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High-throughput screening of stable sulfide semiconductors for solar cell conversion

Jinjin Yang,a Zhongxiang Sun,a Dao-Xin Yaoa and Man-Rong Lia,b,c

The application of chemically stable oxide perovskite solar cells confronts substantial obstacles, such as large band gap and high internal voltage loss, despite the rapid technical development of device fabrication. Alternatively, the design and screening of innovative sulfide materials, which is less explored compared with the oxide counterparts, becomes a burgeoning research area. Here, screening of new solar cell absorber materials in RE3BB’S2 (RE = La, Y; B/B’ = Ti - Cu in the 3d row) is performed via high-throughput calculation. The filtration criteria are thermodynamic/kinetic stability, band gap, carrier effective mass, defect tolerance and optical absorption behavior, which are key parameters to determine whether the material is suitable for semiconducting solar cell absorber or not. Based on the screening criteria, we narrow down two appealing candidates, RE3CoCrS2 (RE = La, Y), with potential application in photoelectrochemical devices. These findings established solid theoretical foundation for the development and implementation of sulfide solar cells in practical applications.

1. Introduction

Efficient harvest of solar energy is urgent to solve the impending energy and environmental crisis. The prerequisite is the screening of materials that have high-performance solar energy conversion.1-3 Perovskite materials have demonstrated advantages as light absorber in solar cell, owing to the outstanding stability in highly oxidizing circumstances, widely-tunable band gap (Eg), high optical absorption rate, long carrier diffusion length, and high carrier mobility. However, two insurmountable problems exist in perovskite oxides: (1) the large Eg for sunlight absorbers due to the low energy of O 2p orbital contributing to the valence band maximum (VBM), and (2) the anodic VBM with respect to the water redox level resulting in large internal voltage loss in devices.4 Fortunately, both aforementioned issues can be resolved by substituting oxygen with sulfur, which can reduce Eg and make the VBM more cathodic to closer to the water redox level. In addition, sulfide perovskites are more environmentally friendly option compared to lead halide analogs, and reduce instability and toxicity commonly associated with halide perovskites. Semiconducting perovskite sulfides have been theoretically predicted and experimentally synthesized, showcasing superior electrical and optical qualities that make them ideal for low-cost tandem solar cells. A number of sulfides, such as A2ZrS3 (A = Ca, Sr, Ba), SrTiS, CuTaS, CaSnS3 and SrSnS2, have shown intense interest in the context of photovoltaic (PV) solar cells.5 Recently, Ruddlesden-Popper (R-P) sulfides A3BB’S2 (also known as A2BB’S3 if B and B’ are the same elements) have theoretically and experimentally received great attention as solar conversion materials.6 Such as A3Zr2S5 (A= Ca, Ba) and Ca3Sn2S5, which demonstrate stable ferroelectricity at room temperature with small Es values (< 2.2 eV), are well suited for significant visible-light absorption. The R-P type Ca3Zr2S5 material with low Es suitable for visible light absorption is anticipated to exhibit stable ferroelectric polarization as a promising ferroelectric photovoltaic material along with high energy conversion efficiency (PCE), where effectively separating photo-generated electron-hole pairs.7 Moreover, the charge recombination rate in Ca3Sn2S5 can be experimentally tuned to simulate its superior infrared detection performance, showing small carrier effective mass (0.04 m0), ultrahigh room-temperature carrier mobility (6.7×104 cm2 V-1 s-1), Fermi velocity (3×108 m s-1), and optical absorption coefficient (105 cm-1).8,9 Also, the strained ferroelectric BaZr2S5 thin film possesses a suitable Es of 1.6 eV for PV application, absorbing sunlight in a wide range of visible-light spectrum. Thus, A3BB’S2 sulfides represent novel and cost-effective material class for solar cells, offering greater stability compared to oxide counterparts.10

