Generation of low-symmetry perovskite structures for \textit{ab initio} computation

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Abstract

Ion displacements are the fundamental cause of ferroelectricity in perovskites. By properly shifting ions, \textit{ab initio} computations have been extensively used to investigate the properties of perovskites in various structural phases. In addition to the relatively simple ion displacements, perovskites have another type of structural distortion known as antiferrodistortion or oxygen octahedron tilting. The interplay between these two types of distortions have generated abundant structural phases that can be tedious to prepare for \textit{ab initio} computation, especially for large supercells. Here, we design and implement a computer program to facilitate the generation of distorted perovskite structures, which can be readily used for \textit{ab initio} computation to gain further insight into the perovskite of a given structural phase.

Keywords: perovskite materials, structural distortion, ferroelectricity, \textit{ab initio} calculation, symmetry

(Some figures may appear in colour only in the online journal)

1. Introduction

Perovskites of the general formula $\text{ABX}_3$ have been used in many areas due to their excellent physical properties [1], including the detailed investigation of their dielectric, magnetic, electrical, optical, and catalytic properties [2–4]. Their piezoelectricity and ferroelectricity have been used for ultrasonics, transducers, pressure sensors, infrared thermoelectric detector, and high density information storage for a long time and such applications have gradually matured over time [5]. Recently, it was also found that organic and inorganic (halide) perovskites are good candidates for solar cells and light emitting devices [6]. In particular, perovskite solar cells have been intensively investigated in search of greater conversion efficiency in addition to their simple preparation process and low manufacture cost [7–9].

Predicting the stable phases of perovskites (and their stability) remains a challenge in the investigation of related perovskites for photovoltaics and electrocatalysts [10, 11]. All-inorganic perovskite materials [e.g., halide perovskites $\text{CsBX}_3$ ($B = \text{Sn and Pb}; X = \text{I, Br, and Cl}$)], without any volatile organic components [12–15], exhibit superior thermal stability comparing to organic–inorganic composite perovskite materials. However, understanding the stability of their structural phases is also critical [16]. For instance, cubic phase $\text{CsPbI}_3$ has a suitable band gap of 1.7 eV for high-efficiency photovoltaics, but it is not a thermodynamically stable phase at...
Perovskites often exhibit a wide range of structural distortions originating from lattice instabilities of their prototype cubic structure [19]. For instance, while a large number of perovskite ferroelectrics have uniform polar distortions (e.g., in PbTiO$_3$, BaTiO$_3$, KNbO$_3$), others can have more complex phases involving antiferroelectric ion displacements and oxygen octahedron tilting (e.g., in PbZrO$_3$ and SrTiO$_3$). The solid solution Pb$_2$(Zr$_{1-x}$Ti$_x$)$_2$O$_5$ embodies such complexity with its ever-changing structural phases with $x$ [20–22]. Given the infinite possibilities of perovskite compounds, the determination of their most stable structural phase is not a trivial work. The oxygen octahedron tilting is particularly difficult to treat and analyze due to relatively small amplitudes and energies caused by the distortions [23].

In order to find the most stable phase, one common practice is to calculate the phonon spectra, obtain the eigenvectors of the unstable phonon modes, shift the ions accordingly, and finally relax the constructed structure using ab initio computation to obtain its energy [24–28]. In addition, the effective Hamiltonian approach has also been successful in predicting and suggesting low-energy phases [20, 29, 30]. This approach relies on the fact that low-energy phases are often derived by ion displacements with respect to the original cubic cell (with the $Pn3m$ space group) and some distortion of the cell shape. With the cubic phase as the reference structure, two sets of parameters, which are (i) the local mode for ion displacements [20, 29–33] and (ii) the antiferrodistortive mode for oxygen octahedron tiltings [23, 34–38], are used to describe the distortion. The effective Hamiltonian approach uses both local mode and local oxygen tilting as the dynamic variables to construct the energy terms, which are the basis for subsequent Monte-Carlo and molecular dynamics simulations.

