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New hybrid lead iodides: From one-dimensional chain to two-dimensional layered perovskite structure

Kecai Xiong [a],[1], Wei Liu [a], Simon J. Teat [b], Litao An [a], Hao Wang [a], Thomas J. Emge [a], Jing Li [a],*

[a] Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, United States
[b] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

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ABSTRACT

Two new hybrid lead halides (H_2BDA)[PbI_4] (**1**) (H_2BDA=1,4-butanediammonium dication) and (HNPEIM)[PbI_3] (**2**) (HNPEIM=N-phenyl-ethanimidamidine cation) have been synthesized and structurally characterized. X-ray diffraction analyses reveal that compound **1** features a two-dimensional corner-sharing perovskite layer whereas compound **2** contains one-dimensional edge-sharing double chains. The N-phenyl-ethanimidamidine cation within compound **2** was generated in-situ under solvothermal conditions. The optical absorption spectra collected at room temperature suggest that both compounds are semiconductors having direct band gaps, with estimated values of 2.64 and 2.73 eV for **1** and **2**, respectively. Results from the density functional theory (DFT) calculations are consistent with the experimental data. Density of states (DOS) analysis reveals that in both compounds **1** and **2**, the energy states in the valence band maximum region are iodine 5p atomic orbitals with a small contribution from lead 6s, while in the region of conduction band minimum, the major contributions are from the inorganic (Pb 6p atomic orbitals) and organic components (C and N 2p atomic orbitals) in compound **1** and **2**, respectively.

1. Introduction

In the past two decades, inorganic–organic hybrid semiconductors have been one of the focusing areas of materials development due to their potential utility in optoelectronic applications [1,2]. The physical and structural properties of these materials can be fine tuned by substituting or tailoring the organic ligands, or by modulating the inorganic modules. One of well investigated hybrid families is based on lead halides, in which organic ligands are incorporated/inserted in the three dimensional inorganic parent structure to break it down to two, one, or zero dimensions. The lead halides family can be classified in four different classes [3–5]. The hybrid perovskites of the form $APbX_3$ (where A is ammonium cation; X=Cl, Br, I) features a three-dimensional network, many of which absorb sun energy effectively and are promising for use in solar cells [3]. The $A_2^1A_{n-1}^2Pb_nX_{3n+1}$ and $A_2^1A_m^2Sn_mX_{3m+2}$ classes, which have the two-dimensional layered structures [4], can be structurally derived from the three-dimensional analog by slicing along specific crystallographic planes and inserting organic amines between the slices. The interlayer separation and the thickness of the inorganic layers can be controlled through the choice of organic cations. And some one-dimensional chain-like structures and zero-dimensional molecular compounds have also been reported [5]. Selected examples are listed in Table 1. These organic–inorganic hybrid materials are unique in that they incorporate both the organic and inorganic components in a single crystal lattice, therefore giving rise to combined physical properties due to the individual components as well as new features that are not possible with either component alone. The inorganic components offer useful optoelectronic and magnetic properties, substantial mechanical hardness and heat resistance. The organic cations can greatly improve the strutural tunability, material processability and flexibility. The structural conformations and charge properties of the organic cations also play important roles in directing and tailoring the structure types of the resulting hybrid materials. Inspired by the previous success in pervoskite-type hybrd materials, we have recently focused on the reactions of 1,4-butanediammonium diiodide (H_2BDAI_2) and benzeneammonium iodide (BZAI) with PbI_2 for the construction of new hybrid lead halides. Herein, we report the solvothermal synthesis of two new members, (H_2BDA)[PbI_4] (**1**) (H_2BDA=1,4-

Table 1
Selected list of hybrid lead/tin halide compounds.

Dimensionality	Hybrid lead/Tin halide	Chemical formula	Reference
3D	MAPbI$_3$	APbX$_3$	3
2D-monolayer	(N-MPDA)[PbBr$_4$]	BPbX$_4$	4a
2D-bilayer	[NH$_2$C(I)=NH$_2$]$_2$(CH$_3$NH$_3$)$_2$Sn$_2$I$_8$	A$_2^1$A$_m^2$Sn$_m$X$_{3m+2}$ (m=2)	4b
2D-trilayer	(MA)$_2$ (PEA)$_2$ [Pb$_3$I$_{10}$]	A$_2^1$A$_{n-1}^2$Pb$_n$X$_{3n+1}$ (n=3)	4c
1D-chain	[((R)-C$_8$H$_{12}$N) PbI$_3$]	APbX$_3$	5a
1D-double-chain	[(MPL-H)$_6$·I$_3$)(Pb$_2$I$_9$)]	A$_6$Pb$_2$ × $_9$C	5b
0D	(NHAr)$_2$Pb$_2$I$_2$·1.5 C$_6$H$_5$CH$_3$	A$_2$Pb$_2$ × $_2$	5c

A=ammonium cation; B=diammonium dication; C=anion;
MA=methylammonium cation; MPL=morpholine;
N-MPDA=N^1-methylpropane-1,3-diammonium dication;
PEA=phenethyl ammonium cation; (R)-C$_8$H$_{12}$N=C$_6$H$_5$CH(CH$_3$)NH$_3$$^+$.

butanediammonium dication) and (HNPEIM)[PbI$_3$] (**2**) (HNPEIM=N-phenyl-ethanimidamidine cation), their structure characterization by both single crystal and powder X-ray diffraction methods, as well as their thermal and optical properties.

