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Perspective

Atomistic models of metal halide perovskites

Aron Walsh[1,2,3,*]

SUMMARY

Metal halide perovskites exhibit a variety of weird and wonderful macroscopic properties, but it can be challenging to connect them to the underlying microscopic structure. Computer simulations at the atomic scale, based on classical and quantum techniques, have been valuable for making this connection. Beyond computing the optoelectronic properties of known compositions and structures, perovskite modeling has become increasingly predictive in the description of emergent properties at surfaces and interfaces, as well as providing important directions for the exploration of new crystal chemistries in perovskite-inspired materials.

INTRODUCTION

The crystal structure of perovskite[1] is deceptively simple. The ideal ABX_3 cubic polymorph can be described by a primitive lattice with an A-site cation placed at ($^1/_2$, $^1/_2$, $^1/_2$), a B-site cation at (0, 0, 0), and an X-site anion at (0, 0, $^1/_2$) in the repeating crystallographic unit cell. The original perovskite mineral is formed from A = Ca^{2+}, B = Ti^{4+}, and X = O^{2-}. However, the key to the success and popularity of perovskites in materials science is their flexibility. The compositions can vary with the X site filled by simple anions such as iodide (I^-) or complex molecular anions such as formate ($COOH^-$). The structure can also be deformed, through displacements and rotations of the atomic building blocks, which leads to an extended family of lower-symmetry polymorphs and phenomena related to reversible strain (ferroelasticity) and electric polarization (ferroelectricity).[2,3] The chemical identities of A, B, and X can also be tuned to enable exotic properties including multiferroic (e.g., $BiFeO_3$) and superconducting (e.g., the cuprate family) states.[4]

Before the intensive study of metal halide perovskites that stemmed from the seminal 2009 solar cell report,[5] the physicochemistry of metal oxide perovskites was well explored.[6] These materials form a significant fraction of the earth's crust and have established applications ranging from catalysts to solid-state electrolytes. While there has been significant transfer of knowledge from the metal oxide community to the field of metal halide perovskites, the halides bring their own set of peculiarities and complexities. The lower formal oxidation states of the constituent ions, e.g., $Cs(I)Pb(II)I_3$ versus $Ca(II)Ti(IV)O_3$, result in softer crystals that are more sensitive to their environment and to thermal, chemical, and mechanical stressors.[7] Their unusual materials and device behavior has led to descriptions including "soft as jelly"[8] and the use of terms such as "plastic crystal" and "liquid crystal duality."[9]

As technologies based on metal halide perovskites have rapidly developed, so too has our understanding of the underpinning materials chemistry and physics. There has been close collaboration and interplay between experimental measurements and materials modeling throughout this process. The impacts of *in silico* methods

Progress and potential

Materials modeling can provide a connection between the microscopic structure and macroscopic properties of crystals. The predictive power for computer simulations of metal halide perovskites depends on several factors, including: (1) representation of the crystal structures, which are often disordered and contain high concentrations of defects; (2) description of interatomic interactions, in which non-local exchange-correlation effects and relativistic spin-orbit coupling play important roles; and (3) treatment of the relevant length scales and time scales, which can range from picoseconds for lattice vibrations to nanoseconds for charge carrier trapping. Due to their complexity, these materials have become a test bed for a wide range of advanced computational techniques.

have ranged from understanding the microscopic nature of chemical bonding, through to the macroscopic crystal response and the exploration of new chemical spaces.[10] This includes studies involving lattice vibrations and molecular rotations, charged point defects and dielectric response, to descriptions of emergent behavior including current-voltage hysteresis and light-induced phase transformations. In this article, I provide my perspective on the growth and continued evolution of the field.

PAST

Quantum mechanical simulations of metal halide perovskites were reported almost two decades ago. Electronic band structure calculations of the $CsPbX_3$ and $CH_3NH_3PbX_3$ (X = Cl, Br, I) series were published in 2004,[11] followed by reports on Sn-based compounds,[12] and the behavior of Pb and Sn compounds under pressure.[13] In 2013, a handful of computational studies were published,[14–18] covering the structural, dielectric, and electronic properties. By then it was recognized that these materials were semiconductors with small electron and hole effective masses, large static dielectric constants, and wherein spin-orbit coupling played an important role in shaping the conduction band of Pb-containing compounds. These studies have been followed by a rapid growth in research outputs covering a range of modeling techniques and atomistic processes.