The basic construct of the effective Hamiltonian is the ‘local mode’ on each lattice site (often denoted by $u_i$), these local modes on all the lattice sites together can simulate the unstable optic phonon branches and reproduce relevant physics [31]. With the local mode (and later the oxygen octahedron tilting) and properly constructed energy terms, Monte-Carlo or molecular dynamics simulations can predict the low energy structures of a given perovskite [39, 40]. Afterward, ab initio calculations [41] can be employed to verify if a proposed structure is indeed the ground state by comparing it to other structural phases. The comparison here requires the construction of various crystal phases for ab initio computation.

In constructing various structural phases, ion displacements are easy to understand and monitor. For instance, while BaTiO$_3$ has a complex sequence of ferroelectric phase transitions, the resulting tetragonal, orthohombic, and rhombohedral ferroelectric phases can all be understood in terms of the Ti ions shifting along different directions. On the other hand, the second type of distortion (which could also be part of the overall phase transition) involves small tiltings or rotations of the BX$_6$ octahedra (usually the oxygen octahedra), which is more difficult to deal with due to the corner sharing of the X on neighboring sites that constrains possible movements [42–44]. For instance, the TiO$_6$ octahedra in SrTiO$_3$ are not independent of each other and can only exhibit certain patterns. One possibility is that the TiO$_6$ rotate about the $c$-axis with neighboring octahedra rotating in opposite directions. Some perovskites (e.g., CaTiO$_3$) can demonstrate even more complex rotation patterns and it was Glazer who first proposed a systematic notation to describe such patterns [34, 35], now commonly known as Glazer’s notation.

Some software packages (e.g., POTATO and SPuDS [45, 46]) were developed to handle the octahedron tiltings in perovskites. However, since ion displacements associated with local modes are not included, their structural prediction may miss phases arising from ion displacements. In addition, the use of bond valence theory may not be as accurate as ab initio computation. The Python program PyTilting we will show here facilitates more accurate search of the stable structural phases. The program can systematically generate different structural phases encompassing distortions involving both the local mode and the octahedron tilting. The automation of the structure generation process will constitute an essential step in high-throughput ab initio computation [47–49].

## 2. Structural distortions

The perovskite structure contains a network of corner-sharing octahedra. Considering such constraints, the following rules apply to tilting: (i) the axis of the tilting can be parallel to any crystallographic axis, which requires a vector $\omega = (\omega_x, \omega_y, \omega_z)$ to describe it; (ii) the amplitude of each tilting may be different from the others, that is, $\omega_x$, $\omega_y$, and $\omega_z$ can be independent of each other; (iii) two subsequent layers being stacked along the tilting axis may be tilted in-phase or anti-phase. However, neighboring octahedron on the plane perpendicular to the tilting axis has to be in anti-phase.

For a $2 \times 2 \times 2$ supercell with periodic boundary conditions, there are 23 tilting patterns that can derive from the cubic perovskite [34, 36]. However, when ion displacement is involved and combined with these tiltings, the situation becomes quite complicated. It is not trivial in many cases to translate a desired distortion into a structure setup with proper space group and symmetry that can be readily employed in ab initio calculations. To address this challenge, we have designed programs to realize such distortions in terms of ion displacements, obtaining the low-symmetry structures from the cubic high-symmetry structure. In this section, we will first discuss the general features of octahedron tilting and ion displacement.

### 2.1. Octahedron tilting

Glazer’s notation has become the standard way to describe tilting distortions, concisely summarizing tilting patterns into strings such as $a^0b^+b^+$ and $a^0b^+b^-$. To decipher such strings, we first note that they can be categorized into three groups,
phase or out-of-phase rotation). A negative superscript (in adjacent layers are in the same or opposite directions (in-phase) tiltings around the $a$-axis, but counting along the $c$-axis, neighboring unit cells have the opposite (out-of-phase) tiltings around the $c$-axis.

