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Introduction to Perovskite

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1.1 Evolution of Perovskite

Perovskite refers to a crystalline structure and extends to all the materials sharing this structure, despite the fact that it can present very different nature and properties. Initially, perovskites just denoted metal oxide minerals with a crystallography family of ABO_3 stoichiometry. The beginning of perovskite dates back to the discovery of chlorite-rich skarn at the Ural Mountains by the mineralogist German Gustav Rose in 1839. The component $CaTiO_3$ was found in this mineral and named after the notable Count Lev A. Perovski (1792–1856), president of the Russian Geological Society. Thereafter, many metal oxides with perovskite structures, such as $BaTiO_3$, $PbTiO_3$ and $SrTiO_3$, were widely studied. Many of the oxide perovskites were found to exhibit ferroelectric or piezoelectric properties [1–3].

More than 50 years after the discovery of oxide perovskite, a series of lead halide compounds with the general formula $CsPbX_3$ (X = Cl, Br, I) were synthesized by Wells [4]. These metal halides were later proved to have a perovskite structure, ABX_3, which is cubic at high temperatures and transforms from a tetragonally distorted structure at a lower temperature. The tunable photoconductivity of $CsPbX_3$ has drawn much attention to the electronic property study, and also evolved the idea of organic molecules addition [5, 6]. Weber discovered that the organic cation methylammonium ($CH_3NH_3^+$) substitutes for Cs^+ form $CH_3NH_3MX_3$ (M = Pb, Sn, X = I, Br) and published the first crystallographic study on organic lead halide perovskites [7, 8].

At the end of the twentieth century, abundant organic–inorganic halide perovskites were synthesized by Mitzi et al. [9–11]. Organic molecules, such as small and large organic cations, breathe new life into halide perovskite, embracing more diverse structures and physical properties in optoelectronic, photovoltaic, ferro- and antiferromagnetic, and non-linear optical fields. In addition to flexible components and versatile functionality, the low-forming energy makes halide perovskites facile

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to be fabricated into films, which makes them a promising material for commercialization in next-generation semiconductors, and their interest in the development of light-emitting diodes (LEDs) and transistors was demonstrated.

1.2 Structure of Perovskite

In a traditional view, perovskite represents a crystallographic family with the chemical formula ABX_3, in which A and B are cations and X is an anion. The ideal perovskite is a cubic structure, having B cations as sixfold coordination surrounded by an octahedron of X anions, and A cations as 12fold cuboctahedral coordination, see Figure 1.1. Taking inorganic perovskite $CsPbI_3$ as an example, the Cs^+ cations are shown at the corners of the cube, and Pb^{2+} cations are in the center with I^- anions in the face-centered positions. In three-dimensional (3D) perovskites, all six anions at the corners of the octahedra, with Pb at the center, are shared with the six nearest octahedra, see Figure 1.1. When large cations are included in the structure, not all the six halides can be shared with other octahedra, forming 2D, 1D, or 0D perovskite-inspired materials. Many composition types of perovskites have been reported, involving lead halide perovskite, all-inorganic cesium/rubidium lead halide perovskite, lead-free or lead-low halide perovskite, and halide double perovskite, as it will be extensively discussed in this book.

In the case of organic–inorganic perovskite, at least one of the ions in ABX_3 is organic, e.g. $MAPbI_3$ and $FAPbI_3$ (MA is methylammonium, $CH_3NH_3^+$; FA is formamidinium, $HC(NH_2)_2^+$). Recently, metal-free perovskite has also been synthesized with the chemical formula ANH_4X_3, where A is a divalent organic cation, and X is halogen ions, e.g. MDABCO–NH_4I_3 (MDABCO is *N*-methyl-*N*′-diazabicyclo[2.2.2]octonium).