In rare earth (RE) ions, the abundant 4f/5d orbit electrons could generate different intermediate energy states to induce unique photo-physical behavior, rendering excellent potential in PV based devices. Accordingly, the electronic properties of solar cell materials can be modulated by proper RE ions.11 In particular, the incorporation of RE ions has a major effect on the charge carrier mobility, band structure, and absorption/fluorescence properties, resulting in modified charge transport dynamics as exemplified in perovskite-related solar cells.12 More significantly, the up-conversion...
takes place in materials containing trivalent RE ions by the process of ground- and excited-state absorption of multi-photons from actual energy levels. In general, when utilizing trivalent RE doped materials as up-converting layers, a single junction connected to an ideal up-conversion layer can achieve a maximum PCE of approximately 47.6% for non-concentrated sunlight and 63.2% for concentrated sunlight. For examples, the Er/Yb doped M$_2$O$_5$S (M = Gd, Y, La) are used as a reference to show the enhancement of up-conversion emission efficiency under 1550 nm excitation, and Tb$_3$-Yb$_3$ co-doped silicate glass can improve the PCE of monocrystalline silicon solar cells by 8.6%. Along this line, RE$_3$BBS$_2$I$_7$ is expected to be excellent light absorbers to enhance the PCE of solar cells, considering its chemical and structural similarity with the reported solar energy conversion materials. Ruled by charge balance, the valence state of B-B’ in RE$_3$BBS$_2$I$_7$ can be either monovalent-tetravalent (I-IV) or bivalent-trivalent (II-III) combination. So far, the most prevalent cases adopt the monoivalent-tetravalent (I-IV) B = Cu, Ag; B’ = Si, Ge, Sn) combinations in RE$_3$B$_2$S$_2$I$_7$ and mostly crystallize in the La$_3$SiCuS$_2$-type P6$_3$ hexagonal structure, such as Y$_3$CuGeS$_3$; and Sm$_3$CuGeS$_3$ identified as outstanding infrared nonlinear optical material. In contrast, the bivalent-trivalent (II-III) combination $RE_3^{2+}B^{3+}S_2$I$_7$ is barely studied as a research object of this work, leaving a vast chemical space to explore new candidates. The structural, magnetism and electrical transport data of La$_3$B$_3$Fe$^{3+}$S$_2$I$_7$ (B = Mn, Fe, Co, Ni) have been experimentally reported, providing experimental validation of upcoming calculations. La$_3$B$_3$Fe$^{3+}$S$_2$I$_7$ crystallize in the non-centrosymmetric hexagonal space group P6$_3$ with Z = 2, where crystal structures consist of parallel chains of face-sharing B-centred octahedra and stacking of Fe-centred tetrahedra with seven-coordinated La atoms in the intervening spaces. Based on previous magnetic and electric test, La$_3$B$_3$Fe$^{3+}$S$_2$I$_7$ (B = Mn, Fe, Co, Ni) sulfides are p-type semiconductors and have higher magnetic moment at high-temperature than at low temperatures, except for the nickel compound, because of the probable interaction between octahedral site B and tetrahedral site Fe. The performance of solar cell light absorbing materials depend not only on the process of device fabrication, but also the electrical and optical properties of the original materials. However, it is difficult and costly to measure the microscopic mechanisms of materials experimentally. There is a need for theoretical prescreening to reveal the intrinsic mechanisms and inherent properties of new potential candidates for light absorption layer in solar cell. Nowadays, data-driven and high-throughput computing (HTC) assisted approaches have facilitated significant time and cost savings. The key points are to explore the correlations of band structure, light absorption, carrier mobility and defect tolerance to guide and accelerate the discoveries of new light absorption layer materials. In this work, we present a comprehensive screening of 128 possible candidates in $RE_3^{3+}B^3B^{2+}S_2$I$_7$ (RE = La, Y; B and B’ are Ti - Cu in the 3d row of periodic table of elements) to attentively seek suitable solar cell absorption materials. We perform density functional theory (DFT) based HTC, considering formability of 672 different $RE_3^{3+}B^3B^{2+}S_2$I$_7$ candidates in seven potential polymorphs along three magnetic configurations. The screening workflow is displayed in Fig. 1, including data-mining and HTC. Note that some compounds in $RE_3^{3+}B^3B^{2+}S_2$I$_7$ system have been experimentally reported, which boosts the examination and validation of suggested approaches through initial computation test. Our screening unveils a short list of potential thermodynamically and kinetically stable candidates with suitable $E_g$ for solar cell absorbers, giving two final winners. RE$_2$CoCrS$_2$ (RE = La, Y) with appropriate $E_g$ of 1.02 (La based) and 1.00 (Y based) eV are predicted small carrier effective masses of electrons and holes at the VBM and conduction band minimum(CBM) causing high mobility and low recombination rate of photo-generated charge carriers, which are necessary for efficient solar cell conversion. The proposed two candidates are identified to be tolerant to vacancy, since the introduction of defect does not give rise to deep gap recombination sites. A strong light absorption coefficient in the visible region is proposed as evidenced by their calculated optical absorption.