The starting point for most materials modeling studies of metal halide perovskites has been from crystal structures solved using diffraction techniques. The presence of light (C, N, H) and heavy (I, Pb) atoms in the same material makes complete structure determination challenging for organic-inorganic crystals. High-quality refined structures for several halide perovskites have been reported from both X-ray diffraction[19,20] and neutron diffraction[21,22] techniques. It must be recognized that the resulting crystal structures are models averaged over space and time, where disorder in the orientation of molecular cations is represented by partial occupancy of crystallographic sites or large anisotropic thermal displacements. Such statistical descriptions of disorder can pose difficulties for mapping onto a static structure model suitable for running atomistic computer simulations.

An important theme in the first wave of modeling studies on metal halide perovskites was therefore the understanding of structural dynamics and the connection to optoelectronic properties of relevance to applications in solar cells and light-emitting diodes. This involved going beyond static crystal models, which are the norm for first-principles studies of materials based on density functional theory (DFT). A number of routes were explored including molecular dynamics (time evolution following classical mechanics),[23] lattice dynamics (harmonic and anharmonic descriptions of crystal vibrations),[24,25] and Monte Carlo (finite sampling of the configurational phase space).[8] At the same time, approaches for going beyond DFT were being explored for description of the electronic band structures and optical spectra, including quasiparticle GW corrections (more sophisticated quantum mechanical treatments of electron-electron interactions).[26–28]

Three of my personal highlights are illustrated in Figure 1. The first involves the librations and rotations of methylammonium inside the inorganic cage, where calculated picosecond time constants for molecular motion could be compared with measured inelastic neutron scattering[29] and time-resolved infrared spectroscopy.[30] In more recent work, solid-state nuclear magnetic resonance has proved a valuable measurement tool to probe dynamics for a range of cations.[31] The second highlight represents the flexibility of the inorganic cage itself, where low energy and slow

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[1]Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK

[2]Department of Materials Science and Engineering, Yonsei University, Seoul 03722, South Korea

[3]Twitter: @lonepair

*Correspondence: a.walsh@imperial.ac.uk

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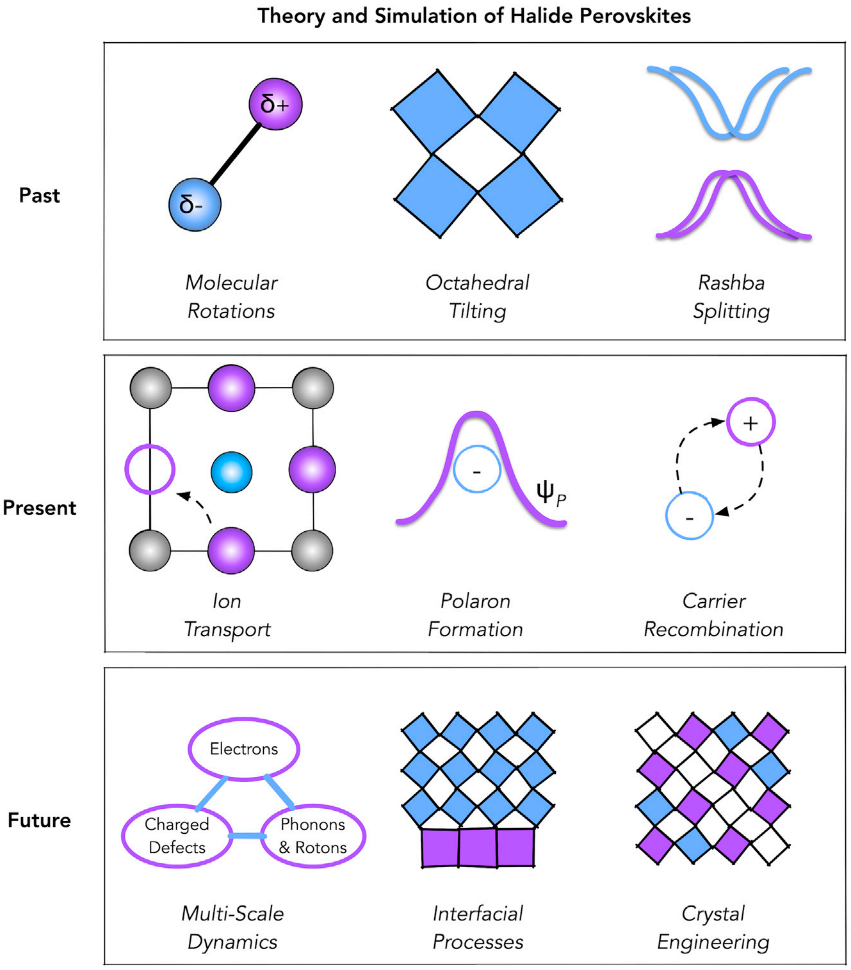