Several conditions must be satisfied in order for perovskite structure to be formed. Generally, the valences of A and B cations must total to three times those of the X anion to preserve charge balance. Furthermore, the perovskite structure can only

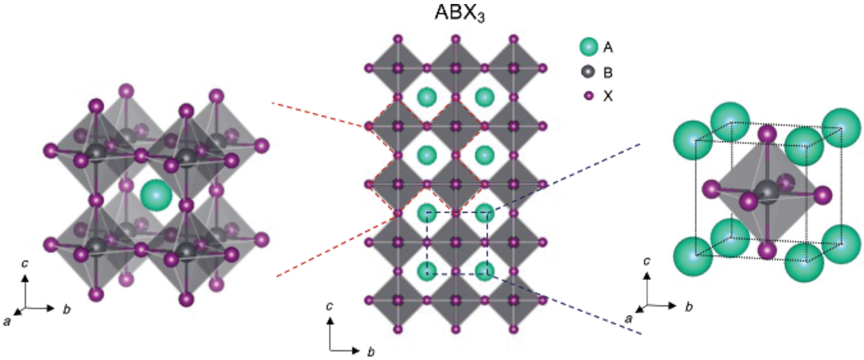

Figure 1.1 Crystal structure of 3D cubic perovskite. Cation A is located in the void between the BX_6 octahedra. In a crystal unit cell, A is located in the corners, B is in a body-centered position, and X is in a face-centered position.

tolerate particular ion combinations because of the size restrictions between ions in order to preserve the anion-corner-sharing structure. This ionic size relationship is expressed in terms of the Goldschmidt tolerance factor τ, which is correlated to the ionic radii r_A, r_B, and r_X [12]:

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

where τ is an empirical index to predict the different structures of ABX_3. When $0.9 < \tau < 1$, the perfect cubic perovskite structure is formed; when $0.8 < \tau < 0.9$, the distorted perovskite structure with tilted octahedra is preferred; when $\tau < 0.8$ or $\tau > 1$, the structure is non-perovskite [13]. Another factor is the octahedral factor,

$$\mu = {}^{r_B}/{r_X}$$

which determines whether the B atoms will favor the octahedral coordination of X atoms over greater or lower coordination numbers; this criterion is met for values between 0.4 and 0.9 [14]. In addition to size and charge, the coordination preference of metal ions is also taken into consideration.

Nowadays, many structural variants of perovskite have been synthesized, and they are all derived from the original 3D perovskite structure based on the corner-sharing BX_6 structure. Although the ABX_3 perovskite structure has rigid constraints, the low-dimensional perovskite allows for broader structural and compositional tunability. When the 3D perovskite is conceptually excised into slices, the size restrictions for the A', which is the interlayer cation, are lifted for low-dimensional derivatives. According to the connectivity, the segregated component made of BX_6 octahedra is usually present 2D, 1D, or even separately 0D types, see Figure 1.2. From the perspective of the dimensions of morphologies, perovskite materials can be categorized into 3D bulk, 2D nanoplatelets, 1D nanowires, and 0D nanocrystals.

In the case of 2D perovskite, such structures are made up of a cation monolayer or bilayers alternating with sheets of the corner-sharing BX_6 octahedra. The 2D perovskite features mono- or diammonium cations A', showing the chemical formulas of A'_2BX_4 and $A'BX_4$, which are frequently referred to as Dion–Jacobson (divalent A') or Ruddlesden–Popper (monovalent A') phases [15]. In A'_2BX_4 formed by monovalent cations, such as PEA^+ (phenethylammonium, $C_6H_5(CH_2)_2NH_3{}^+$) and BA^+ (butylammonium, $C_4H_9NH_3{}^+$), a van der Waals gap was generated by a bilayer of monovalent cations from two neighboring lead halide sheets. Instead, in the $A'BX_3$ system, each pair of cations can be substituted by a single divalent cation with tethering groups at each end to attach to neighboring halide sheets. The other low-dimensional perovskite derivatives feature much more separated BX_6 links, including 1D "pillar"-like BX_6 octahedra connected chains and 0D isolated "dot"-like octahedra, respectively; see Figure 1.2. Especially, the BX_6 connectivity can also be separated by the different compositions, which form the mixed perovskites known as *pseudo* members.

