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Research Highlight

Lead-free organic-inorganic halide perovskites grown with nontoxic solvents

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A Perovskite is any material with the same type of crystal structure of $CaTiO_3$, a mineral discovered in 1839 [1], with the chemical formula of ABX_3, where A and B are two cations and X is an anion. Inorganic metal trihalide perovskites, $CsPbX_3$ (X = Cl, Br, and I), were synthesized almost 60 years later by reacting PbX_2 and CsX salts in aqueous solutions [2]. In the ideal cubic-symmetry structure, the A ions in 12-fold cuboctahedral coordination are much larger than the B ions in 6-fold octahedral coordination. Because perovskite does not possess a close packed anion sub-lattice with flexible bond angles, many types of distortions from the ideal structure can occur including the tilt and distortion of octahedra and displacement of cations out of the centers of their coordination polyhedra, leading to lower symmetries: tetragonal, orthorhombic, rhombohedral and monoclinic. Layered perovskites, also known as two-dimensional perovskites, are formed when thin sheets intrude and separate ABX_3 structure. Complexity of both chemical composition and crystal structure often renders great challenges in the synthesis and formation of single crystalline stoichiometric perovskite phase without co-existence of undesirable parasitic phases.

The non-close packing anion sub-lattice in perovskite structure permits the ready creation of solid solutions, $A_{1-x}A'_xB_{1-y}B'_yX_{3-z}X'_z$, in within all three A, B, and X sites to modify the various components in a vast number of permutations for engineering structure-property relationships, facilitating development of multifunctional compounds with tunable physical, chemical, optical, and electronic properties. For example, the band gap of organic-inorganic lead halide perovskite is sensitive to composition of the anion. Within a homologous set of compounds, the band gap follows the trend Cl > Br > I; the optical bandgap of $CH_3NH_3PbX_3$ varying from 1.6 to 2.9 eV depending on halide content [3].

Perovskites possess many unique and intriguing properties such as ferroelectricity, piezoelectricity, superconductivity, colossal magnetoresistance, ionic conductivity, and optoelectronic. Oxide perovskites were first found application as pigments in paints and other coatings, while the intensive research was triggered by the demonstration of ferroelectricity in $BaTiO_3$ in 1945 [4]. In 1958, vibrant colors of $CsPbX_3$ compounds motivated the first study of metal halide perovskite electronic properties, which revealed a frequency-dependent photoconductive response [5]. In 1986, Bednorz and Müller [6] reported high critical temperature superconductivity in Cuprate perovskites and further development has pushed the critical temperature of oxide perovskites above 90 K (−183 °C). In 2009, 170 years after the natural oxide perovskite was discovered, Miyasaka and co-workers [7] reported that organic-inorganic lead halide perovskite was found to be able to absorb sunlight and generate electricity.

Enormous research efforts have been devoted to the fundamental understanding of material science and device fabrication of the organic-inorganic lead halide perovskite solar cells immediately following Miyasaka's groundbreaking work [7], and it was quickly realized that organic-inorganic lead halide perovskites possess high optical absorption coefficient, long free carrier diffusion length, and low exciton binding energy with tunable optical bandgap. To date, the highest power conversion efficiency of perovskite solar cells (PSCs) that based on low temperature solution-process above 22% have been achieved [3], approaching the record efficiencies of monocrystalline silicon-based solar cells (25.6%) and thin film single-crystalline GaAs cells (28.8%).

Now PSCs have reached high power conversion efficiency, challenges including the hysteresis of photocurrent density–voltage and the instability of perovskite, remain to be solved for their wide-spread practical applications for the solar energy harvesting. Surface modification or engineering may eliminate the hysteresis and new device architecture and package may provide solutions to circumvent the instability as well. However, above approaches are not feasible to sidestep the lead toxicity and toxic solvents (e.g., *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)) required during the preparation.

Developing lead-free and stable organic-inorganic halide perovskite materials becomes imperative for the further advancement in PSCs and other applications including lasers, light-emitting diodes (LED), photocatalysis, and catalysis. Tin, bismuth, and antimony-containing organic-inorganic halide perovskites such as $(CH_3NH_3)_3Bi_2I_9$ and $(CH_3NH_3)_3Sb_2I_9$ have been synthesized, however, the research on such lead-free organic-inorganic halide perovskites is in its infancy [8].

Zuo and Ding [9] reported a family of perovskite materials, $(NH_4)_3Sb_2I_xBr_{9-x}$ $(0 \le x \le 9)$. These materials present good solubility in ethanol, which is an eco-friendly solvent. $(NH_4)_3Sb_2I_9$ single crystal was prepared by using an anti-solvent vapor-assisted crystallization method (Fig. 1a). Fig. 1b shows a single crystal with a thickness of 2.1 mm and side lengths around 5.7 mm. The single crystal exhibits an absorption onset at 645 nm, corresponding to an optical bandgap of 1.92 eV. The photoluminescence (PL)

