Ruddlesden–Popper perovskite sulfides $A_{3}B_{2}S_{7}$: A new family of ferroelectric photovoltaic materials for the visible spectrum


As Published: http://dx.doi.org/10.1016/j.nanoen.2016.02.036

Publisher: Elsevier

Persistent URL: http://hdl.handle.net/1721.1/105243

Version: Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

Terms of use: Creative Commons Attribution-NonCommercial-NoDerivs License
Ruddlesden–Popper perovskite sulfides $A_3B_2S_7$: A new family of ferroelectric photovoltaic materials for the visible spectrum

Hua Wang $^{a}$, Gaoyang Gou $^{a,*,}$, Ju Li $^{a,b,c,**}$

$^a$ Frontier Institute of Science and Technology, and State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China
$^b$ Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States
$^c$ Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Perovskite ferroelectric materials exhibit the novel ferroelectric photovoltaic effect, where photon-excited electron–hole pairs can be separated by ferroelectric polarization. Especially, semiconducting ferroelectric materials with small band gaps ($E_g$) have been extensively studied for applications in solar energy conversion. Traditional route for creating semiconducting ferroelectrics requires cation doping, where $E_g$ of the insulating perovskite ferroelectric oxides are reduced via substitution of certain cations. But cation doping tends to reduce the carrier mobility due to the scattering, and usually lead to poor photovoltaic efficiency. In the present work, based on first-principles calculations, we propose and demonstrate a new strategy for designing stoichiometric semiconducting perovskite ferroelectric materials. Specifically, we choose the parent non-polar semiconducting perovskite sulfides $AB_2S_7$ with $Pnma$ symmetry, and turn them into ferroelectric Ruddlesden–Popper $A_3B_2S_7$ perovskites with spontaneous polarizations. Our predicted Ruddlesden–Popper $Ca_2Zr_2S_7$ and other derived compounds exhibit the room-temperature stable ferroelectricity, small band gaps ($E_g < 2.2\, eV$) suitable for the absorption of visible light, and large visible-light absorption exceeding that of Si.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Due to the unique ferroelectric–photovoltaic (FE-PV) effect, ferroelectric materials have been extensively investigated for photovoltaic applications. Unlike the traditional semiconductor PV devices, which rely on p–n junctions to generate photocurrent, ferroelectric materials have spontaneous polarization, built-in depolarization field, and unconventional mechanisms for the separation of photo-excited electron–hole pairs [1,2]. As a result, heterogeneous p–n junctions are not required in FE–PV devices. Various ferroelectric materials, including LiNbO$_3$ single crystal [3] and BiFeO$_3$ thin films [4–9] can produce PV responses along their polarization directions. Moreover, ferroelectric materials exhibit the electric switchable PV responses [6,10] and their output photovoltages can greatly exceed $E_g$ of the system [11]. These unique properties allow FE–PV devices to potentially have energy conversion efficiency beyond the Shockley–Queisser limit [12].

However, most ferroelectric materials known to date are perovskite oxides with large $E_g$ above 3.3 eV. The poor absorption of the visible-light spectrum limits these ferroelectric materials for PV applications. Thus some research efforts have focused on developing effective approaches to reduce $E_g$ of ferroelectric oxides for absorption of more visible light. Cation doping method has been widely adopted for this purpose [13–15]. After substitution of perovskite B-site cations by other transition metals, many semiconducting ferroelectric oxides have been created [10,16–19]. For example, a small $E_g$ of 1.39 eV has been reported in ferroelectric [KNbO$_3$]$_{1−x}$[BaNi$_{1/2}$Nb$_{1/2}$O$_3$]$_{x}$ solid solutions [10]. Double perovskite Bi$_2$FeCrO$_6$ has a tunable $E_g$ between 1.4 and 2.7 eV [19]. While cation substitution method can indeed reduce $E_g$ of ferroelectric oxides, it will also produce structural disorder, non-stoichiometric defects or oxygen vacancies into the systems. As a result, cation-doped ferroelectric oxides usually have low carrier mobility and poor transport properties. In fact, except for very few cases [19], most cation-doped semiconducting ferroelectric oxide solid-solutions still have low output photocurrent densities on the order of $\mu A/cm^2$ and energy conversion efficiency less than 1% [1].

