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The Atomic and Electronic Structure and Tunability of Ruddlesden-Popper Phases for Photovoltaic Applications

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The Atomic and Electronic Structure and Tunability of Ruddlesden-Popper Phases for Photovoltaic Applications

By

Britt A. Tyler

Accepted in Partial Completion of the Requirements for the Degree Master of Science

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Britt A. Tyler

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The Atomic and Electronic Structure and Tunability of Ruddlesden-Popper Phases for Photovoltaic Applications

A Thesis
Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

by
Britt A. Tyler
August 2019
Abstract

There is an increasing need for alternative energy sources that reduce the global reliance on fossil fuels. Since their demonstration in 2009, perovskite solar cells (based on compounds with the formula ABX₃, such as CH₃NH₃PbI₃) have become an extremely promising and active research area. Still, there are obstacles to the widespread use of these technologies, including their instability and the environmental impacts of lead. It is therefore important to find ways to modify and tune the structure and properties of perovskites to optimize their stability and photovoltaic performance. This research explores a family of perovskite relatives known as Ruddlesden-Popper (RP) phases. Density functional theory (DFT) calculations are used to study the structural energetics and electronic structure of RP phases varying in composition (A=Rb, Cs; B=Ge, Sn, Pb; X=Cl, Br, I), structural distortion, and biaxial strain. Among the goals are to explore and understand how strain can be used as a tool for stabilizing RP phases, and to make concrete predictions for routes to tune the structure and properties of perovskite photovoltaic materials.
Acknowledgements

This work would not have been possible were it not for assistance from numerous members of the chemistry department at Western Washington University. I would particularly like to thank the members of my thesis committee, Drs. Robert F. Berger, Emily Borda and Tim Kowalczyk for guidance, and support. A special thanks to Dr. Robert F. Berger for all of his individual instruction, guidance and many hours of work. I would also like to thank the Berger research group as well as the Kowalczyk research group. Additional thanks to Dr. Muñiz and the Muñiz research group for bringing me to this point. Thanks to the National Science Foundation for summer funding, Award Number:1726071 and thanks to the Research Corporation for Science Advancement, Cottrell Scholar Award for financial support.
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Chapter 1

Introduction

1.1 The Need for Renewable Energy

The current world population is approximately 7.7 billion people and is estimated to climb to 8.6 billion by 2030.[1] With growing population comes growing energy consumption. Since 1990, energy consumption has increased by approximately 50%. Yet, there has been little change in the types of energy sources that are utilized. Approximately 67% of the energy consumed in 2016 came from fossil fuels, which is only about a 2% decrease from 1990 (Figure 1).[2]

![Figure 1: World energy consumption, showing how little the distribution of energy sources has changed in the past three decades.](image)

Fossil fuels are a finite resource, and the cost and energy put into retrieving fossil fuels is increasing and will continue to increase. M. King Hubbert, a Shell research scientist who made numerous contributions to petroleum geology, said “So long as oil is used as a source of energy,
when the energy cost of recovering a barrel of oil becomes greater than the energy content of the oil, production will cease no matter what the monetary price may be.”[3]

Furthermore, the combustion of fossil fuels is a major contributor to the carbon cycle and thus a contributor to global warming. The Paris climate accord stipulated that the world needs to take major steps to curb the rate at which global warming is taking place. In order to limit the increase of the global temperature to below 2°C, some drastic (and perhaps unrealistic) steps would need to be taken. It is predicted that the world will need to develop 10 to 30 terawatts of clean-energy capacity by 2050. According to a recent technology review, in order to provide for this need, the world would have to construct 30,000 nuclear power plants or manufacture and install the equivalent of 120 billion 250-watt solar panels.[4]

The world needs to invest in non-fossil fuel energy sources with minimal impact on the carbon cycle. Of the renewable energy sources, hydroelectricity is the largest provider but is unlikely to be an area of significant growth in the future. Another renewable energy source of note is wind power. The renewable energy source on which we focus, and the one with perhaps the largest potential for growth, is solar energy. The solar cell technologies that currently dominate the market are silicon-based. A variety of emerging technologies, including the perovskites described in the next section, are areas of very active research. If these new classes of photovoltaic technologies can strike a suitable balance of low cost, high efficiency, sustainable lifecycle, and high stability, they can potentially make a huge impact on the world’s energy supply.
1.2 Principles of Solar Energy Conversion by a Semiconductor