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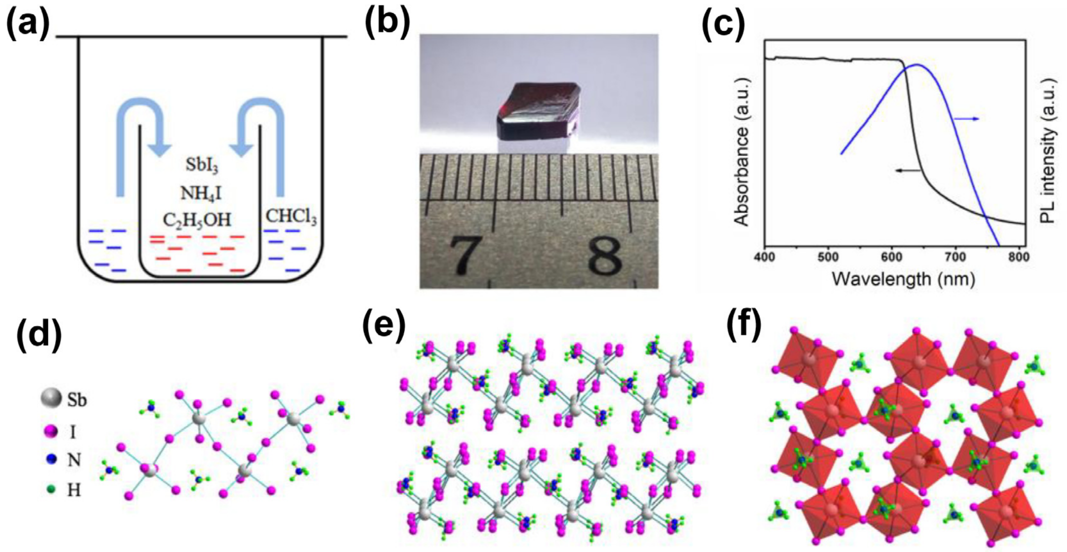

Fig. 1. (Color online) $(NH_4)_3Sb_2I_9$ single crystals. (a) Schematic illustrating the preparation approach. (b) Photograph of the grown single crystal, $(NH_4)_3Sb_2I_9$. (c) Light absorption and photoluminescence spectra. (d) Structure overview (001 plane). (e) Layered structure (010 plane). (f) The polyhedrons formed by iodine and hydrogen atoms: NH_4 tetrahedra and SbI_6 octahedra (001 plane). Reprinted with permission from Ref. [9], Copyright© 2017 Wiley.

spectrum for the single crystal presents a peak at 639 nm (Fig. 1c). The crystal structure was analyzed by using single crystal X-ray diffraction (XRD) (Fig. 1d–f). According to the crystal structure, $(NH_4)_3Sb_2I_9$ can be classified as a two-dimensional perovskite material [8]. The hole and electron mobility for $(NH_4)_3Sb_2I_9$ single crystal were measured by using the space charge limited current (SCLC) method. The single crystal exhibits a hole mobility of 4.8 $cm^2/(V\ s)$ and an electron mobility of 12.3 $cm^2/(V\ s)$, sufficiently large for most optoelectronic applications, though lower than the mobility of $CH_3NH_3PbI_3$ counterpart.

Single crystal reflects the intrinsic properties of a material, while in most cases thin films are used in many devices. $(NH_4)_3Sb_2I_9$ film shows an absorption onset at 558 nm. There is an 87 nm blue shift as compared with that of its single crystal counterpart. The absorption for $(NH_4)_3Sb_2I_9$ film can be readily tuned by substituting I with Br. The absorption onsets for $(NH_4)_3Sb_2I_6Br_3$, $(NH_4)_3Sb_2I_3Br_6$ and $(NH_4)_3Sb_2Br_9$ films are 516, 486 and 453 nm, respectively. In the XRD pattern, the stronger (002), (004) and (006) diffraction peaks result from the oriented growth of $(NH_4)_3Sb_2I_9$ crystals during the film formation. The film has a hole mobility of $1.2 \times 10^{-4}\ cm^2/(V\ s)$ and an electron mobility of $1.5 \times 10^{-4}\ cm^2/(V\ s)$. Solar cells using $(NH_4)_3Sb_2I_9$ as the light absorber generate a V_{oc} of 1.03 V with a power conversion efficiency (PCE) of 0.51%. The V_{oc} is much higher than that of other lead-free perovskite solar cells. Improving the quality of $(NH_4)_3Sb_2I_9$ film may lead to higher power conversion efficiency as well as other application performance. The application of the material in LED, photodetector, and the other optoelectronic devices needs further exploration.

Quest for new materials with desired physical properties through low-cost and environmental friendly synthesis and processing routes is a perpetual endeavor prompting the advancement of materials science and engineering, and enabling new technologies to serve and benefit our society. Perovskite crystals have surprised us with various unique properties and found applications in many key technologies. The synthesis of lead-free $(NH_4)_3Sb_2I_xBr_{9-x}$ perovskites with eco-friendly solution processing indicates that there are a lot of space to enrich the perovskite family. Organic-inorganic halide perovskite material with better and desired properties, higher stability, lower toxicity, and easier to prepare is the key to advance its wide applications including solar cells and other optoelectronic devices.

Conflict of interest

The author declares that he has no conflict of interest.

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