In our work, instead of using cation doped solid solutions, we will design and predict a new family of stoichiometric perovskite...
compounds as semiconducting FE-PV materials. Wide band gaps of ferroelectric oxides result from the large electronegativity difference between metals and oxygen [10]. Compared with oxides, other perovskite systems, such as perovskite sulfides, containing the less electronegative sulfur atoms should have smaller $E_g$. In fact, semiconducting perovskite sulfides have been experimentally synthesized and theoretically predicted [20–23], but none of them are reported to be ferroelectric. Thanks to a new mechanism of hybrid improper ferroelectrics (HIF) recently discovered [24–26], there are opportunities to create ferroelectric perovskite sulfides. Typically, in a paraelectric $ABX_3$ perovskites with orthorhombic $Pnma$ symmetry, there exist a $a^2-c^2$ and $a^2b^2c^2$ octahedra rotation modes. These two coupled modes can induce non-zero ferroelectric polarization, known as HIF, in layered Ruddlesden–Popper $A_3B_2X_7$ perovskites. Such rotation-driven ferroelectricity has been theoretically predicted [25,27] and then experimentally realized in various Ruddlesden–Popper perovskites [28–31]. As $Pnma$ perovskite sulfides $ABS_3$ already exist in nature [32], once crystallized in Ruddlesden–Popper $Pnma$ phase, they can be novel ferroelectrics with diverse functionalities. Without introducing doped cations or non-stoichiometric defects, these stoichiometric single-phase Ruddlesden–Popper ferroelectric sulfides can be promising FE-PV materials, as they potentially have good carrier transport properties as stoichiometric compounds, and large absorption of visible light due to direct band gap [23]. Moreover, the design strategy we proposed should be transferable to other non-polar orthorhombic perovskites, such $Pnma$ halide perovskite $CsSnI_3$ [33,34].

Our paper is organized as follows: we start with experimental $Pnma$ perovskite sulfides $ABS_3$ and investigate their octahedral rotation patterns. We then extend to Ruddlesden–Popper $A_3B_2S_7$ sulfides and examine how ferroelectricity is induced by coupled octahedral rotation modes. Electronic structures and optical absorption properties of Ruddlesden–Popper $A_3B_2S_7$ will also be computed. Based on our simulations, ferroelectric sulfides with optimized $E_g$ and electric polarizations can be obtained. Finally, we will discuss the possible experimental synthesis of ferroelectric sulfides.

2. Computational methods

Our first-principles calculations are performed within density-functional theory as implemented in the QUANTUM ESPRESSO code (QE) [35] and the Vienna ab initio Simulation Package (VASP) [36,37]. For calculations within QE code, we use the nonlocal optimized norm-conserving pseudopotentials [38,39] and a 60 Ry plane-wave energy cutoff. PBEsol exchange-correlation functional [40] is used for the calculations, as it can provide improved structural results for perovskite systems [41,42]. $8 \times 8 \times 6$ and $8 \times 8 \times 4$ Monkhorst–Pack $k$-point grids [43] are used to simulate $Pnma$ $ABS_3$ and Ruddlesden–Popper $A_3B_2S_7$ perovskite sulfides respectively. Stable $ABS_3$ and $A_3B_2S_7$ phases are obtained by performing structural relaxations on soft-mode generated structures until the Hellmann–Feynman forces for each atom is less than 0.1 meV/Å and the stresses less than 0.1 kbar. Soft-mode frequencies and eigen-vectors are calculated based on density functional perturbation theory (DFPT) [44,45]. The electronic contribution to the polarization is calculated following the Berry phase formalism [46].