2. Methods

In the frame of DFT, Vienna ab initio simulation package (VASP) adopted projector-augmented wave (PAW) in structural relaxation and electronic structure investigation, and Generalized gradient approximation (GGA) implemented in the Perdew-Burke-Ernzerhof (PBE) method was employed. The convergence of cut-off energy, k-points and Gaussian broadening were tested to make sure the accuracy of conclusion. The plane wave cut-off energy was 700 eV. The k-point mesh was 9 × 9 × 9 for monoclinic (C2/m and P2_1/c) and tetragonal (P4_2/mnm and I4/mmm) symmetry, 7 × 7 × 9 for hexagonal (P6_3) symmetry, and 5 × 3 × 5 for orthorhombic Pbam and Cccm symmetry, ensuring that the geometric optimization and static electronic calculations are minimized in the constraint of periodic boundary condition. The energy and force convergence threshold were set as 1.0 × 10$^{-6}$ eV and 1.0 × 10$^{-3}$ eV/Å. The exchange correlation energy was treated by GGA-PBE. To lessen the inaccuracy brought by strong on-site Coulomb interactions, electron-electron Coulomb repulsion interactions (U) for 3d transition metal elements were considered in the rotationally invariant form (GGA+U), which go beyond the conventional local-density approximation. Standard Hubbard U corrections were adopted to Ti (4.0 eV), V (3.25 eV), Cr (3.7 eV), Mn (3.9 eV), Fe (5.3 eV), Co (3.32 eV), Ni (6.2 eV) and Cu (7.0 eV) as discussed in details in literatures and existing Materials Project (MP) database. Given standard set of Hubbard U corrections would be suitably transferrable to magnetic characteristics. Heyd-Scuseria-Ernzerhof (HSE06) was employed to systematically improve the calculation accuracy on electronic structure. The phonon dispersion was calculated using Phonopy package with the finite displacement method along the main symmetry directions in three-dimensional Brillouin zone.
3. Results and discussion