As we can see, it requires some effort to decipher the tilting patterns specified by Glazer’s notation. To reduce this unnecessary work, our program fully understands the exact meaning of Glazer’s notation, can decode them, and construct the desired structure for an arbitrary (but properly chosen) supercell. For instance, it can easily reproduce the 23 simple tilting systems with a $2 \times 2 \times 2$ supercell, generating all the cases in which the oxygen octahedra have rotations on one, two, or three axes. Large supercells with more exotic tilting patterns can also be specified with minimal additional programming.

2.2. Ion displacement

Having considered tilting, we now focus on the ion displacement, which is easier because, unlike tilting, ion displacements on each unit cell can be independently specified by three numbers $u = (u_x, u_y, u_z)$ on each unit cell where $u_x$, $u_y$, and $u_z$ are the magnitudes of ion shifting along the $a$-, $b$-, and $c$-axis. With the information of the local mode, which specifies how the ions inside each unit cell relatively shift, the ion displacements can all be specified throughout the system.

To be compatible with the periodic boundary condition, patterns of the local mode over the $2 \times 2 \times 2$ supercell can be specified by using the high-symmetry points inside the Brillouin zone: $\Gamma = (0, 0, 0)$, $X = (1, 0, 0)$, $M = (1, 1, 0)$, and $R = (1, 1, 1)$ (or other points with larger supercells). For instance, the $\Gamma$ point specifies a uniform $u$ over the whole supercell. We note that the local mode patterns for $u_x$, $u_y$, and $u_z$ can be specified independently. Practically, the local mode can be determined from phonon eigenvectors (or eigenvectors of the force constant matrix) [30]. Here, for convenience, we usually just displace the B atom to achieve the desired low-symmetry structure. Employing more complex local modes is often inconsequential since the resulting structure will be further relaxed by ab initio softwares, most of which can be set to respect the starting symmetry of a given system.

3. Implementation

Figure 2 shows the flow of the program. It comprises of several steps from top to bottom: (i) first, the initial configuration is defined with the most basic parameters (e.g., atomic symbols), setting the ions to their ideal cubic position. A Python class Puc (primitive unit cell, PUC) is defined for this task; (ii) next, the unit cell information is inherited by the class Distortion, which builds a supercell by repeating the unit cell according to the grid and lattice constant parameters; (iii) in the next step, the program determines the structural distortion given by the user. If no distortion is desired, the system defaults to the parent phase ($Pm\bar{3}m$), otherwise the user’s input regarding the distortion is read; (iv) Glazer’s notation is decoded by the function
After setting up the PUC, the Distortion class builds a supercell encompassing many identical PUCs and setup the distortion on the supercell level, accommodating possible structural phases. The parameter grid = (n_x, n_y, n_z) specifies how many unit cells repeat along the a-, b-, and c-axis.

In summary, the program includes some basic constructs consisting of several parameters: (i) the atom symbols for ABX_3; (ii) the lattice constant; (iii) the grid parameter for supercell; and (iv) the a/c ratio. Other parameters specifying the actual distortions and their uses are discussed below.

3.2. Specifying distortions

Based on the two distortion mechanisms discussed in section 2, tilting and ion displacement need to be specified as input for the program.

3.2.1. Decoding Glazer’s notation. For tilting, the program needs to properly change the positions of oxygen atoms. Since Glazer’s notation is the standard way to describe the tilting in a perovskite system, it is natural to use it as the input for the program and their meaning needs to be properly decoded in the program.

In a Glazer’s notation, the superscript 0, +, or − corresponds to no tilting, in-phase, and out-of-phase tilting of neighboring oxygen atoms, respectively. Such tilting patterns correspond to high-symmetry points in the Brillouin zone that are Γ (k = [0, 0, 0]), M (k = [0, 1, 1]) and R (k = [1, 1, 1]). Due to the constraint of the corner sharing of octahedra, the supercell determines which point to choose. Let us use the tilting around the a-axis as an example (i.e., ω_x in the first group of a Glazer’s notation): (i) the superscript − means k_ω = [1, 1, 1] (R), i.e., ω_x changes its sign whenever it moves to the next nearest neighbor; (ii) the superscript + means k_ω = [0, 1, 1], i.e., ω_x changes its sign whenever it moves to the next first nearest neighbor along y or z, but keep the same sign when it moves along x; (iii) the superscript 0 means k_ω = [0, 0, 0], i.e., the same tilting on all sites, which is how Glazer’s notation is flawed. Similarly, the other two groups specify how ω_y and ω_z are arranged over the whole crystal.