Using the QE predicted sulfide structures, we further use Heyd–Scuseria–Ernzerhof (HSE) hybrid density functional with screened exact exchange interaction [47,48] implemented in VASP for the electronic structure and optical absorption properties calculations. An energy cutoff of 500 eV and a plane-wave basis set within the projector augmented wave (PAW) [49] method are used for VASP calculations. Spin-orbit coupling (SOC) is excluded in HSE calculations, as the band gap changes due to SOC effect in perovskite sulfides are negligible [23]. It is noted that quasi-particle GW method [50,51] can predict the band gap of a system with better accuracy, but the computational cost for well-converged GW calculations of Ruddlesden–Popper $A_3B_2S_7$ (48 atoms in one unit cell) is unaffordable [23,52]. As a result, HSE hybrid functional calculation becomes an efficient yet accurate approach for electronic structure calculations of perovskite sulfides.

3. Results and discussion

3.1. Structural and ferroelectric properties

$Parent ABS_3$ perovskite sulfides. Experimentally synthesized $ABS_3$ perovskite sulfides crystallize in various perovskite phases, which exhibit the corner-, edge- or face-sharing $BS_6$ octahedra networks [21,32,53,54]. Based on the experimental work of Lelieveld and Ildo [32], we will study the experimental corner-sharing perovskite $ABS_3$ with $A=Ca$, $Sr$ and $Ba$, $B=Zr$ and $Hf$. These $ABS_3$ sulfides belong to the orthorhombically distorted perovskite family with the $Pnma$ symmetry (No. 62). Our calculated crystal symmetry and lattice parameters agree well with experimental results (Table SI of the supporting information).

As shown in Fig. 1, $Pnma$ $ABS_3$ exhibits $a^2-c^2$ and $a^2b^2c^2$ $BS_6$ octahedra rotations in Glazer notation [55]. Due to the three-dimensional connectivity of the corner-sharing perovskite structure [27,56], octahedra rotations in $Pnma$ $ABS_3$ will also induce the anti-ferroic distortion (AFD) mode, where $A$-site cations from two neighboring cation layers are displaced by the same magnitude but along the opposite direction (Fig. 1(b)). As a result, $Pnma$ $ABS_3$ sulfides have zero net polarization.
Similar to perovskite oxides, the magnitudes of structural distortion or rotation of octahedra in $AB_2S_3$ sulfides can be characterized by the well-established tolerance factor $\tau$, defined as:

$$\tau = \frac{R_A + R_S}{\sqrt{2}(R_A + R_S)}$$

where $(R_A + R_S)$ and $(R_A + R_S)$ correspond to $A$-$S$ and $B$-$S$ bond lengths (detailed results in Table SII). For $Pmna ABSS_3$, with the pronounced octahedra rotations, their tolerance factors $\tau < 1$. An obvious structural trend is found when we plot the magnitude of crystallographic modes of $AB_2S_3$ as a function of the tolerance factor in Fig. 1(c); $AB_2S_3$ with smaller tolerance factor (e.g. CaZrS3) has the stronger octahedra rotation magnitudes (larger rotation angles, Fig. S1), and also exhibits the larger anti-ferroic distortion amplitudes. Therefore a question arises: can these octahedral rotations with large amplitudes lead to the enhanced polarization in Ruddlesden–Popper perovskite sulfides?

Ruddlesden–Popper $A_2B_2S_7$ sulfides. With the existence of $\text{a}^-\text{a}^-\text{a}^+$ and $\text{a}^+\text{a}^+\text{a}^-$ octahedra rotations in $Pmna ABSS_3$, it is likely to achieve the rotation induced ferroelectricity (HIF) in layered Ruddlesden–Popper perovskites [25,27]. Considering that Ruddlesden–Popper $\text{Ba}_2\text{ZrS}_3$, has already been synthesized experimentally [57,58], we will extend our investigation to Ruddlesden–Popper $A_2B_2S_7$ sulfides derived from the parent $Pmna ABSS_3$, and study their rotation induced ferroelectricity.