3.1 Data-mining and initial computing models

Distribution of preliminarily screened by energy above convex hull ($E_{\text{null}}$) of formation energy and PBE $E_{\Gamma}$ for 203 known $A_2BB'_5S_7$ and $A_2BB'_5S'_4$ chemical formula found in Inorganic Crystal Structure Database (ICSD), MP database and reported literature as our initial database is plotted in Fig. 2a. Obviously, compounds with higher $E_{\text{null}}$ values are more unstable and likely anticipated to be metallic. To further motivate the choice of structures and chemical combinations considered in the calculations based on the known $A_2BB'_5S_7$ and $A_2BB'_5S'_4$ from data-mining,\textsuperscript{22,30-32} seven possible polymorphs as initial structural models for $A_2BB'_5S_7$ are shown in Fig. 2b. The corresponding lattice parameters, perovskite-related tolerance factors, and basic properties of representative compounds in each polymorph are summarized in Table S1. As shown in Fig. 2b- i : (1) The monoclinic $C2/m$ layered structure, as found in $Y_3YSi_2$ ($A = B = B'$ $= Y$) where the face-sharing pyramidal $BS_7$ extends along the $b$-axis forming a linear chain.\textsuperscript{31} (2) The monoclinic $P2_1/c$ exemplified by $Ba_2SnS_7$ (Fig. 2b-ii.).\textsuperscript{34} The corner-sharing $BS_5$ tetrahedra run along the $b$-axis. (3) Orthorhombic $Pbam$ as shown in $Eu_2SnS_7$ (Fig. 2b-iii.),\textsuperscript{35} where the corner-shared $BS_5$ form one-dimensional chain along the $c$-axis. (4) The hexagonal $P6_3$ as reported in $La_2SiCuS_7$ (see Fig. 2b-iv) consists of six-coordinated $B$ cations aligned along the $c$-axis, forming a chain structure by face-sharing $BS_5$ octahedra.\textsuperscript{21} Hexagonal $P6_3$ is the most frequently identified structure in contrast to the rest six rare ones. (5-7) Three perovskite-type structures related to $R-P$ phase are shown in Fig. 2b- v, vi, vii, where the crystal structures are exemplified by three distinct polymorphs of $Ba_2ZrSn_2S_7$\textsuperscript{8,36,37} namely orthorhombic $Cccm$ (Fig. 2b- v), tetragonal $P4_2/mmm$ (Fig. 2b- vi), and $I4/mmm$ (Fig. 2b-vii), respectively. These series consist of perovskite structure blocks separated by extra rock-salt layers along [001] direction. The orthorhombic $Cccm$ is a distorted variant related to the perovskite structure\textsuperscript{38} while the tetragonal $I4/mmm$ with an ideal body-centered structure can be regarded as double layers of $BS_5$ octahedra along the $c$-axis separated by rock-salt layer. In the slightly distorted tetragonal $P4_2/mmm$ structure, the perovskite slabs and rock-salt layers stagger along [001] direction. Within the perovskite layers, the octahedra are corner-shared along [1 1 0] and [1 -1 0] and tilted along one of the in-plane directions. Here the above seven structural prototypes are the most possible polymorphs for $A_2BB'_5S_7$, and thus are adopted as the initial structural models in subsequent HTC.

Chemical screening of all possible polymorphs of ($A^{3+}$)$_2$(B$^{4+}$)($B'$$^{4+}$)S$^{2-}$, chalcogenides, where $A$, $B$, and $B'$ can be 23, 48, and 30 conceivable elements under charge balance, respectively, and the combinations of theoretical 33,120 (23 × 48 × 30) candidates are shown in Fig. 2c. According to charge neutrality, the sum of cationic oxidation states should be +14 corresponding to the value of -14.
from the sulfur anion. The targeted 128 \((RE^{1+})(B^{2+})(B^{3+})(S^{2-})\) compounds \((RE = La, Y; B/B' = Ti - Cu in the 3d row in a periodic table) over the chemical space are restricted by charge balance and geometrical confinement, seeing Fig. 1 (Data-mining). So far, any significant portion of virtual chemical combinations has not been studied yet. Thus, it is urgent to implement further validation for the synthetizable and practical chemical combinations following the workflow in Figs. 1 and S1 (Electronic Supplementary Information).

Contribution of spin-spin interaction (magnetic structure) in 3d transition metals has proven to be critical to calculate the minimum workflow in Figs. 1 and S1 (Electronic Supplementary Information).

Determining magnetic configuration is a highly nontrivial task, and one can only locate the magnetic ground state within the space of a limited number of initial configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations. In this work, we restrict the collinear magnetic structures to feature HTC, since there are numerous possible configurations.
breaking displacement during structural optimization, then in some cases the crystal structure undergoes dramatic changes.