The actual implementation to decode Glazer’s notation is shown in figure 3. Combining k_ω_x, k_ω_y, and k_ω_z, we know how the octahedron tilts in each unit cell. After determining the arrangements of ω_x, ω_y, ω_z, the program also checks if the input tilting angles are consistent with the arrangement, and if ω_x, ω_y and ω_z shall be equal to each other. For instance, the notation \(a^+c^-c^+\) can be a possible representation of a tetragonal crystal system where the lattice parameter a is equal to b, which gives \(ω_x = ω_y ≠ ω_z\). If inconsistency is encountered, the program will print warnings and stop its further execution.

3.2.2. Displacement. Two matrices are used to characterize ion displacements. The eigenvector of the local mode (soft mode) in perovskites can be characterized by four parameters: \(ΔA(ξ_A), ΔB(ξ_B), ΔO_p(ξ_{O_p})\) and \(ΔO_q(ξ_{O_q})\) [30], which corresponds to displacements of the A atom, B atom, the O atom forming the B–O bond along the displacement direction, and
Figure 3. Decoding Glazer’s notation. \( k_{\alpha y} \) and \( k_{\alpha z} \) are similarly treated as \( k_{\alpha x} \) shown here.

Figure 4. Mathematical representation of the displacement.

the other two O atoms forming the B–O bonds perpendicular to the displacement direction. Considering the fact that the \( x, y, \) and \( z \) directions are equivalent (for the cubic phase used as the reference structure), the displacements can be mathematically represented by a \( 5 \times 3 \) matrix \( dpq \) as shown in figure 4. The amplitude of the local mode is denoted by \( u = (u_x, u_y, u_z) \), which contains displacements along \( x (u_x) \), \( y (u_y) \), and \( z (u_z) \) directions represented by a \( 3 \times 3 \) diagonal matrix \( du \). The actual displacement for each atom can be realized by the matrix product of \( dpq \) and \( du \) as shown in figure 4.

Similar to setting the patterns for tilting, we also need to set the \( k \) vectors to specify how local mode \( du \) changes from one unit cell to the next. With \( k_{ux}, k_{uy}, \) and \( k_{uz} \) being independent of each other, for a \( 2 \times 2 \times 2 \) supercell, \( k_{ux}, k_{uy}, \) and \( k_{uz} \) can be chosen from \( \Gamma = (0,0,0), X = (1,0,0), M = (1,1,0), \) or \( R = (1,1,1) \).

3.3. Example input

To illustrate the use of the program, we show how to stepwise construct of bismuth ferrite (BiFeO3). It is known that BiFeO3 can have ferroelectric (R3c) and antiferroelectric phases (Pnma) in combination with its magnetic properties, making it a popular multiferroic material [50–53]. The R3c phase (space group: #161) can be thought of as stretching the ideal cubic structure in the [111] direction, which is made more complex by the \( a' - a' - a' \) tilting, resulting in a rhombohedral phase [52, 53].

```python
def decode_glazer(s):
    if len(s) != 6:
        print("Glazer notation has the form 'a-a-a-', your input seems incorrect.")
        exit()
    k_ox = [1,1,1]
    if s[1] == '-':
        k_ox = [1,1,1]
    elif s[1] == '+':
        k_ox = [0,1,1]
    elif s[1] == '0':
        k_ox = [0,0,0]
    else:
        print("Glazer notation has the form 'a-a-a-', your input seems incorrect.")
        exit()

Figure 3. Program input to setup basic properties of BiFeO3.