Ruddlesden–Popper $A_2B_2S_7$ sulfides have the general chemical formula $A_3[ABSS_3]_3$, where the $ABSS_3$ perovskite blocks (P-blocks) are stacked along [001] direction, inserted by an extra $A$ layer for every $n$ perovskite units, and inter-layer $A$ cations are coordinated with the terminal $S$ atoms to form rock-salt blocks (R-blocks) [59]. Shown in Fig. 2 are $n=2$ Ruddlesden–Popper $A_2B_2S_7$ sulfide structures. We choose the distortion-free $14/mmm$ (No. 139) phases as the paraelectric reference for $A_2B_2S_7$, from which the soft phonon modes and corresponding structural instabilities can be identified. Two primary soft modes corresponding to $\text{a}^-\text{a}^-\text{a}^+$ and $\text{a}^+\text{a}^+\text{a}^-$ octahedra rotations are found in $14/mmm$ phase. After performing structural relaxation on these two soft modes generated structures, ground state Ruddlesden–Popper $A_2B_2S_7$ phases can be obtained.

All of the Ruddlesden–Popper $A_2B_2S_7$ sulfides are optimized to have orthorhombic polar $A_2Bam$ (No. 36) symmetry. As shown in Fig. 2, $A_2Bam$ sulfides inherit $\text{a}^-\text{a}^-\text{a}^+$ octahedra rotations from the parent $Pmna ABSS_3$. Besides, they also exhibit the spontaneous polarizations along pseudocubic [110] direction. The origin of rotation induced ferroelectricity in $A_2Bam$ can be revealed in cation-layer resolved polarization ($P_{\text{sym}}$) plots (Fig. 2(a) and (b)).

Octahedra rotations in orthorhombic $A_2Bam$ also induce AFD-type cation displacement, where $A$-site cations from the neighboring layers are displaced oppositely. But as octahedra connectivity along [001] direction between different P-blocks are disrupted, in each P-block, two of the three cation-layer dipoles are directed along pseudo-cubic [110] direction, while the third is anti-parallel to the others. Therefore, a net polarization arises in Ruddlesden–Popper $A_2Bam$. The polarizations in $A_2Bam$ are mainly contributed by the $A$-site cation displacement, while the latter depends on the magnitude of the octahedra rotations. It is therefore apparent that CaZrS3 and Ca3HfS3 with small $\tau$ and significant octahedra rotations exhibit large magnitude of polar displacement (Fig. 2(c)).

To quantify the octahedra rotation induced ferroelectricity in Ruddlesden–Popper $A_2Bam$, we further calculate their spontaneous polarizations ($P$) using the Berry phase method (Fig. 3(a)). By recording the variation of spontaneous polarizations and the total energy of $A_2Bam$ with respect to the change of amplitudes for structural distortion connecting the paraelectric and ferroelectric phases, the typical double-well $P-E$ profiles are obtained (Fig. 3(b)). Two potential wells correspond to two ferroelectric $A_2Bam$ phases of different polarization directions, while the paraelectric state is located at the saddle point. When the potential well gets deep enough, $A_2Bam$ can be stabilized in a stable ferroelectric phase. Therefore, the energetic stability of ferroelectric $A_2Bam$ can be evaluated via ferroelectric stabilization energy $\Delta E_F$, which measures the energy difference between the paraelectric and ferroelectric states. As shown in Fig. 3(a), our calculated $P$ and $\Delta E_F$ for $A_2Bam$ decrease continuously as the tolerance factor increases. The extremely small $P$ and $\Delta E_F$ in $Ba_2ZrS_3$ indicate that it has a very low Curie temperature ($T_C$) and its ferroelectricity cannot be stable at room temperature, which naturally explains why experimental synthesized $Ba_2ZrS_3$ crystals in a paraelectric $14/mmm$ structure [58]. On the other hand, CaZrS3 has a large $\Delta E_F$ of 2.5 eV/f.u. vs. $\Delta E_F = 0.5$ eV/f.u. for Ruddlesden–Popper Ca3Ti2O7, whose measured $T_C$ reaches 1100 K [60]. As a result, CaZrS3 should have a stable and experimentally measurable polarization ($P = 18.1 \mu C/cm^2$) at room temperature, which can be an ideal ferroelectric sulfide for experimental study at room temperature and above.