In a photovoltaic cell (a “solar cell”, which converts sunlight to electricity), the absorption of light is accompanied by the excitation of an electron from the valence band to the conduction band (Figure 2). The energy difference between these two bands (analogous to the HOMO-LUMO gap of a molecule) is called the band gap. If a material has a band gap that is too wide, it will not absorb many photons in the solar spectrum. However, if a material has a band gap that is too narrow, most of the absorbed energy will be lost when the excited electron relaxes to the bottom of the conduction band. According to Shockley and Queisser’s analysis, the optimal band gap for a photovoltaic absorber is close to 1.4 eV.[5] This number is a useful reference later in this thesis, when we report band gaps.

Figure 2: Schematic illustration of how a solar cell material absorbs a photon to excite an electron.

In recent decades, dye-sensitized architectures have significantly changed the way that solar cells are produced. In a dye-sensitized solar cell, a thin layer of a photosensitive dye is the component that absorbs sunlight. Because only a thin layer is needed, those devices are
relatively cheap to produce. In 2009, Miyasaka et al. first used organometal halide perovskites, whose structures are discussed in the next section, as the light-absorbing layer in dye-sensitized solar cells.[6]

In order for new technologies to replace silicon-based solar cells, they must strike the right balance of high energy conversion efficiencies, high stabilities, and low manufacturing costs. Perovskite solar cells are indeed cost-effective, and allow for thin and flexible design. While perovskite solar cells do not yet quite match the energy conversion efficiency of silicon, Figure 3 (data reproduced from the National Renewable Energy Laboratory [7]) shows that their efficiency has improved remarkably in the past decade. Note that the efficiency of perovskite solar cells (red circles filled in with yellow) has improved in a decade as much as silicon-based devices have improved since the 1970s.

Figure 3: The progression of world record solar cell efficiencies over time for various technologies. This figure is curated by the National Renewable Energy Laboratory.[7]
Some concerns do exist in this class of materials in terms of their stability and the environmental impacts of their use of lead. In the interest of optimizing the stability and efficiency of perovskite materials while reducing their lead content, it is important to explore the compositional and structural degrees of freedom of these compounds.

1.3 Perovskites

In 1839, a mineral with the formula CaTiO₃ was found in the Ural Mountains by Gustav Rose. Rose named the mineral “perovskite”, after mineralogist Lev Perovski.[8] More generally, “perovskites” now refer to solids with the stoichiometry ABX₃ that have the same crystal structure as CaTiO₃. Typically, cations occupy the A and B sites, while anions occupy the X site. An example of such a compound (CsPbI₃) relevant to the research in this thesis is shown in Figure 4.

![Figure 4: The cubic unit cell of CsPbI₃, a perovskite compound used in solar cells. The structure is shown with a) all atoms as spheres, and b) the Pb and I atoms as an octahedron.](image)

Perovskites are studied for a wide variety of applications, including solar energy conversion, superconductivity, and ferroelectricity.[9] The research presented here focuses on light-absorbing perovskite compounds for photovoltaics devices. These materials are
semiconductors that generally have large (sometimes polyatomic) cations at the A site, Pb$^{2+}$
cations at the B site, and halide anions at the X site. A prototypical example is CH$_3$NH$_3$PbI$_3$,
which was one of the first compounds introduced by Miyasaka et al.[5]

Perovskites are known for being highly tunable in a variety of ways. In terms of their
composition, the atoms within a halide perovskite can be doped and substituted at the A, B, and
X sites. The likelihood that a given combination of elements will form a stable perovskite
compound is largely determined by the sizes of the atoms. The classic framework for predicting
perovskite stability is the Goldschmidt tolerance factor (Equation 1), a ratio of atomic sizes that
is close to 1 when elements fit together well in the perovskite structure.[10] In the equation, $r_A$
is the ionic radius of the A-site cation, $r_X$ is the ionic radius of the X-site anion, and $r_B$
is the ionic radius of the B-site cation.

Equation 1. Definition of the Goldschmidt tolerance factor, [10] a metric for predicting the
stability of a perovskite compound. The r’s represent the ionic radii at each crystallographic site.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Another way in which perovskites can be tuned is through temperature-controlled phase
transitions. While perovskites often take on the cubic structure shown in Figure 4 at high
temperatures, many perovskites exhibit distortions at room temperature. Relevant to this
research, germanium-halide perovskites (which have smaller B-site cations and larger values of
t) have polar distortions (Figure 5a), while lead- and tin-halide perovskites (which have larger B-
site cations and smaller values of t) typically have octahedral rotations (Figure 5b).

