine radiatively with holes from the valence band maximum. However, in polycrystalline semiconductors used in thin-film solar cells the PL peak is often observed at a lower energy than the band gap energy (Stokes shift). An example is $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), where the PL peak is systematically shifted by 100–200 meV with respect to the band gap energy, even in solar cells with efficiency above 10%⁸³. This can be due to trap- and tail states caused by impurities or native defects. To make a meaningful comparison, Figure 9 shows the PL spectrum of the LaYS_3 film together with the PL spectrum of a fully sulfurized $\text{Cu}_2\text{ZnSnS}_4$ film that was later processed into a solar cell with 5.2% conversion efficiency⁸⁴. The PL acquisition parameters were the same for both materials. In the $\text{Cu}_2\text{ZnSnS}_4$ film, the PL peak is located 200 meV below its band gap⁸⁴. On the other hand, the PL peak in our LaYS_3 film is centered at 1.9 eV, which is 100 meV lower than the band gap extracted from ellipsometry (Figure 8). We also note that the related binary compound La_2S_3 has a much larger offset of 600 meV between its band gap (2.7 eV) and its PL peak position (2.1 eV)⁸⁵. The above discussion indicates that LaYS_3 could be a successful high-band gap photoabsorber for tandem water splitting devices.

5 Conclusions

In the current study we have explored different polymorphs of sulfur perovskites with ABS_3 stoichiometry as potential light absorbers for solar energy conversion - in particular as the large band gap material for a tandem photoelectrode. As compared to oxide perovskites explored in previous works, sulfur perovskites tend to have smaller band gaps pertinent for visible light absorption. Our results are based on a systematic screening procedure using a chain of simple descriptors. The procedure takes into account stability (through the formation energy), light absorption (the band gap), mobility (effective masses), and defect sensitivity (defects states in the gap). The outcome is a list of promising candidate materials as PV and PEC light absorbers. Among them, LaYS_3 is synthesized as a thin film for the first time, showing excellent agreement with the calculated structure and direct band gap. Additionally, a preliminary study by photoluminescence hints towards favorable defect properties in LaYS_3 thin films, which is also consistent with the computational results for defect sensitivity in that material. The screening procedure is certainly not complete. Several properties are not fully accounted for by the descriptors. One example is the mobility, where the electron or hole effective mass only describe one aspect of the mobility. A deeper understanding and a more accurate calculation would require consideration of scattering from phonons, electron, and impurities beyond what can be achieved in a screening study. However, the excellent agreement with experimen-

tal data from our synthesized LaYS_3 compound and from the already known compounds lends credibility to the approach. Further experimental studies will be undertaken to capitalize on these findings and investigate their full potential including schemes for protection and interfacing.

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