```
The program first needs the lattice constant and atom symbols to identify the material to be calculated. We set the lattice constant of BiFeO$_3$ to be 3.96 Å, with a $2 \times 2 \times 2$ supercell. The parameter $c/a$ accounts for the possible lattice stretch along the $c$ axis, which can be convenient sometimes but not always necessary ($c/a$ defaults to 1.0). The setup at this stage is shown in figure 5.

In the second stage, with the Glazer notation for BiFeO$_3$’s $R3c$ phase being $a' a' a'$, we enter the tilting angle $\omega = (0.1, 0.1, 0.1)$ in radian, which is just an estimate of the magnitude of tilting and complete setup for the tilting distortion as shown in figure 6. We also need to endow a small displacement by inputting the magnitude ($u$) and vector (local_mode) of the local modes. Assuming the amplitude of the local mode is given by $u = (u_x, u_y, u_z)$ as mentioned in the section 2.2, the program automatically calculates and actuates the displacement for each ion in a unit cell as shown in figure 4. Meanwhile, the wave vector for the local mode is imported as a matrix $k$ with the rows representing $k_{ux}$, $k_{uy}$, and $k_{uz}$. Knowing that the $R3c$ phase has polarization along the (111) direction, we set $u = (0.1, 0.1, 0.1)$ and the wave vector at the $\Gamma$ point ($k = [0, 0, 0]$) as shown in figure 6.

Finally, we generate the atoms object that can be used directly by ASE, GPAW, or exported to cif file. The symmetry of the generated structure can be checked by ASE as shown in figure 7.

4. Application

In this section, we apply the program to identify the most stable phase of a halide perovskite, that is CsSnI$_3$. Halide perovskite has attracted much attention for their use in solar cells for their high energy conversion efficiency and tunable band gaps [54, 55]. CsSnI$_3$ is an unusual perovskite that undergoes a series of complex phase transitions and exhibits near-infrared emission at room temperature. The phase-stabilized CsSnI$_3$ is important for its application in the photovoltaic and optoelectronic fields [54, 56, 57].

4.1. Phonon analysis

In order to reduce the number of possible structural phases, we perform a screening to eliminate certain phases in order to save time and computing resource by calculating the phonon band structure and performing some initial analysis that focuses on the unstable modes. For instance, negative (or imaginary) frequencies at the $\Gamma$ point are associated with uniform global displacement of ions, which often implies ferroelectricity.

For ion displacement, in addition to the $\Gamma$ point, other points from the Brillouin zone can also be used to specify the dipole patterns (possible choices are constrained by the size of the supercell). On the other hand, only two points are important for tilting, which are (i) the $M$ point, $q = (1/2, 1/2, 0)$ and (ii) the $R$ point, $q = (1/2, 1/2, 1/2)$.

The above analysis can be summarized into the flow chart in figure 8, where we assume the $M$ and $R$ point are only related to tiltings and the $\Gamma$ and $X$ point are related to displacements. The possibility that $M$ and $R$ points accommodate antiferroelectric phases requires additional analysis of the phonon eigenvectors at these two points.

If the phonon spectrum only has a virtual frequency at the $\Gamma$, the stable phase is most likely ferroelectric; with the $X$ point, other antiferroelectric phases also need to be considered.
For pure tilting, there are three scenarios: (i) the virtual frequency only appears at the $M$ point, resulting in six cases (out of 23) that need to be considered; (ii) the virtual frequency only appears at point $R$, then again resulting in six cases (out of 23); (iii) if both the $M$ and $R$ points have virtual frequencies, all 23 tilting patterns need to be considered. The most complicated scenario occurs when all the high symmetry points have virtual frequencies, resulting in the superposition of tilting and displacement that requires further analysis.

4.2. Results

The phonon calculation for CsSnI$_3$ was done using Phonopy [58] with GPAW. To get accurate results, we have used $2\times2\times2$ supercell in the phonon calculation, which agrees with reference [59] very well. The phonon spectrum shown in figure 9 clearly demonstrates that CsSnI$_3$ has the instabilities at the $M$ and $R$, and all the tilting patterns are involved. On the other hand, there is no instability at the $\Gamma$ or $X$ point, which eliminates many possible structural phases.