2. Experimental section

2.1. Materials and measurements

All chemicals are of reagent-grade quality and obtained from commercial sources and are used without further purification. Lead(II) iodide (98.5%, Alfa Aesar), hydriodic acid (57%, w/w, Alfa Aesar), 1,4-butanediamine (98%, Alfa Aesar), aniline (99%, Alfa Aesar).

Powder X-ray diffraction (PXRD) analyses were carried out on a Rigaku Ultima-IV automated diffraction system using Cu Kα radiation (λ=1.5406 Å). The data were collected at room temperature in a 2θ range of 3–50° with a scan speed of 1°/min. The operating power was 40 kV/40 mA.

UV–vis diffuse reflectance spectra were measured at room temperature on a Shimadzu UV-3600 UV/VIS/NIR spectrometer. The reflectance data were converted to Kubelka–Munk function, $\alpha/S=(1-R)^2/2R$ (α is absorption coefficient, S is scattering coefficient and R is reflectance), and used to estimate the bandgap. Samples for reflectance measurements were prepared by evenly distributing ground powder sample between two quartz slides.

2.2. Syntheses of H$_2$BDAI$_2$ and BZAI

1,4-butanediammonium diiodide (H$_2$BDAI$_2$) and benzeneammonium iodide (BZAI) were prepared according to a method similar to that reported for the synthesis of methyammonium iodide [6]. 1,4-butanediammonium diiodide (H$_2$BDAI$_2$) was synthesized by reacting 10 mL of 1,4-butanediamine and 33.0 mL of hydroiodic acid in a 100 mL round-bottom flask at 0 °C for 6 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 °C. The yellow powder was washed with diethyl ether by stirring the solution for 30 min. After filtration, the yellow solid was collected and dried at 60 °C in a vacuum oven for 24 h. Benzeneammonium iodide (BZAI) was synthesized by reacting 10.0 mL of aniline and 18.0 mL of hydroiodic acid in a 50 mL round-bottom flask at 0 °C for 6 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 °C. The white powder was washed with diethyl ether by stirring the solution for 30 min. After filtration, the white solid was collected and dried at 60 °C in a vacuum oven for 24 h.

2.3. Syntheses of compounds 1–2

Compound 1: Hydriodic acid (57%; 1.0 mL) was added to the mixture of PbI$_2$ (46 mg, 0.10 mmol) and 1,4-butanediammonium diiodide (34 mg, 0.10 mmol) at room temperature in a heavy-walled Pyrex tube. The reaction mixture was sonicated for 5 min to disperse the mixture. The tube was frozen under liquid nitrogen for 10 min before sealed under vacuum and placed inside an oven at 120 °C for 7 days. Yellow single crystals of **1** were obtained in 63% yield based on PbI$_2$.

Compound 2: Acetonitrile (1.0 mL) was added to the mixture of PbI$_2$ (46 mg, 0.10 mmol) and benzeneammonium iodide (22 mg, 0.10 mmol) at room temperature in a heavy-walled Pyrex tube. The reaction mixture was sonicated for 5 min to disperse the mixture. The tube was frozen under liquid nitrogen for 10 min. And then it was sealed under vacuum, and placed inside an oven at 120 °C for 7 days. Yellow single crystals of **2** were obtained in 45% yield based on PbI$_2$.

2.4. Single crystal X-ray data collection and structure determination

Single crystal synchrotron X-ray diffraction data of compounds **1** and **2** were collected at 100 K on a D8 goniostat equipped with a Bruker PHOTON100 CMOS detector on beamline 11.3.1 at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory, using synchrotron radiation tuned to λ=0.7749 Å. Data were also collected for compound **1** at room temperature (298 K) on the same beamline. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the Bruker SHELXTL package [7]. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were located at geometrically calculated positions and refined using a riding model. The low temperature structures were deposited in the Cambridge Structural Database (CSD), with CCDC-1053651 (**1**) and −1053652 (**2**). Details of the crystal data are summarized in Tables S1–S2.

3. Results and discussion

3.1. Crystal structures and phase purity

Analysis using the single crystal data collected at 100 K shows that compound **1** crystallizes in the triclinic space group P $\bar{1}$, with the 2D layered structure feature of lead-iodine perovskite. In the asymmetric unit (Fig. 1), there are two crystallographically distinct