3.2 HTC
For more predictive and affordable screening results, the chemically-screened dynamics and thermodynamically stable compounds are initially calculated in all possible polymorphs over the whole chemical space under charge balance. Only the stable combinations with targeted suitable $E_g$ are remained, and the mobility of electron ($e$) and hole ($h$) is also taken into account by calculating the carrier effective mass ($m_{el}^*$, $m_{eh}^*$). Finally, the defect tolerance of survival compounds is studied to distinguish potential defect state that does not contribute to deep-gap recombination sites. The distribution of the absorption spectrum in the visible region indicates the absorption intensity of potential $RE_3BB'S_7$ ($RE = La, Y$; $B/B' = Ti - Cu$ in the 3d row) solar cells absorber candidates to achieve the best PCE.

3.2.1 Stability

3.2.1.1 Formability filtration
It is instructive to analyze the energy distance of the most stable polymorph to the energy convex hulls $E_{\text{hull}}$ constituted by the stable compounds ($E_{\text{hull}} = 0 \text{ meV/atom}$) approved in MP. Namely, the thermodynamic stability is evaluated by considering all reactions in which the compound decomposes into stable components. Only the compounds with $E_{\text{hull}}$ lower than thresholds are supposed to be synthesizable. In order to ensure the reported $La_3BFe'^{II}S_7$ ($B = Mn$, Fe, Co, Ni) compounds locate on or even below the convex hulls, 97.656 meV/atom for $La_3FeMnS_7$, the maximum value of known series in this category, is set as the threshold for screening potential thermodynamically stable or metastable compounds. It should be pointed out that the MP database does not contain all possible decomposition products for some compounds, so that the calculated energy above $E_{\text{hull}}$ serves only as a lower bound and actual thermodynamic stability could be lower than predicted. Detailed calculation results of the 128 $RE_3BB'S_7$ in magnetic polymorphs ground state are listed in Tables S3 and S4, where the cases including on/below $E_{\text{hull}}$ are displayed in Fig. S1 (HTC 1). As shown in Fig. 3a, b, the instability considerably increases with lengthened energy distance to the convex hull. Employing the bounds on energy above hull narrows down the search space for synthesizable 94 (128 minus 34) candidates, including 56 La- and 38 Y-based compounds on or below the threshold, indicating they are thermodynamically stable at 0 K. The $E_{\text{hull}}$ benchmark rules out 34 (including 8 La- and 26 Y-based compounds) of the 128 combinations, since they dock above the convex hull and are thermodynamically not synthesizable. Preliminary screening on the electronic structure show that only 22 (11 La- and 11 Y-based) out of the 94 combinations in the perfect ground state.

![Fig. 3](image-url)

Fig. 3 The stability of the considered combinations. Distribution of the distances to the convex hull of (a) $La_3BB'S_7$ and (b) $Y_3BB'S_7$. (c) Phonon dispersion and variations of representative $La_3TiCuS_7$. (d) The total potential energy with respect to simulation time during AIMD simulations of $La_3TiCuS_7$. 

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3.2.1.2 Kinetic and thermodynamic stability

In condensed-matter physics, phonons are used to describe the simple harmonic vibrations of lattices. Thereby, phonon spectrum is a good characteristic method to evaluate the kinetic stability evaluated from finite-difference phonon calculations. When the phonon spectrum is all above 0 cm$^{-1}$, it means the material has no imaginary frequency and is relatively stable. We subsequently investigate the kinetic stability of these 22 combinations with non-zero $E_g$. The phonon spectra of La$_3$TiCuS$_7$ without virtual frequency is exemplified in Fig. 3c. Partial phonon dispersion of selected stable partial sulfides without imaginary frequency are shown in Fig. S3. Among the 22 calculated combinations, 18 (8 La-based and 10 Y-based) compounds are found to have no imaginary phonon modes, being dynamical lattice stable at $T = 0$ K. La$_3$(MnCoS)$_5$, La$_5$V$_2$S$_7$, La$_6$(Ni$_3$S)$_7$, and Y$_3$V$_2$S$_7$ are discarded because of the strong virtual frequency.