To find the most stable structural phase, we use the program to generate all the 23 tilting patterns for ab initio calculation using the projector augmented plane wave (PAW) method as implemented in the GPAW software package [60, 61] with the Perdew–Burke–Ernzerhof (PBE) functional [62]. A $2\times2\times2$ Monkhorst–Pack [63] sampling is used for the $k$-space integration. The valence orbitals used in the first-principles calculations are: Cs (5s6s5p), Sn (5s5p4d) and I (5s5p). The structures are relaxed with a plane-wave cutoff of 900 eV until atomic forces fall below 0.05 eV Å$^{-1}$. As shown in table 1, it is clear that the highest energy belongs to the parent phase of Pm$\bar{3}$m, while the phase with the lowest energy has the tilting $a^+b^-b^-$.

Table I shows all the 23 tilting patterns for CsSnI$_3$ with its Glazer notation and symmetry group. We note the results are consistent with the tilting systems proposed by Glazer, except no. 5 ($a^+b^+b^-$) and No.7 ($a^+a^-a^-$). These two systems should have the P4$_2$/nmc phase (space group: 137) instead of the Pmma phase (space group: 59) that was initially proposed [34], which has been confirmed by other literature [23, 36, 38, 64].

The energy of the four systems no. 8 to no. 11 is quite close to each other in energy, with a difference of $\sim 2.52$ meV. Coincidentally, this phenomenon also appears for no. 1 to no. 3, and their energy difference is as small as $\sim 1$ meV, and no. 8 and no. 10 with difference less than 1 meV. It is also worth mentioning that even if some configurations have the same space group, their tilting patterns can still be different (see no. 1, 2 and 15 in table 1), resulting in different energies.

5. Discussion

5.1. CsSnI$_3$

The space groups and the most stable structure predicted here agree well with experimental and other theoretical or computational results [54–57, 59]. For CsSnI$_3$ crystal (black phase), it is known to undergo a number of successive phase transitions with temperature, corresponding to rotations and rearrangements of the SnI$_6$ octahedron. The cubic phase (B-$\beta$) is only stable at high temperature, which turns into the tetragonal P4/mmb phase at 380 K (B-$\beta$), then to the orthorhombic Pnma at 300 K (B-$\gamma$).

Table 1. 23 tilting systems for CsSnI$_3$ and their energies (the energy of the Pm$\bar{3}$m phase is used as the reference energy).