3.2. Electronic structures and optical absorption properties

Non-polar $Pmna ABSS_3$ perovskite sulfides can be ferroelectric if they are synthesized in Ruddlesden–Popper $A_2Bam$ structures. To explore the application of ferroelectric $A_2Bam$ as the ferroelectric photovoltaic materials suitable for visible light absorption, their
electronic structures, especially band gaps ($E_g$) should be precisely determined. Due to the deficiencies of LDA or GGA method in predicting the energy band gaps, a more accurate HSE hybrid functional [47,48] is used for calculations. HSE calculation provides an accurate prediction of band gaps for perovskite sulfides. For example, HSE predicted band gap for BaZrS$_3$ is only 0.1 eV lower than experimental value [21] (Table SIII).

AB$_3^2$S$_7$ sulfides are predicted to have direct band gaps within the energy range between 1.8 and 2.4 eV, comparable with medium-bandgap semiconductors such as CdSe and GaP. Besides, Puma AB$_3^2$ sulfides are also predicted to be semiconductors with small $E_g$ (Fig. S2 and Table SIII). The following band gap trends are identified in $A_3B_2S_7$ (Fig. 4): $E_g[A_3ZrS_7] < E_g[A_3HS_7]$, and for each individual $A_3ZrS_7$ and $A_3HS_7$, its $E_g$ decreases monotonically with the tolerance factor. The band gap trend in $A_3B_2S_7$ can be understood from the nature of their electronic structures. Similar to ferroelectric oxides [61], there are pronounced hybridization of electronic states between $B$-site cations and anions in $A_3B_2S_7$. Typically in $Ca_3ZrS_7$, Zr-4d and S-3p states are hybridized/overlapped over the energy range around the Fermi level. The conduction band of the system is mainly contributed by the empty Zr-4d states, while the occupied S-3p states are distributed throughout the entire valence band. Band gap of $Ca_3ZrS_7$ refers to the energy difference of band edges between occupied S-3p and empty Zr-4d states.

The electronic structures of $A_3B_2S_7$ are mainly determined by the hybridization/orbital overlap between Zr-4d (Hf-5d) and S-3p states. As shown in Fig. 4, Zr–S–Zr bond overlap will be maximized when Zr–S–Zr bond angle reaches 180°, giving rise to the largest orbital bandwidths. But due to the octahedral rotations, bent Zr–S–Zr bonds in $A_3B_2S_7$ will reduce the magnitude of Zr–S orbital overlap and electronic bandwidths derived from them [62,63]. Therefore, band gap changes in $A_3B_2S_7$ are mediated by the octahedral rotations [64]: compared with Sr$_3Zr_2S_7$, $Ca_3Zr_2S_7$ exhibits larger magnitude of octahedra rotation and smaller orbital band.
Ca3Zr2S7 is a direct band gap semiconductor, where both valence band maximum and conduction band minimum are located at Γ point. The arrows mark the position of band gap for Ca3Zr2S7. The dash line corresponding to experimental optical absorption coefficient for bulk Si measured at room temperature [67] is used for comparison. The gray area refers to the standard AM 1.5G solar spectrum (in arbitrary units) [68].

3.3 Photovoltaic properties

Ruddlesden–Popper Ca3Zr2S7 can effectively absorb visible light with wavelength below 568.7 nm. As the solar spectrum is dominated by visible light, high absorption of visible light is essential for achieving high PV efficiency [69]. To evaluate the photovoltaic performance of Ca3Zr2S7 as an ideal solar cell, its PV conversion efficiency needs to be simulated.

PV efficiency of an ideal thin film solar cell can be simulated using the spectroscopic limited maximum efficiency (SLME) method [70]. Such a method takes into account the optical absorption spectrum, energy dependent carrier recombination loss and the thickness of the absorber layer (see supporting information for details). SLME method has been widely and successfully applied for many solar-cell materials, including the perovskites photovoltaic materials [69,71]. Fig. 6 shows our calculated short-circuit current density Jsc, open-circuit voltage Voc and maximum photovoltaic conversion efficiency η for ideal Ca3Zr2S7 solar cell, as a function of absorber film thickness.