A third way in which perovskite compounds can be tuned is by applying strain. Strain
can be introduced via epitaxial growth on mismatched substrate surfaces, or in a variety of
nanostructures.[11] The structure of a thin film can be stretched out if grown on a substrate with a larger unit cell or compressed if grown on a substrate with a smaller unit cell. In practice, the in-plane axes of a perovskite thin film can be strained by up to about 3% of the unit cell size in either direction. Throughout Chapter 3 of this thesis, we will explore the effects of each of these modes of tunability – elemental substitution, distortion and strain – and the structural layering described in the next section.

![Diagram](image)

**Figure 5:** Common structural distortions in perovskite compounds: a) The germanium atom is shifted slightly away from the center of the octahedron, representing a polar distortion in CsGeI\(_3\). b) The arrows indicate the direction of octahedral rotations occurring in CsPbI\(_3\).

1.4 Ruddlesden-Popper Phases

Beyond the ABX\(_3\) perovskite, there also exist related classes of layered compounds such as Ruddlesden-Popper (RP) phases.[12,13] RP phases have the general formula \(A_{n+1}B_nX_{3n+1}\), for which the \(n=1\) case is illustrated in Figure 6. In these compounds, blocks of \(n\) perovskite layers are spaced by an extra AX layer. These structures can be viewed as consisting of alternating regions of the perovskite structure and the NaCl-type structure. RP phases are currently being studied for use in photovoltaics, and have been demonstrated to have better long-term stability.
than the corresponding perovskites.\cite{14} Their stability in the presence of water is attributed to the hydrophobic organic molecules used to space the perovskite layers. The efficiency of solar cells based on RP phases has also improved, recently exceeding 15\%.\cite{15} A tandem junction solar cell utilizing two-dimensional RPs was shown to have an efficiency of 28\%, which rivals the current record-holding tandem solar cell efficiency of 32.8\% of a (more expensive) gallium indium phosphide/gallium arsenide monolithic device.\cite{7}

![Diagram](image)

Figure 6: \(\text{Cs}_2\text{PbI}_4\), an example of the \(n=1\) Ruddlesden Popper structure, represented as a) ball-and-stick and b) octahedral models. Regions within the RP structures are highlighted that resemble the perovskite and NaCl-type structures.

1.5 Goals of This Research

In this research, we computationally study the extent to which the atomic and electronic structure of perovskite photovoltaic materials can be tuned through the growth of Ruddlesden-Popper (RP) phases. This is done to provide potential candidates for synthesis and to elucidate trends that exist amongst these RP phases. After establishing our computational methods in
Chapter 2, we present and discuss results in Chapter 3. We first explore which combinations of elements are likely to form stable RP compounds. We do this by comparing the structural energies of RP compounds (without and with common distortions) to a variety of competing binary and ternary phases. Next, we examine and rationalize how biaxial strain, which can be achieved experimentally in epitaxial thin films and other nanostructures, can help to stabilize RP phases. Finally, we consider how these structural changes – layering in RP phases, substitution of various elements, distortion, and strain – affect the band gaps of these compounds. Taken together, these results aim to create a coherent picture of how RP compounds can be used and tuned for solar cell applications.
Chapter 2

Computational Methods

In this work, plane-wave density functional theory (DFT) is used to compute structural energies, electronic band structures, and band gaps. All calculations use the Vienna Ab Initio Simulation Package (VASP) [16-19], the projector augmented wave (PAW) method [20], and a plane-wave basis set cutoff of 500 eV. Images of crystalline unit cells are generated using VESTA.[21]

When performing DFT calculations, a key methodological choice is which density functional to use to account for electron exchange and correlation. Based on past precedent in the computational literature on perovskite photovoltaics, most of our calculations utilize the Perdew-Burke-Ernzerhof (PBE) functional [22,23], a generalized gradient approximation. PBE has been demonstrated to accurately capture the structural energetics of halide perovskites with respect to strain and distortion, as well as trends in their band gaps.[24-27] While the PBE functional does a reasonable job capturing the shifts in band gap that come with distortion, strain, and elemental substitution, PBE (and other simple DFT functionals) has a well-known tendency to significantly underestimate absolute band gaps relative to experiment.[28] In order to correct for this, some of our calculations use higher levels of theory that incorporate additional physics. Where specified, our calculations include spin-orbit coupling and the hybrid functional PBE0.[29]

