

Organic perovskites

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The family of perovskite materials derived from the crystal structure of the mineral CaTiO_3 , which was first reported in 1839^[1]. Then a series of materials with perovskite structure were discovered. Most perovskite materials have the ABX_3 stoichiometry, in which A is monovalent or divalent cation, B is divalent or tetravalent cation, and X is monovalent or divalent anion. Perovskite materials play important roles in various functional devices due to their unique optical, electronic and optoelectronic properties. Inorganic perovskites such as BaTiO_3 and PbTiO_3 have been widely used in ferroelectric and piezoelectric devices, actuators, capacitors, and nonlinear optical devices^[2]. The emergence of organic-inorganic hybrid perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ triggers a new wave of research about perovskite-based devices, such as solar cells, light-emitting diodes (LEDs), photodetectors, lasers, and field-effect transistors^[3, 4]. Motivated by the outstanding performance of perovskite materials, a variety of perovskite derivatives were developed, such as two-dimensional perovskites, double perovskites, and vacancy-ordered perovskites^[5, 6].

Though there are many different perovskites, almost all of them contain metal cations, such as Pb^{2+} , Ba^{2+} , and Ti^{4+} . The metal-containing perovskites can not fully degrade, making it hard to dispose of the waste. Moreover, some metal cations are highly toxic, limiting their application, especially the application in wearable devices, which are in fast-growing demand. Metal-free perovskites, composed of organic components, can solve the above issue^[7]. Organic perovskites were thought to be inexistent before the report of $\text{C}_4\text{N}_2\text{H}_{12}\cdot\text{NH}_4\text{Cl}_3\cdot\text{H}_2\text{O}$ in 2002^[8]. However, no new organic perovskites was found in the next 15 years.

Xiong *et al.* reported a series of metal-free perovskites, which have a formula of $\text{A}(\text{NH}_4)\text{X}_3$ (A: divalent organic cation; X: Cl^- , Br^- , or I^-)^[2]. The metal-free perovskites have similar crystal structure with the traditional perovskites, but there is clear difference about the relative position of the ions in the lattice. The standard perovskites take the structure shown in Fig. 1(a), in which six anions (X) form an octahedron, the highly-charged cation locates at the center of the octahedron. In another type of perovskites, the octahedron forms by six cations (Fig. 1(b)), and the A and B sites are occupied by anions, e.g. Li_3OBr . This type of perovskites is called “antiperovskite”^[6]. For the metal-free perovskites reported by Xiong *et al.*, the A-site cation has more charges than the B-site cation (Fig. 1(c)), which are different from both the standard

perovskites and the antiperovskites. The metal-free perovskites show similar structure with the inorganic perovskite BaLiF_3 , called “inverse perovskite”^[6].

Organic perovskites can be developed due to the chemical diversity of the organic cations. Xiong *et al.* studied the ferroelectric property of MDABCO- NH_4I_3 , which showed a ferroelectric phase at 293 K (Fig. 1(d)). The ferroelectric phase transformed into paraelectric phase at 448 K, and this phase-transition temperature is higher than that of the inorganic perovskite BaTiO_3 (390 K). What's more, MDABCO- NH_4I_3 has a large spontaneous polarization ($P_s = 22 \mu\text{C}/\text{cm}^2$), close to that of BaTiO_3 ($P_s = 26 \mu\text{C}/\text{cm}^2$). These results suggest that organic perovskites have potential use in ferroelectric devices instead of inorganic perovskites. The organic perovskites can also be used in X-ray imaging. Zhao *et al.* made X-ray detectors by using large single crystals of DABCO- NH_4Br_3 ^[9]. The detectors presented a good sensitivity of $173 \mu\text{C Gy}_{\text{air}}^{-1} \text{cm}^{-2}$. Organic perovskites used in solar cells and LEDs were not reported due to their large bandgap ($> 5 \text{ eV}$).

Compared with the inorganic perovskites, the organic perovskites have the advantage of low-temperature processing, which avoids the fracture caused by high-temperature annealing. The organic perovskites can decompose to non-toxic products, making them suitable for biocompatible and implantable devices like biosensors and bioelectronics. More organic perovskites and new applications may be developed in the future due to the chemical diversity of organic materials.

Acknowledgements

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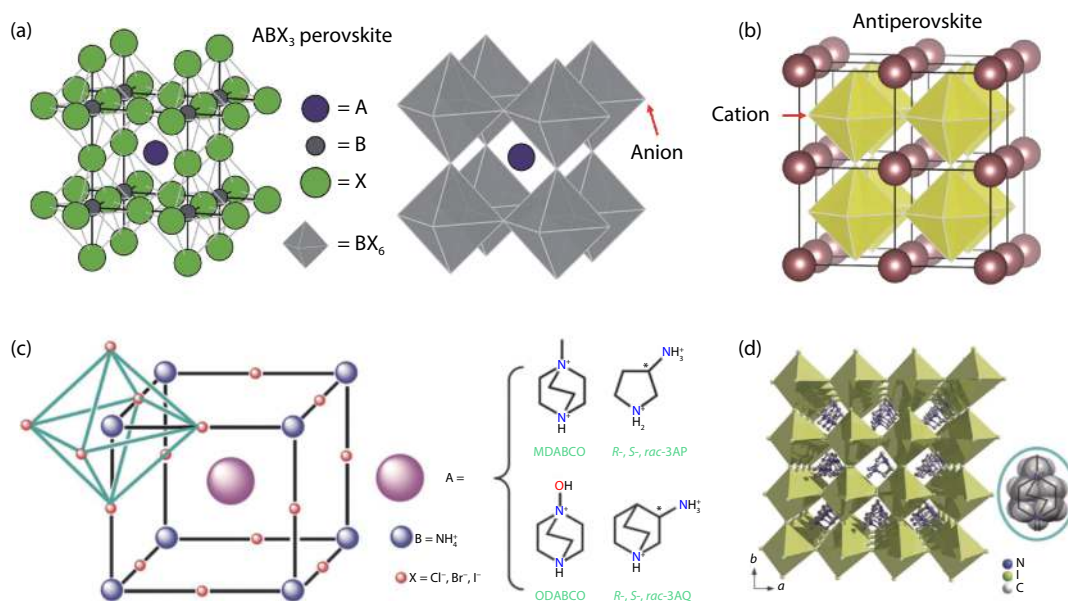


Fig. 1. (Color online) (a) Structure of the standard perovskite. (b) Antiperovskite. Reproduced with permission^[6], Copyright 2020, American Chemical Society. (c) Structure of the organic perovskites A(NH₄)X₃. (d) Ferroelectric phase of MDABCO-NH₄I₃. Reproduced with permission^[2], Copyright 2018, American Association for the Advancement of Science.

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