Figure 1. Illustration of the evolution in atomistic computer simulations of metal halide perovskites

(<1 THz) octahedral tilting can persist even in the nominally cubic phase, which can be observed from measured pair-distribution functions.[32] Local structural deformations are now established to occur in both hybrid and inorganic perovskites.[33] The third highlight is the consequence of the crystal disorder and symmetry lowering: spin splitting of the electronic band-edge states, which was first predicted and later observed in the lead halide perovskites.[34] The so-called Rashba-Dresselhaus effect involves spin-orbit coupling in a non-centrosymmetric environment and can be measured directly through angle-resolved X-ray photoemission. It is worth noting that as the technique probes filled electronic states, valence band splitting is more easily observed than conduction band splitting, while the latter is calculated to be much larger in these crystals.[34]

One question that these and related explorations created was how the apparent atomic-scale disorder and high device performance of halide perovskites could coexist. The short answer is that, serendipitously, the dominant structural distortions result in local band-gap increases rather than decreases.[35] This behavior of perovskites contrasts with conventional perceptions of disorder in covalent semiconductors, which is linked to the formation of deep states and large Urbach tails.[36] Here, no sub-band-gap states are generated that are active for electron-hole recombination. In fact, several beneficial effects can be inferred, including an enhancement of the dielectric screening that helps to separate excitons and limit carrier scattering by charged point defects. In addition, the associated electrostatic potential fluctuations can emulate a bulk heterojunction within a single-phase material[7]—the topology of these fluctuations will determine whether their effect is beneficial or detrimental to photovoltaic performance.

PRESENT

As the microscopic understanding and models of the structural behavior improved, new directions were stimulated by anomalies that were being observed in the photophysical response of halide perovskite crystals and films. These include the notorious current-voltage hysteresis in solar cells[37] and slow cooling of hot carriers in solar cells,[9] as well as phase separation that occurred upon illumination.[38] A breakthrough at the time, but not unexpected from the older literature on metal halides, was recognizing that these materials are mixed ionic-electronic conductors.[39,40] Rather than being straightforward semiconductors, where electron and hole transport is dominant, charged defects can also drift and diffuse. The mixed ionic-electronic conduction character has implications and opportunities that are still being studied, in particular using impedance spectroscopy to build effective circuit diagrams that capture both bulk and interfacial contributions to polarization and device operation.[41]

As the field matured and shifted to more quantitative predictions, special attention was paid to the selection of theoretical models necessary to describe optoelectronic processes in metal halide perovskites. When applying DFT to crystals, one can generally expect that standard exchange-correlation functionals within the local density approximation (LDA) and generalized-gradient approximation (GGA) provide a reasonable description of crystal structure parameters and thermodynamic quantities. However, there are three critical issues that can affect optoelectronic properties: (1) band-gap underestimation; (2) band-edge misalignment; and (3) wavefunction delocalization. These three issues are important for electronic application of perovskites in general, but are compounded for point defect processes, for which the description of electronic transitions between localized defect states with respect to the delocalized valence and conduction band edges of the host material are critical. It quickly became apparent that even the qualitative description of defects in lead halide perovskites requires a higher level of theory than LDA or GGA.[42] The use of a hybrid exchange-correlation functional including spin-orbit coupling has become the standard, albeit at great computational expense. Some studies make strong claims based on lower levels of theory, but their conclusions should be treated with caution.