Unlike calculations of molecules, calculations of crystalline solids utilize a grid of k-points, which specify the phase of a crystal wavefunction from one unit cell to the next.[30] A finer grid of k-points facilitates a more exact calculation, but at greater computational expense. Because k-points exist in reciprocal space and crystal structures in real space, the number of k-
points has an inverse relationship with unit cell size for the same quality of calculation. Consistent with previous work in our group [31], our calculations use a $6\times6\times6$ k-point grid for a 5-atom cubic perovskite unit cell, and proportionally fewer k-points for larger unit cells.

Some of our calculations model crystal structures under biaxial strain, resembling that which can be achieved by the growth of epitaxial thin films or other nanostructures. When computing strained structures, the size of the unit cell is fixed along two Cartesian axes, while the third axis and atomic positions are allowed to relax.
Chapter 3

Results and Discussion

3.1 The Energetic Stability of Ruddlesden-Popper Phases

We begin by studying the energetic stability of a variety of Ruddlesden-Popper (RP) compounds relative to competing phases, in order to determine what combinations of elements are most likely to be synthesized (Table 1). When searching for stable compounds, there is no computational method that guarantees finding the lowest-energy configuration for a given stoichiometry. Instead, the usual approach is to use chemical intuition and knowledge of existing structures to guide the computation and comparison of a variety of most likely candidate structures.

In order to compute the stabilities of RP phases, we compare the energies of the relaxed RP structures to various alternative arrangements of the same atoms: combinations of perovskites, binary salts, and other structures. An example of such a comparison is shown in Figure 7, in which the energy of an $n=1$ RP phase ($\text{Rb}_2\text{GeCl}_4$) is compared to the combined energies of a perovskite ($\text{RbGeCl}_3$) and a NaCl-type binary salt ($\text{RbCl}$).

Figure 7: An example of our approach to computing the stability of a RP phase. The structural energy of the RP phase is compared to those of the corresponding perovskite and NaCl-type salt.
To provide some context, a negative energy in Table 1 (and in Figure 7) indicates that the $n=1$ RP phase is more energetically stable than a given competitor. In a row of three numbers in Table 1, the most positive number (i.e., the comparison to the most stable competitor) is shown in blue. Therefore, if a blue number is negative, the $n=1$ RP phase is more stable than all of its most likely competitors and is a promising candidate for synthesis.

Table 1: Computed energies of $n=1$ RP phases, relative to competing structures. “ABX$_3$” refers to a perovskite, while “nonperovskite” refers to the so-called “yellow phase”, a competing structure with stoichiometry ABX$_3$.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Energy Difference Between RP n=1 and Competitor (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Undistorted</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Cl</td>
<td>Ge</td>
</tr>
<tr>
<td>I</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Rb</td>
</tr>
<tr>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Pb</td>
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<tr>
<td>Cl</td>
<td>Ge</td>
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<tr>
<td>I</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Cs</td>
</tr>
<tr>
<td>Ge</td>
<td>Br</td>
</tr>
<tr>
<td>I</td>
<td>-0.048</td>
</tr>
<tr>
<td>Cl</td>
<td>Cs</td>
</tr>
<tr>
<td>I</td>
<td>-0.007</td>
</tr>
<tr>
<td>Cl</td>
<td>Pb</td>
</tr>
<tr>
<td>I</td>
<td>-0.018</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Aside from the structures shown in Figure 7, the other known competitive structures to which each RP phase is compared are shown in Figure 8. The structure that we refer to as “nonperovskite” is the so-called “yellow phase”, a competing structure with stoichiometry ABX$_3$ (Figure 8a).[32] The BX$_2$ structure is the PbI$_2$-type salt structure (Figure 8b).
Figure 8: a) The nonperovskite (‘‘yellow’’ phase) of RbGeCl$_3$. b) The PbI$_2$-type salt structure.