Additionally, $E_{\text{ull}}$ and phonon dispersions calculations should be noted that these are zero-temperature calculations, and the stability could be altered by finite temperature contributions to the free energy. In other words, the entropy factors in free energy may cause some of the compounds that are anticipated to be unstable at 0 K to turn out to be stable at ambient temperature. The consideration of finite temperature stability can be undertaken as further efforts. Based on ab initio molecular dynamics (AIMD) examination, the energy and temperature in the molecular dynamics simulation process are extracted to prove thermodynamic stability. As the finite energy fluctuations, it is supposed to be relatively stable at 300 K, when the structure is changed without destroyed. For example, the AIMD simulation results and variations of the total potential energy for La$_3$TiCuS$_7$ is exemplified in Fig. 3d, which exhibits small energy fluctuation and hardly distorted crystal structure. The calculated AIMD results of other partially squeezed stable compounds are shown in Fig. S4. Overall, the 18 (8 La- and 10 Y-based compounds) combinations with finite energy fluctuations and robust structure at 300 K are listed in Table 1 and Fig. S1 (HTC 3).

As the finite energy fluctuations, 18 compounds with desirable stability and non-zero $E_g$ are now passed to the next step to examine the electronic structure with further filtration.

3.2.2 Electronic structure

Governed by the well-known Shockley-Queisser limit, the limit efficiency for a single $p-n$ junction based solar-cell semiconductor is related to the $E_g$ value at standard illumination conditions. When $E_g$ is too large, it is unable to absorb sunlight in the visible light band. If the $E_g$ is too small, the open circuit voltage of the cell will decrease and result in in faded efficiency. As solar cell absorber materials, the $E_g$ value is required to be within a specific range of 1.0-1.6 eV. Within this $E_g$ range, the materials can equilibrate the number and the energy obtained by absorbed photons. The $E_g$ values of current potential candidates. It is well known that the methods have been most commonly used for successfully estimating $E_g$ of semiconducting materials up to this point are GGA+U, HSE06, and GW approximation (GWA). However, the HSE06 or GWA cannot handle the computationally intensive computations of defect characteristics, which call for the utilization of massive supercells. As a consequence, the electrical, and defect characteristics are computed in this work using GGA+U.

In order to screen the target $E_g$, we examine the electronic characteristics of the 18 (8 La- and 10 Y-based) stable cases to gauge the band structures and electronic density of states (DOSs). 9 (5 La- and 4 Y-based, seeing Fig. 51 (HTC 4)) promising compounds with $E_g$ of 1.0-1.8 eV among the 18 stable compounds are singled out. As listed in Table 1, the 9 candidates in bold are reserved for the next screening process, and the rest are removed due to inappropriate $E_g$.

In most cases the gaps are indirect, but for some systems the gaps are direct, seeing Fig. S5. The latter ones are particularly relevant for thin photo-absorbers because of the higher absorbance. Specifically, for these 9 compounds, we further calculate the $E_g$ using the HSE06 functional. In the GGA+U method, the $E_g$ of La$_3$CoCrS$_7$ and Y$_3$CoCrS$_7$ are 1.02 and 1.00 eV, closing to the 1.75 and 1.69 eV obtained by the HSE06 method, respectively, shown in Fig. 5a, b. La$_3$CoCrS$_7$, see Figs. 4a, b and S6a, b. In addition, for Y$_3$TiCuS$_7$, the $E_g$ values are 1.56 and 1.93 eV from GGA+U and HSE06 methods, respectively, shown in Fig. 5a, b. GGA+U calculations show good agreement with those from HSE06 computations, indicating that GGA+U can offer trustworthy insights into this family. The three compounds mentioned above meet the screening criteria of optimal $E_g$. Next, the distributions of electron structure are taken into account. A comprehensive and rational explanation has been provided for the analysis of the valence electron state density in 3d transition metal elements. This elucidation serves as a sound basis for the design of new solar cells.