As shown in Fig. 5, Ca3Zr2S7 has a direct band gap of 2.18 eV. Compared with CaZrS3 (band structure shown in Fig. S2) with three-dimensional (3D) corner-sharing octahedra connectivity, 2D layered Ca3Zr2S7 only exhibits the largely dispersed energy bands along the in-plane polarization directions (Γ–X and Γ–Y), while the out-of-plane bands along Γ–Z are almost dispersionless.

Our calculated imaginary dielectric function ε2 and absorption coefficient α of Ca3Zr2S7 are also given in Fig. 5. Experimental absorption coefficient of Si is also included for comparison. The onset of the optical absorption in Ca3Zr2S7 occurs at an energy point exactly same as its fundamental band gap (marked as arrows in Fig. 5), indicating that there is a direct optical transition from valence band maximum to conduction band minimum in Ca3Zr2S7. More importantly, within the visible light energy range (photon energy <3.4 eV), Ca3Zr2S7 exhibits optical absorption coefficient much larger than that of the single crystal Si (Fig. 5).
PV efficiency reaches the maximal value (\(\sim 24\%\)) at large \(L\). At a typical absorber thickness of \(L=0.5\ \text{µm}\), the calculated \(J_{sc}\) is at the order of mA/cm\(^2\) and efficiency \(\eta\) is about 23%. Such a value is comparable with the calculated PV efficiency for other photovoltaic materials, such as GaAs and CH\(_3\)NH\(_3\)PbI\(_3\) (\(\eta\approx 15\%\) and 23%, when \(L=0.5\ \text{µm}\) [69]). The overall good PV performance of Ca\(_3\)Zr\(_2\)S\(_7\) originates from its direct semiconducting band gap and high absorption of visible light [70]. It is worth noting that the experimentally measured efficiency of a solar cell can be affected by many extrinsic effects, such as thin-film preparation, defects, etc. Still our calculated ideal PV properties for Ca\(_3\)Zr\(_2\)S\(_7\) can be a useful guideline for future experimental investigations.

### 3.4. Extension to cation-ordered Ruddlesden–Popper sulfides

We have shown that Ruddlesden–Popper Ca\(_3\)Zr\(_2\)S\(_7\) with the smallest tolerance factor exhibits the largest polarization and band gap (Figs. 3 and 4) among all A\(_2\)ZrS\(_3\) sulfides we studied. From the experimental point of view, tuning the band gaps of the semiconducting ferroelectric materials will be crucial for optimizing their performance characteristics as solar cells [19]. In this subsection, we will demonstrate the tunability of band gap and ferroelectricity in Ruddlesden–Popper Ca\(_3\)Zr\(_2\)S\(_7\) via A-site cation ordering.

Fig. 7 shows the crystal structure for A-site ordered Ruddlesden–Popper A\(_2\)S[CaZrS\(_3\)]\(_2\) derived from Ca\(_3\)Zr\(_2\)S\(_7\), where Ca cations in the middle of perovskite blocks are substituted by other A cations with larger radius (A = Sr and Ba). Compared with pure Ca\(_3\)Zr\(_2\)S\(_7\), electric dipoles from A\(_2\)S cation layers are smaller, which cannot cancel out with the Ca\(_3\) dipoles [27]. As spontaneous polarization in Ruddlesden–Popper sulfides are mainly contributed by A-site cations, A-site ordered (Sr,Ca\(_2\))Zr\(_2\)S\(_7\) and (Ba,Ca\(_2\))Zr\(_2\)S\(_7\) exhibit enhanced electric polarizations over Ca\(_3\)Zr\(_2\)S\(_7\) (Table 1). Moreover, the ferroelectric stabilization energies \(\Delta E_p\) in (Sr,Ca\(_2\))Zr\(_2\)S\(_7\) and (Ba,Ca\(_2\))Zr\(_2\)S\(_7\) are still large enough to guarantee their ferroelectricity are stable at room temperature. Substitution of Ca by Sr or Ba will also lead to an increase of the average tolerance factor of the system. Based on the \(\tau - E_p\) relation we established, A\(_2\)S[CaZrS\(_3\)]\(_2\) have larger \(\tau_{avg}\) than Ca\(_3\)Zr\(_2\)S\(_7\) (Table 1), and their band gaps can be further reduced. For example, (Ba,Ca\(_2\))Zr\(_2\)S\(_7\) has a direct band gap below 2 eV, which can absorb visible light with wavelength below 626.2 nm. Therefore, A-site ordered A\(_2\)S[CaZrS\(_3\)]\(_2\) have enhanced polarizations and reduced band gaps than pure Ca\(_3\)Zr\(_2\)S\(_7\).