In the left half of Table 1, the perovskite and RP structures are constrained to their highest symmetry; that is, they have neither octahedral rotations nor polar distortions. While these undistorted structures are not typically seen at low temperatures, they represent an idealized starting point that is simple to compute and to understand. There are two main points to take from the left half of the table. First, for most compounds with A=Rb, the nonperovskite ABX$_3$ phase is significantly more stable than either the perovskite or the RP phase, often by tenths of an eV per formula unit. This is consistent with the small tolerance factors of these combinations of elements, and the experimental reality that they generally do not exist as perovskites. It is similarly unlikely that RP phases with A=Rb will outcompete this nonperovskite structure, and we therefore focus most of our attention on compounds with A=Cs. Second, the combinations of elements for which the RP phase is most stable tend to have larger A sites (Cs), smaller B sites (Ge or Sn), and smaller X sites (Cl or Br). While the CsPbX$_3$ compounds are computed to have a slight thermodynamic preference for the nonperovskite phase (indicated by the positive numbers at the bottom of the third column of Table 1), these
combinations of elements are nonetheless worth studying for possible RP formation, as they are known to exist as perovskites.

In the right half of Table 1, the perovskite and RP structures are allowed to relax with the types of distortions that are known to exist in the room-temperature perovskites phases – polar distortions for B=Ge, and octahedral rotations for B=Sn and Pb. This presents a more complex, and more realistic, picture of the true energetic competition among these structures. Again, there are two main points to take from the right half of the table. First, for A=Rb, the nonperovskite structure again dominates, though not by nearly as wide an energetic margin. In cases where the RP phase comfortably outcompetes the perovskite phase (RbSnX$_3$ and RbPbX$_3$), it is not out of the question that RP phases could be synthesized under epitaxial growth conditions. Second, for A=Cs, there are again several combinations of elements for which all energies are negative (CsSnCl$_3$, CsSnBr$_3$, CsPbCl$_3$, CsPbBr$_3$), and others that are close. Given their energetic stability relative to a variety of competing structures, these cesium-containing RP phases appear to be a family of compounds with many promising targets for synthesis and tuning.

3.2 Using Biaxial Strain to Stabilize Ruddlesden-Popper Phases

As explained in Chapter 1, the structure and properties of perovskite compounds can be tuned via epitaxial strain. Epitaxial strain refers to growth conditions in which the two in-plane axes of a compound are constrained to certain lengths, typically by the geometry of a substrate surface. Epitaxial strains of approximately 3% of the unit cell size (in both the compressive and tensile directions) have been experimentally demonstrated for a variety of perovskites.[11] We hypothesize that epitaxial strain may also help to stabilize RP phases relative to perovskites, and facilitate the growth of some RP phases that could not otherwise be grown. Because RP phases
can be viewed as alternating regions of the perovskite structure and NaCl-type AX structure (Figure 6), we expect that a RP compound is most stable relative to the corresponding perovskite when its in-plane unit cell vectors are constrained to a size close to that of the corresponding NaCl-type AX compound. In all combinations of elements studied here, this corresponds to compressive strain. We explore this idea of using strain to stabilize RP phases below.

We test our hypothesis and the results of our investigation are shown in Figures 9-11 for perovskite and RP structures that are not allowed to distort. In these calculations, we consider compounds with A=Cs, a variety of divalent cations at the B site (B=Ca$^{2+}$, Ge$^{2+}$, Sr$^{2+}$, Sn$^{2+}$, and Pb$^{2+}$) and halide anions at the X site (X=Cl$^-$, Br$^-$, and I$^-$). Though Ca$^{2+}$ and Sr$^{2+}$ are not used for solar cell applications, we include them to test the hypothesis that RP stability is closely related to unit cell size. The chlorides, bromides, and iodides are shown in Figures 9, 10, and 11, respectively. In these figures, each curve represents the energy of an $n=1$ RP compound (relative to the respective strained perovskite and NaCl-type AX compound) ranging from its fully relaxed structure (right side of the curve) to compressive strains up to -10% (left side of the curve). Realistically, it is difficult to achieve strains beyond -3% of the unit cell size experimentally in thin films, but larger strains are still useful toward our conceptual understanding of the effects of strain.