| Number | Tilting | Symmetry | Energy (meV) |
|--------|---------|----------|--------------|
| 3 tilts |         |          |              |
| 1      | $a^+b^+c^+$ | Immm (#71) | −83.7 |
| 2      | $a^+b^+b^+$ | Immm (#71) | −83.0 |
| 3      | $a^+a^-a^+$ | Imh (#204) | −82.5 |
| 4      | $a^+b^-c^+$ | Pmma (#59) | −130.2 |
| 5      | $a^+a^-c^+$ | P4$_2$/nmc (#137) | −118.6 |
| 6      | $a^+b^-b^+$ | Pmma (#59) | −124.9 |
| 7      | $a^+a^-a^+$ | P4$_2$/nmc (#137) | −118.9 |
| 8      | $a^+b^-c^+$ | P2$_1$/m (#11) | −150.4 |
| 9      | $a^+a^-c^+$ | P2$_1$/m (#11) | −144.2 |
| 10     | $a^+b^-b^-$ | Pnma (#62) | −151.2 |
| 11     | $a^+a^-a^-$ | Pnma (#62) | −148.8 |
| 12     | $a^-b^-c^-$ | P1 (#2) | −97.8 |
| 13     | $a^-b^-b^-$ | C2/c (#15) | −92.6 |
| 14     | $a^-a^-a^-$ | R3c (#167) | −91.4 |
| 2 tilts |         |          |              |
| 15     | $d^+b^+c^+$ | Immm (#71) | −91.6 |
| 16     | $d^+b^+b^+$ | Imm (#139) | −88.8 |
| 17     | $d^+b^+c^-$ | Cmcn (#63) | −124.6 |
| 18     | $d^+b^-b^-$ | Cmcn (#63) | −122.1 |
| 19     | $d^+b^-c^-$ | C2/m (#12) | −103.9 |
| 20     | $d^+b^-$ | Imma (#74) | −100.8 |
| 1 tilt |         |          |              |
| 21     | $d^+d^+c^+$ | P4/mmb (#127) | −82.9 |
| 22     | $d^+d^-$ | P4/mcm (#140) | −83.9 |
| 23     |         | Pm$\bar{3}$m (#221) | 0.0 |
The tolerance factor $t$ is a powerful predictor of tilting distortions. It turns out that the case size for the Cs atom in the ideal cubic phase, which is set by the Sn–I octahedron size, is slightly too large by the definition given by Benedek and Fennie [65], $t = R_{AC}/\sqrt{2}R_{BC}$ with $R_{AC}$ and $R_{BC}$ being the ideal bond lengths. Using the ideal bond lengths based on Shannon ionic radii [66], we find $t = 0.90$ for CsSnI$_3$, indicating that tilting can suppress ferroelectricity, consistent with the general trend of adopting the Pnma phase with $t < 1$. The driving force for this stabilization is to optimize the environment for the A cation (Cs atom here) [59]. Moreover, the $\alpha \rightarrow \beta$ phase transition corresponds to the Glazer tilting $a^\alpha d^\alpha c^\alpha$, and the $\gamma$ phase is characterized by both octahedral twists about the $c$ axis and tilts about the tetragonal $a$ axis, which refers to the Glazer notation $a^\gamma b^\gamma b^\gamma$.

It is important to note that structural distortions can remarkably change the electronic properties of a perovskite. For instance, using local-density approximation (LDA), Huang and Lambrecht [56] have shown that $\alpha$-CsSnI$_3$ has a band gap of 0.29 eV, while the distortion associated with the $\gamma$-CsSnI$_3$ increases the band gap to 0.503 eV. They also employed the quasiparticle self-consistent GW method, leading to good agreement with experiments [56, 67]. Such results clearly show that the distortion $a^\alpha b^\alpha b^\alpha$ in the orthorhombic $\gamma$ phase has substantial impact on CsSnI$_3$’s electronic properties. With the structural phases generated by PyTilting, the influence of tilting and ion displacement can be readily investigated with additional ab initio calculations.

### 5.2. Tilting

Our results indicate that the tilting patterns can be divided into several groups, reflecting their geometry features: (1) $a^\alpha b^\alpha c^\alpha$ (no. 1–3); (2) $a^\alpha b^\alpha c^\alpha$ (no. 4–7); (3) $a^\alpha b^\alpha c^\alpha$ (no. 8–11); (4) $a^\alpha b^\alpha c^\alpha$ (no. 12–14); (5) $a^\alpha b^\alpha c^\alpha$ (no. 15, 16); (6) $a^\alpha b^\alpha c^\alpha$ (no. 17, 18); (7) $a^\alpha b^\alpha c^\alpha$ (no. 19, 20); (8) $a^\beta d^\beta c^\beta$ (system no. 21) and (9) $a^\beta d^\beta c^\beta$ (system no. 22). The tilting patterns of the same group tend to have extremely close energy, as demonstrated in figure 10 because their mutual conversion only requires a certain adjustment of the tilting angle rather than a change of the tilting pattern, and such adjustment can be actuated in ab initio calculations. For instance, $a^\alpha b^\alpha c^\alpha$ could become very close to $a^\alpha b^\alpha b^\alpha$, $d^\beta b^\beta c^\beta$ similar to $d^\beta b^\beta b^\beta$. This is likely because, after relaxation, the structure changes towards a high-symmetry configuration, in which the occurrence of certain symmetry elements gives rise to the same tilting angles along different axes.