Nonetheless, there is a growing body of studies providing deep insights into the point and extended defect properties of perovskites, for example, probing variations in the activation energies for charged vacancy-mediated diffusion in response to external stimuli such as pressure[43,44] or the charge transitions associated with interstitial defects.[45–47] I had a particular fascination with the formation of open-shell spin-$^1/_2$ defect complexes associated with I–I bond formation due to their known occurrence in binary metal halides. Such dimers can form from native hole trapping that brings two X-site anions in close contact (V center) or is mediated by an interstitial defect (H center).[48] For $CH_3NH_3PbI_3$, Ambrosio et al. showed that formation of V centers in the bulk was unfavorable; however, trapping is more likely at surface terminations.[49] We have recently probed the energy landscape for a

Shockley-Read-Hall process involving the iodine interstitial.[50] Electron trapping at the neutral interstitial site is rapid, with a large structural distortion that is facilitated by distortions in the BX_3 octahedral networks. The magnitude of the response is seen in the Huang-Rhys factor, S. While a value of $S < 1$ is associated with weak electron-phonon coupling and $S = 75$ is found for the extreme example of the DX center (Si in GaAs),[51] a value as large as $S = 350$ is predicted for electron trapping by the iodine interstitial in $CH_3NH_3PbI_3$. This study was demanding in terms of both human and computing time owing to the softness of the energy landscape for defect formation with a variety of saddle points and local minima that can be accessed by a single defect species. The search and identification of stable and metastable defect structures is a topic of growing importance in computational materials science.[52]

PROBLEMS

There is now a reasonable understanding of the nature of charge carriers in metal halide perovskites, where the interplay between electronic band dispersion and dielectric polarization gives rise to large polarons.[53] These are diffuse charge carriers that interact weakly with the lattice—the associated scattering between electrons and optical phonon modes limits the room temperature mobility.[54] There are exceptions, in particular, for lower-dimensional perovskite-related materials where charge localization is more likely to occur.[55] However, current microscopic theories are incomplete and fail to incorporate the full range of time and length scales relevant to these materials. Most theories of electron-phonon scattering are valid in the small displacement limit: here we have large amplitude displacements and strong phonon-phonon interactions, coupled with a complex potential energy landscape that features correlated disorder. On top of this is the distribution and transport of charged defects, and the influence of temperature and illumination. Improved models for multiscale carrier dynamics at room temperature may draw from the successes of charge transport modeling in the fields of amorphous semiconductors and conducting polymers.

Another problem is the treatment of extended defects including surfaces and interfaces, where the structure and stoichiometry may deviate largely from the bulk crystal. There are published models of perovskite grain boundaries[56] that are now supported by advances in high-resolution microscopy, which provide deeper insights into crystal orientations and terminations.[57] An additional layer of complexity beyond the coexistence of perovskite polymorphs (different tilting patterns) is the mixing of polytypes (different stacking sequences).[58] Such phase inhomogeneity is likely connected with defect distributions and issues associated with scale-up from small-area to practical large-area perovskite devices. This is an area where atomistic models can surely help to provide valuable insights and direction.

POSSIBILITIES

While the foregoing perspective mainly concerned regular ABX_3 perovskites, there is a growing family of perovskite-related and perovskite-inspired materials.[59] In some cases, these are related to regular perovskites through modification of the structure (e.g., in vacancy ordered $A_2B_3X_9$ crystals), while in others they share common precursors and adopt non-perovskite structures (e.g., A_2BX_4 and A_2BX_6 systems).[60] They can exhibit properties, such as high photoluminescence quantum yields, that surpass the parent ABX_3 systems, and there remains a large composition-structure space to be mapped out. Advancements in combinatorial and automated synthetic exploration are being applied to navigate this new materials space to increase performance, eliminate toxic or unstable components, or enable new functionality. This is a direction whereby the power of materials modeling, in the form of both traditional numerical first-principles approaches and statistical techniques drawing from the machine-learning community, can be showcased.

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AUTHOR CONTRIBUTIONS

A.W. wrote the manuscript.

DECLARATION OF INTERESTS

The author declares no competing interests.

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