In Figure 9, the fact that most data points have negative energy differences suggests that a variety of chloride RP phases are potentially stable, especially under compressive strain. For the RP compound with the largest B-site cation (lead), compressive strains stabilize the RP phases as more strain is applied, up to -10% strain. In contrast, the RP compound with the smallest B-site cation (germanium) is quite stable even without strain, and large compressive strains make the RP phase less stable. While this observation sounds surprising, Figure 9 illustrates why it is true.
The unit cell of the lead-containing RP phase is much larger than that of CsCl, and compressive strain leads to a closer match. The unit cell of the germanium-containing RP phase is already relatively close to that of CsCl, so compressive strain is not productive toward stabilizing it. The minima of the curves in Figure 9 all occur at similar unit cell sizes. While those minima do not exactly match the unit cell size of CsCl (the dashed black line in the figure) as we hypothesized, they are not far from it.

Figure 9: Energetic stability of undistorted $n=1$ Ruddlesden-Popper chloride compounds, relative to the respective strained perovskite and NaCl-type AX compound.
Figure 10: Energetic stability of undistorted \( n=1 \) Ruddlesden-Popper bromide compounds, relative to the respective strained perovskite and NaCl-type AX compound.

With only subtle differences, the results in Figures 10 (the bromides) and 11 (the iodides) resemble those in Figure 9. One slight difference is that, for the bromides and iodides, moderate amounts of compressive strain initially stabilize the germanium-containing compounds. This is consistent with our framework for understanding the stability of these compounds based on unit cell size. Taken together, the results in Figures 9-11 suggest that compressive biaxial strain is a potentially productive route toward the stabilization of a variety of RP phases for perovskite photovoltaics.
Figure 11: Energetic stability of undistorted $n=1$ Ruddlesden-Popper iodide compounds, relative to the respective strained perovskite and NaCl-type AX compound.

While the results in Figures 9-11 are promising, they require closer examination. At room temperature, materials for perovskite photovoltaics have complex energy landscapes of structural distortions, which should be considered when looking at the stability of RP phases. Figures 12-14 are analogous to Figures 9-11, except that both the perovskite and $n=1$ RP phase are allowed to relax with their expected modes of distortion (polar distortions for B=Ge, and octahedral rotations for B=Sn and Pb).
Figure 12: Energetic stability of distorted $n=1$ Ruddlesden-Popper chloride compounds, relative to the respective strained and distorted perovskite and NaCl-type AX compound. The lead- and tin-containing compounds have rotations of their BX octahedra, while the germanium-containing compounds have polar distortions.

In many ways, the results in Figures 12-14 are similar to Figures 9-11, though their meaning is somewhat more ambiguous. While the energy differences are not as negative for the distorted phases as for the undistorted ones, most RP phases do reach negative energy differences under some amount of compressive biaxial strain. Though the curves in Figures 12-14 are not as parabolic as those in Figures 9-11 due to the complex interplay between strain and distortion, most do have minima around the same unit cell size as the corresponding NaCl-type AX compound.
Figure 13: Energetic stability of distorted $n=1$ Ruddlesden-Popper bromide compounds, relative to the respective strained and distorted perovskite and NaCl-type AX compound. The lead- and tin-containing compounds have rotations of their BX octahedra, while the germanium-containing compounds have polar distortions.
Figure 14: Energetic stability of distorted $n=1$ Ruddlesden-Popper iodide compounds, relative to the respective strained and distorted perovskite and NaCl-type AX compound. The lead- and tin-containing compounds have rotations of their BX octahedra, while the germanium-containing compounds have polar distortions.

As seen in Figures 9-14, our hypothesis is confirmed. Straining these RP phases to the AX unit cell size does indeed stabilize them, since the AX region exists within the RP phase, but at a larger size than that of the AX unit cell size singularly. So, the takeaway message is that compressive biaxial strain has the potential to stabilize RP phases for a variety of combinations of elements, perhaps more realistically for smaller B-site cations (B=Ge).

3.3 Methods for Computing the Band Gaps of Perovskites and Ruddlesden-Popper Phases

So far, we have established the energetic stability of RP compounds. In the remaining sections of Chapter 3, we will explore whether these compounds have band gaps that are suitable and tunable for photovoltaic applications. In order to do that, we must first consider what methods are needed to meaningfully compute these band gaps. In the results highlighted in
Figure 15, the band gaps of cubic perovskites are computed using various methods, and compared to experimental values.