According to our results, in each group, two (or three) axes with the same tilting angle, will result in increased energies. In addition, the $R$-point-related tilting patterns seem to have lower energy than $M$-point-related tilting patterns when other factors being equal (e.g. system no. 1 and 12, no. 2 and 10, no. 21 and 22). The 23 tilting systems of CsSnI$_3$ shown in table 1 indicate that the energy of a structure mainly depends on its crystal structure.

Finaly, it should be mentioned that, for some tilting patterns, small distortions (in addition to tilting) of the octahedra must occur to preserve the connectivity of the octahedra. Such a requirement results in symmetries (and space groups) that are different from expectations purely from the consideration of tilting. For instance, the four tilting patterns in group 2 (no. 4 ~ 7) were initially proposed to produce an orthogonal phase (with the space group of 59) [34]. However, later research [23, 36, 38, 64] examined the geometrical constraints and found that two of them have the $P4_2/mmc$ symmetry, requiring extra distortion to the octahedra. In other words, such tilting patterns cannot be accommodated without changing the B–O bond lengths. Due to this type of additional distortion, tilting...
patterns no. 5 and 7 are able to form a more symmetrical tetragonal phase, and resulting in higher energies than no. 4 and 6, respectively.

5.3. The program

Finally, let us briefly discuss the program itself. The program PyTilting is designed to automatically generate low-symmetry structural phases involving distortions of both tilting and ion displacement. The program has the following features and advantages: (i) it can be used to build complex phases of a perovskite, which can be used in ab initio computation to predict the stable ones and serve as the starting point to obtain various physical properties; (ii) it allows the user to set up any supercell size that enables the investigation of complex perovskites with mixed A-site or B-site cations (some additional scripts will be needed); (iii) it is designed to easily interface with the ASE atoms object [68] or export cif files, which can be conveniently imported into other ab initio softwares or directly used as input (for e.g., GPAW [61]). Finally, the whole program and its documentation are freely available online [69].

On the other hand, there are limitations to PyTilting. The program is designed to work best with pure bulk perovskite. For complex perovskites with mixed A-site or B-site cations, after the desired structural phases are generated, one may need to write a small additional program to set the desired atom in each PUC. Since each PUC contains information regarding its location and atoms, this additional program is not hard to write. For thin films, ASE (or other software, e.g. VESTA [70]) can be used to read the output generated by PyTilting and perform necessary operations to obtain a desired thin film. Moreover, the Jahn–Teller distortion, which is directly related to oxygen octahedron distortion (e.g. its elongation) cannot be treated in the present program.

6. Summary

In this work, we have developed a program to generate various tilting patterns for perovskites with the ability to set up ion displacements as well. This program can generate desired configurations for arbitrary superlattices, which is useful to deal with complex structural phases or complex perovskites made by doping or solid solution. The program adopts two strategies to deal with two major distortions with perovskites: (1) for the tilting, we derive 23 tilting patterns based on the Glazer notation; (2) use local-mode-based displacements to form polar phases. The successful combination of these two strategies enables us to generate hybrid structural phases made of both tilting and ion displacement.

To test the program, we have taken CsSnI3 as an example and used the program to find its most stable structural phase. The strategy is to first obtain the phonon spectrum in order to reduce the number of different phases to examine. With the aid of our software package, the 23 tilting systems are built and their energies are calculated. It is found that the Pnma is the most stable phase, corresponding to the $a^{-} b^{+} b^{-}$ tilting with its energy reduced by $\sim 150$ meV from the cubic Pm$\overline{3}$m phase.

The computer program is written in Python, which can directly generate configuration files, or easily be integrated into other software packages for ab initio calculations. It is an open source program which is currently online to be downloaded and used. Since our program can build arbitrary supercells, doping effects on a given structure can be managed by replacing certain ions in the system after the desired structural phases are generated. With the availability of such a tool, we can build a vast number of different structural phases, the next step will be finding effective ways to screen those candidates quickly to provide us the most stable phase of a given perovskite.

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