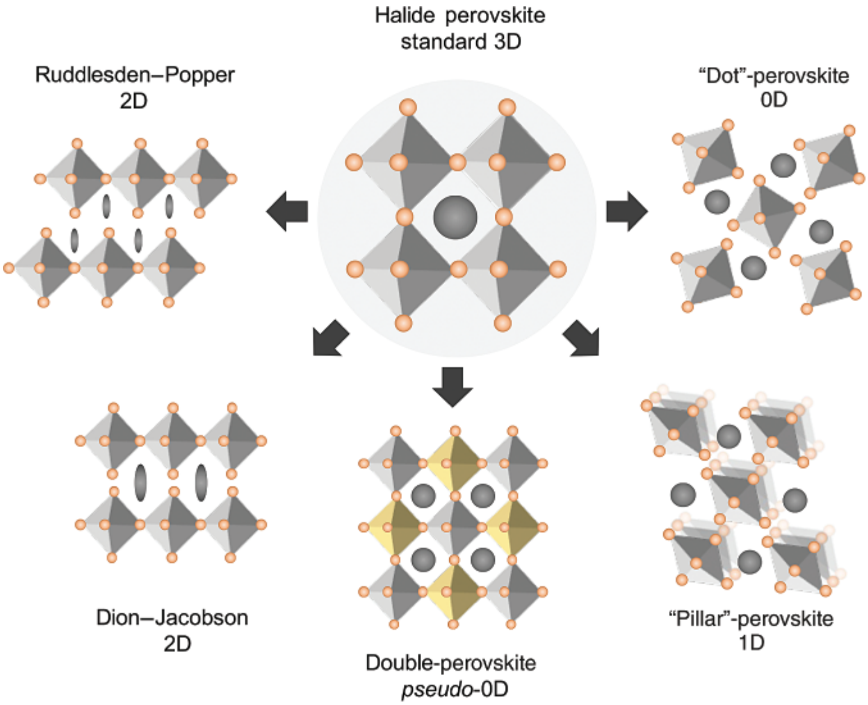

Figure 1.2 Halide perovskite family tree. Schematic illustration of standard 3D perovskite and the low-dimensional derivates, including Ruddlesden–Popper 2D, Dion–Jacobson 2D, "Pillar"-perovskite 1D, "Dot"-perovskite 0D, and the double perovskite *pseudo*-0D perovskite.

1.3 Property and Application of Perovskite

Early research on perovskite oxides focused on the biaxial optical properties and ferroelectric properties. In contrast, halide perovskites open the door to studying the optoelectrical properties because of their unique electronic structures, including direct tunable bandgap, strong absorption, small and balanced electron-hole effective masses, and defect resistance, thereby improving their photoluminescence quantum yield. Moreover, the unprecedented flexibility of perovskite composition can be brought about by organic or inorganic components with optical or electronic functionalities. The most important advantage of halide perovskites is their facile, accessible, high-quality crystals and films, enabling structure–property correlation exploration and prototype device optimization. Thus, halide perovskite semiconductors will hold promise for a variety of fascinating applications, including photovoltaics (PVs), LEDs, photodetectors, memristors and lasers, see Figure 1.3, just to cite the ones that probably receive more attention. In addition to this versatility, it is important to highlight the enormous potential for the development of high-performance devices on flexible substrates, extending the application range of high-performance rigid photovoltaics.