![Fig. 4 The electronic structures of La$_3$CoCrS$_7$. Total DOSs for pristine La$_3$CoCrS$_7$ from (a) GGA+U and (b) HSE06 methods. Total DOSs for La$_3$CoCrS$_7$ with S vacancy concentration of (c) 7.14% and (d) 1.78% from GGA+U method. No additional bands are produced. The zero of the energy is set at the Fermi level.](image-url)
for understanding the electronic structure and behavior of these elements within the context of the mentioned compound, for which the DOSs in La₇CoCrS₇ are plotted in Fig. 4a, b from GGA+U and HSE06 methods. It shows that electron distributions in the vicinity of the Fermi level are Co 3d/Co 3d and S 3p state. The Co 3d/Co 3d state mainly are more localized in lower energy (-4 ~ -1 eV), which results in the Co 3d/Co 3d - S 3p reduced hybridization at a higher energy region (-2 ~ -0.5 eV). It suggests La₇CoCrS₇ has innate iononic and unique covalent bonds, owing to the high covalency of sulphur atoms. Taking the experimentally synthesized La₇FeMnS₇ as a validated example, the band structures and DOSs are obtained with $E_g$ 1.17 and 1.73 eV from GGA+U and HSE06 methods as shown in Fig. 5. It exhibits semiconducting behavior with direct $E_g$ about 1.17 eV, i.e., the CBM and VBM positioned at K point. The presented semiconductor-like properties are in good agreement with the experimental resistivity-temperature curves of La₇FeMnS₇ as an n-type semiconductor. The AFM configuration is the magnetic ground state by comparing the energy of the optimized unit lattice with different magnetic configurations, in line with experimental linear chain antiferromagnetism. In brief, 9 (5 La- and 4 Y-based) hopeful compounds, as shown in Fig. S1 (HTC 4), meet the screening criteria and are passed to the next step in the screening process, namely, the exploration of carrier transport.

### 3.2.3 Carrier effective masses

Carrier separation creates current before recombination, resulting in energy loss in devices. Higher mobility carriers have lower recombination probability and can be used for target screening procedure. Although the carrier mobility ($\mu$) is difficult to calculate, the carrier effective mass is related to carrier mobility ($\propto 1/\mu$). Obviously, the smaller the carrier effective mass, the faster the carrier mobility. Thus, candidates with higher carrier effective mass are ruled out during the screening process. In the current study, we are particularly interested in materials with low effective electron and hole masses, where $m^*_e$ and $m^*_h$ are less than one $m_0$ as listed in Table 1. Carrier effective mass is obtained by fitting parabola to the VBM and CBM according to band structures calculated along high symmetry points. For instance, by fitting the dispersion relationship between VBM and CBM in the band structures diagrams of $Y_7TiCuS_7$ for $E_g$ screening criteria and are passed to the next step in the screening process. The carrier masses of La₇TiCuS₇ are all larger than 1.0 $m_0$ in which the $m^*_e$ is 1.33 $m_0$ and 1.02 $m_0$ for $m^*_h$, so La₇TiCuS₇ is removed from the filtering path. From the obtained electronic band structures of experimentally synthesized La₇FeMnS₇, we find both conduction band edges exhibit tiny amounts of dispersive components, suggesting heavy carrier effective masses. As for La₇FeMnS₇, the electron and hole effective mass are 0.7 and 2.5 $m_0$, due to the half-full electronic configuration of the high-spin d⁷⁻Mn³⁺ in octahedral coordination. Since the d-d transition of this configuration is forbidden in quantum mechanics, La₇FeMnS₇ is ruled out. Finally, 6 (9 minus 3) regretful compounds (La₇TiCuS₇, La₇MnCrS₇, La₇VMnS₇, La₇FeMnS₇, Y₇FeMnS₇ and Y₇VMnS₇) are expelled from our final list because of large carrier effective masses. Seeing Fig. S1 (HTC 5), only La₇CoCrS₇, Y₇CoCrS₇ and Y₇TiCuS₇ satisfy the following condition with $m^*_e$ less than one $m_0$ and are considered as potentially interesting candidates for PV applications to focus of further analysis.