![Band gap diagram](image)

Figure 15: Band gaps of cubic perovskites using the PBE (generalized gradient approximation) and PBE0 (hybrid) functionals, without and with spin-orbit coupling (SOC). Experimental values are taken from References.[33-35]

The simplest density functional, PBE (a generalized gradient approximation), consistently underestimates experimental band gaps. The more computationally expensive hybrid functional, PBE0, widens the band gaps by 1-1.5 eV relative to PBE. It is only when spin-orbit coupling (SOC) is included in the PBE0 calculations that computed band gaps for the lead containing perovskites come into agreement with experimental values. Germanium and tin containing compounds fail to match experimental data, most likely due to the calculations being performed on undistorted compounds. All of these findings are consistent with past work.[36]

While Figure 15 establishes that computationally expensive methods (i.e., a hybrid functional and spin-orbit coupling) bring computed results closer to experiment, it also suggests
that simple PBE calculations can accurately capture trends (i.e., whether the band gap increases or decreases when the structure is changed in a certain way). Figure 16 suggests that this continues to be true for the RP phases. PBE0 band gaps are consistently 1-1.5 eV larger than PBE band gaps. Because our interest lies primarily in tunability and trends of RP band gaps, our calculations in the next subsection are computationally simple PBE calculations.

Figure 16: Computed band gaps of the $n=1$ RP phases using the PBE and PBE0 functionals.

### 3.4 Ruddlesden-Popper Band Gaps and Their Tunability under Strain

Just as the energetic stability of perovskites and RP phases can be tuned by epitaxial strain, their band-edge orbitals and band gaps can also be tuned. Figure 17 illustrates the PBE-computed band gaps for undistorted and distorted perovskite and RP compounds.
Figure 17: Computed band gaps of a) cubic perovskites, b) distorted perovskites, c) undistorted $n=1$ RP phases, and d) distorted $n=1$ RP phases. In all cases, strains range from 0% (unstrained) to -4% (substantial compressive strain).

Compounds are computed under strains ranging from 0% (unstrained) to -4% (the approximate experimental limit of compressive strain). For undistorted perovskite and RP compounds (Figure 17a and 17c), band gaps can be reduced by several tenths of an eV under compressive strain. This is consistent with past work on perovskites, which has attributed narrowing of the gap to the enhancement of antibonding interactions in the valence band maximum as atoms are pushed closer together.[36-39] When distortions are allowed to occur in the perovskites and RP compounds (Figure 17b and 17c), the trends in band gap with strain become less clear. We suspect this is due to competing effects. While compressive strain by itself narrows the band gap, it also enhances the amplitudes of structural distortions, which tend to widen band gaps.
More broadly, the results in Figure 17 highlight the potentially exciting properties of this class of RP compounds. With substitutions at the B and X sites and achievable epitaxial strains, these compounds can be tuned to have band gaps throughout the strongest parts of the solar spectrum. Thus, these compounds could make use of the energy of the photons provided by the sun.
Chapter 4
Conclusions, Limitations, and Future Work

In this work, we have shown that a variety of RP phases are of potential interest for photovoltaic applications. In terms of structural stability, these compounds are competitive with other binary and ternary compounds, and that stability can be enhanced by compressive epitaxial strain. These trends in stability can be explained using simple arguments involving the relative sizes of the elements. The band gaps of these RP phases span the most intense regions of the solar spectrum (i.e., near visible wavelengths), and can be tuned by several tenths on an eV under achievable strains.

It is important to be aware of a few limitations of this research and the conclusions that can reasonably be drawn from it. First, because our studies of stability rely on comparisons to only a few competing structures, we cannot guarantee that any RP phase is the global energy minimum. Second, our structural energy calculations neglect entropy, and are implicitly at zero temperature. When assessing stability, we are therefore making the assumption that entropy contributions to each structure are similar. Third, we have not addressed these compounds' long-term stability against degradation, which is a concern in perovskite solar cells. Finally, by focusing solely on band gap, we are potentially missing other features of the electronic band structure of RP phases (e.g., density of states and effective mass of charge carriers) that could impact photovoltaic efficiency.

As previously noted, there are multiple ways to tune perovskites. There are many more questions for us to explore in order to create a coherent picture of tunability in RP phases. A greater variety of A-site elements can be studied, including the types of organic linkers that have been used experimentally.[14] In order to avoid using lead, a greater variety of B-site elements
can also be explored. Rather than a single element at the B site, ordered mixtures can be used. Finally, all of those RP compounds can be explored for larger values of $n$ (i.e., different layering patterns) for greater structural and electronic tunability.
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