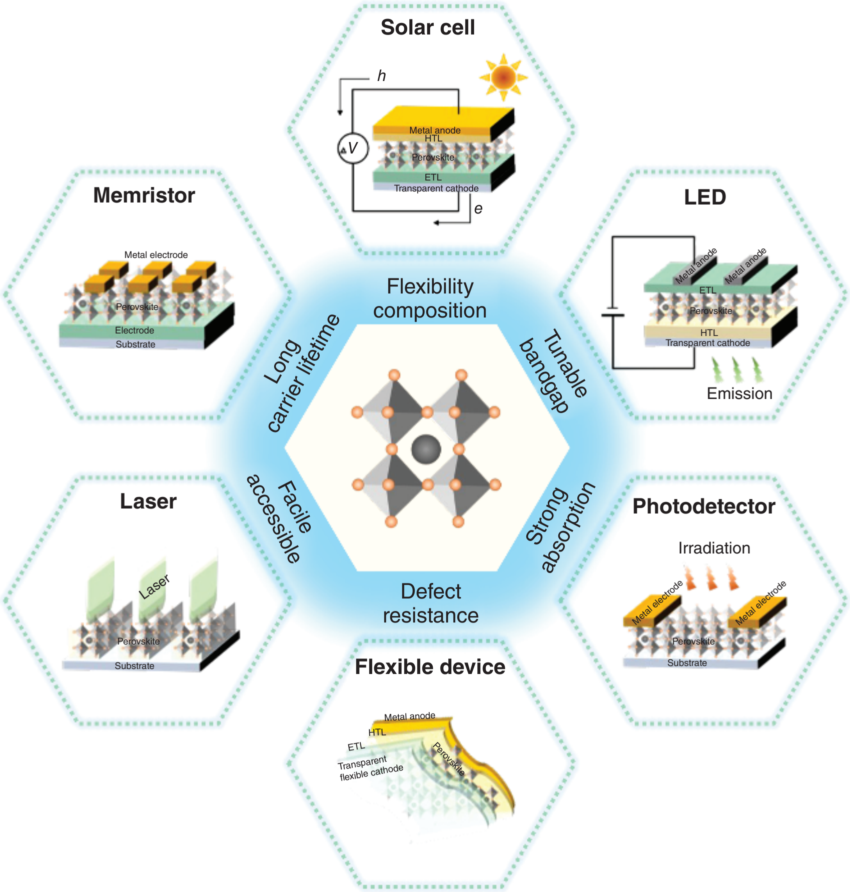

Figure 1.3 Example of properties and applications of halide perovskite. Halide perovskites are promising semiconductors with excellent properties, including flexible composition, facile accessibility, tunable bandgap, strong absorption, long carrier lifetimes, and defects resistance. These merits enable halide perovskite to be competent in solar cells, LEDs, photodetectors, memristors, and lasers. Interestingly, halide perovskite devices can also be developed on flexible substrates due to the good performance of polycrystalline films and low-temperature growth conditions.

The organic–inorganic halide perovskites have received wide attention, mostly due to their high efficiency and low cost in next-generation PVs, which have made these materials start to compete with commercial thin-film cells. Such materials harvest the energy of sunlight efferently because of their high absorption coefficients in both visible and near-infrared light. The first report of the perovskite solar cell was in 2009 [16], and now the record laboratory-scale power conversion efficiency of perovskite film is certified at 25.7% (https://www.nrel.gov/pv/cell-efficiency). Perovskite film-based solar cells are easy to be fabricated at low temperature, more energy-saving, and environmentally friendly than the conventional silicon wafer with a lower payback time [17], but with a lower contrasted long- term stability.

Consequently, further commercialization process of perovskite-based solar cells has been hindered by the stability problem, including degradation due to moisture, oxygen, heat, light, mechanical stress, and reverse bias. These failings do not detract from the overall excellence but focus the research effort on increasing device stability. Halide perovskite materials remain a cost-effective solution to address vast electrical energy supplies.