We conclude by providing some guidelines for experimental synthesis of ferroelectric Ruddlesden–Popper sulfides A\(_2\)B\(_2\)S\(_7\) and fabrication of sulfides-based FE-PV devices. Sulfide Ba\(_3\)Zr\(_2\)S\(_7\) in Ruddlesden–Popper structure has been synthesized using solid-state reaction [57] or flux method [58] decades ago. Structural characterization indicates that Ba\(_3\)Zr\(_2\)S\(_7\) has a paraelectric phase with zero polarization. Therefore, ferroelectric properties of perovskite sulfides have never been experimentally explored. Based on our prediction, Ca\(_3\)Zr\(_2\)S\(_7\) has very stable ferroelectricity at room temperature, semiconducting band gap and large optical absorption coefficient. Ferroelectric Ca\(_3\)Zr\(_2\)S\(_7\) could potentially be made using the similar experimental methods for synthesis of Ba\(_3\)Zr\(_2\)S\(_7\), as both Ca\(_3\)Zr\(_2\)S\(_7\) and Ba\(_3\)Zr\(_2\)S\(_7\) are predicted to have the same ground state structure. Moreover, band gaps and ferroelectricity of Ca\(_3\)Zr\(_2\)S\(_7\) can be further tuned via A-site cation ordering. Using the modern layer-by-layer thin film deposition techniques [18,24,72], it is possible to prepare A-site ordered Ruddlesden–Popper A\(_2\)S[CaZrS\(_3\)]\(_2\). Consequently, multilayered ferroelectric thin-film PV device consisting of Ca\(_3\)Zr\(_2\)S\(_7\), (Sr,Ca\(_2\))Zr\(_2\)S\(_7\) and (Ba,Ca\(_2\))Zr\(_2\)S\(_7\), single layers can absorb wide range of visible light, and an optimized PV conversion efficiency may be achieved [19].

### 4. Conclusion

In conclusion, using first-principles calculations, we design a new family of semiconducting perovskite ferroelectrics – Ruddlesden–Popper perovskite sulfides A\(_2\)B\(_2\)S\(_7\), for ferroelectric photovoltaic applications. Especially, Ruddlesden–Popper Ca\(_3\)Zr\(_2\)S\(_7\) is predicted to have the stable ferroelectric polarization which can efficiently separate the photo-generated electron–hole pairs, and low band gap suitable for visible light absorption. Our calculations further demonstrate Ca\(_3\)Zr\(_2\)S\(_7\) as a promising ferroelectric photovoltaic material with the high photovoltaic energy conversion efficiency. Most importantly, Ruddlesden–Popper perovskite sulfides presented in current work can be created by the standard synthesis techniques. We hope our work will motivate the experimental synthesis of ferroelectric perovskite sulfides and exploration of their ferroelectric and photovoltaic properties.

### Acknowledgments

The authors acknowledge the funding support from National Basic Research Program of China, under Contract no. 2012CB619402, National Science Foundation of China, under Contract no. 11574244, and Program for Innovative Research Team in University of Ministry of Education of China (IRT13034). JL acknowledges support by NSF DMR-1410636. National Supercomputer Center (NSCC) in Tianjin is acknowledged for computational support. The authors thank Prof. Xiaofeng Qian for useful discussion.

### Appendix A. Supplementary data

Supplementary data associated with this paper can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.02.036.