### 3.2.4 Defects tolerance

![Table 1](image)

<table>
<thead>
<tr>
<th>Combination</th>
<th>$E_g$ (eV)</th>
<th>$m^*_e$</th>
<th>$m^*_h$</th>
<th>Combination</th>
<th>$E_g$ (eV)</th>
<th>$m^*_e$</th>
<th>$m^*_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₇TiCuS₇</td>
<td>1.44</td>
<td>0.70</td>
<td>0.59</td>
<td>Y₇CoCrS₇</td>
<td>1.00</td>
<td>0.49</td>
<td>0.31</td>
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<tr>
<td>La₇CoCrS₇</td>
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<td>0.62</td>
<td>0.34</td>
<td>Y₇CrMnS₇</td>
<td>1.07</td>
<td>1.08</td>
<td>0.33</td>
</tr>
<tr>
<td>La₇MnCrS₇</td>
<td>1.47</td>
<td>0.70</td>
<td>0.34</td>
<td>Y₇VMnS₇</td>
<td>1.17</td>
<td>1.17</td>
<td>0.31</td>
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<tr>
<td>La₇FeMnS₇</td>
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<td>0.70</td>
<td>0.34</td>
<td>Y₇CrMnS₇</td>
<td>1.07</td>
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<tr>
<td>La₇FeMnS₇</td>
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<td>0.70</td>
<td>0.34</td>
<td>Y₇CrMnS₇</td>
<td>1.07</td>
<td>1.07</td>
<td>0.33</td>
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</table>

Performance of solar cells is highly dependent on the defect characteristics of absorber. Defects play an important role in semiconductor technologies, such as light-emitting diodes, transistors, and photodetectors, since defects influence the concentration, mobility and lifetime of electric charge carriers.
Finding growth circumstances that favor the desired beneficial defect rather than the undesirable deep level defects is crucial for performance optimization. Actually, defects introduce additional states and restrain the optoelectronic performance. These additional gap states may act as recombination centers and become "traps" for capturing photo-generated carriers (electrons and holes), thus shortening the lifetime of carriers and reducing the charge separation efficiency. Different positions of the additional states have different effects on PV materials. Defect states located deep within the $E_g$ are referred to as defect sensitive, whereas the defect states within the bands or near the band edges are known as defect tolerant. The latter formation of point defects is favorable for PV performance. For instance, the decline in PV energy conversion efficiency with increasing Ga content in ternary chalcopyrite is screening out as potential materials for solar energy conversion applications. 

3.2.5 Optical absorption coefficient

Compared with the recently developed lead halide perovskites, sulfide devices have the potential to utilize even thinner absorbers in order to achieve high PCE. 11, 63 Employing absorbers with exceedingly high optical absorption offers significant advantages to solar cell performance, since photo-generated electrons and holes travel short distance before being collected. By doing so, the linked open circuit voltages will increase and significantly reduce non-radiative recombination. To determine optical absorption coefficient in visible range of $A_7CoCrS_7$ ($A = La, Y$), we calculate optical absorption coefficient as a function of wavelength, following methodology described in theoretical methods section. The calculated spectra of $A_7CoCrS_7$ ($A = La, Y$) with the PBE method are shown in Fig. 6a, b. The spectra exhibit roughly similar behavior represented by high-intensity absorption features appearing in the visible range with broad edges extending to 540 and 580 nm, which the theoretical optical absorption coefficient can reach $10^5$ cm$^{-1}$ in the visible-light region. This value is much higher than perovskite oxides ($10^4$-10$^5$ cm$^{-1}$), and even widely-used silicon ($10^4$ cm$^{-1}$). The [001] direction exhibits a notably higher optical density between 430 and 500 nm compared with the recent development lead halide perovskites.
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**Notes and references**


**Author Contributions**

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