While initial boost of halide perovskite research was the development of photovoltaic devices, the good performance of these solar cells is founded on low nonradiative recombination, which is also beneficial for other optoelectronic devices. Consequently, halide perovskites are also currently impacting the development of a broad range of optoelectronic devices and systems. One significant benefit of halide perovskites used as LEDs is their very high color purity, with full width at a half-maximum of 20 nm for the blue or green–blue electroluminescence spectrum peaks [18]. Unlike traditional inorganic nanomaterials, the exceptional color purity of quantum-well nanoparticles is maintained regardless of crystal size. As a result, halide perovskites have the potential to solve some of the drawbacks of existing LEDs, such as difficult synthesis challenges, high cost, poor color purity of organic LEDs, and high ionization energy of quantum dot LEDs. Since the first demonstration of perovskite LEDs in 2014, the external quantum efficiency (EQE) of these devices has rapidly increased from below 1% to 25.8% for red [19], 28.1% for green [20], and 14.8% for blue [21]. The new LED technology has seen a meteoric rise in device efficiencies, but many scientific and technical obstacles, such as the unsatisfied stability and efficiency of blue LEDs, still stand in the way of perovskite LEDs further advancement into real-world applications.

Halide perovskite-based photodetectors exhibit comparable performance to commercially available photodetectors based on crystalline Si and III–V, offering significant potential for the technology of light-signal detection. The outstanding intrinsic optoelectronic properties of halide perovskites, such as photoinduced polarization, high drift mobilities, and effective charge collection, have contributed to the current growth of cutting-edge material studies in the field of light-signal detection. Halide perovskite semiconductors feature effective light absorption, enabling the detection of a wide range of electromagnetic waves from ultraviolet and visible to near-infrared and even radiations (X-ray, γ-ray, etc.), with low-cost solution processability and high photon yield. This class of semiconductors may empower ground-breaking photodetector technology in the areas of imaging, optical communications, and biomedical sensing; in this last case, further stability in polar solvent media, such as water, could increase enormously the range of applications of these systems.

Moreover, halide perovskites present a high ionic bonding character and ionic conductivity, causing the coexistence and coupling of ionic and electronic components of current and capacitance. This fact is at the base of nonconventional effects on optoelectronic systems, which could be a source of instabilities but can also be exploited. In this sense, halide perovskites exhibited good memristive properties supported by their electronic–ionic conductivity properties [22]. Memristor, that is memory resistor, is a leading candidate with robust capabilities in information storage and neuromorphic computing applications to address the growing challenge of approaching the end of Moore's law and the von Neumann bottleneck. The memristive property of halide perovskite is achieved through the synergistic coupling of photonic, electronic, and ionic processes, which enable perovskite to demonstrate novel functions such as optical-erasing memory, optogenetically inspired synaptic functions, and light-accelerated learning with multifunctionalization and novel photonic, logical, multilevel, and flexible functions.

Aside from the above-mentioned, halide perovskites have much more extensive applications due to their outstanding attributes, such as lasers, X-ray detectors, waveguides, scintillators, gas sensors, spintronics, and photocatalysis.

1.4 Summary and Outlook

The last two decades have seen the rapid development of halide perovskite materials, with researchers in particular pioneering systematic structural and property correlation studies based on halide perovskite composition and phases. The structure of perovskites has also been derived from ABX_3 to various derivatives that are important for changing chemical properties, controlling energy bands, and granting new physical properties. Perovskite materials, as an excellent new generation of semiconductor materials, have been demonstrated to be useful in a wide range of application scenarios, including photovoltaics, displays, and sensing, storage.

However, the environmental and thermodynamic stability of halide perovskite-based applications are two major challenges impeding their development, and some related phenomena and mechanisms should be thoroughly investigated to address perovskite device long-term use problems. Scientists have begun to use multimodal characterization to study the structural changes of halide perovskites, to monitor structural changes related to physical processes using *in situ* technology, and to conduct large-scale studies to establish correlations between components and properties using AI technology. The halide perovskite is like a treasure trove, and more interdisciplinary collaboration will lead to even more unexpected discoveries. This book will overview the intriguing properties of halide perovskites, making this system significantly different from other optoelectronic materials. Properties of materials and devices will be overviewed as well as the perspective on material and device development, always focusing on the fundamental properties.

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