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Synthesis, Structure, and Optical Properties of a Contorted <110>-Oriented Layered Hybrid Perovskite: $C_3H_{11}SN_3PbBr_4$

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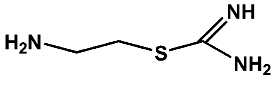
The <110>-oriented perovskite is very rare in the hybrid perovskites family. In this work, an unusual layered <110>-oriented hybrid perovskite, which is stabilized by a special organic ligand, 2-(aminoethyl)isothiourea, has been obtained. This ligand combines a primary amine and a formamidine on the two ends of one molecule. Introduction of the special ligand brings about contorted inorganic sheets in the hybrid perovskite structure. The optical properties of the new <110>-oriented perovskite were studied.

Introduction

Hybrid perovskites with the general composition $(R\text{–}NH_3)_2MX_4$ and $(NH_3\text{–}R\text{–}NH_3)MX_4$ have a very flexible structure, which consists of a wide range of divalent metal ions alternating with a variety of different organic cations.[1] Hybrid perovskites can be classified into different types according to their crystallographic direction. Several possibilities for the orientation of the inorganic slab include <100>, <110>, and <111>.[2] Organic ligands play an important role in constructing perovskite structures with different orientations. The main interactions between organic and inorganic components in hybrid perovskites include electrostatic interactions and hydrogen bonds between the organic ammonium heads and the halogen atoms in the inorganic sheets. The steric framework of organic ammonium heads directly influences the formation of hydrogen bonds that finally determine the structure of the inorganic sheet in hybrid perovskites. The selectivity of certain organic cations toward the formation of specific orientations of the layered perovskite framework is an attractive area of research.

The <100>-oriented perovskite is the most common orientation among hybrid perovskite structures and has been extensively studied. Various organic ammonium groups have been used to construct <100>-oriented perovskites.[3] Confined by the inorganic sheet in hybrid perovskites, most of these organic groups are simple alkylammonium or aromatic ammonium groups. A <110>-oriented perovskite with a different organic ligand has rarely been reported. It is very unusual that the organic ligand can properly stabilize the inorganic components to form a <110>-oriented perovskite. Up to now, only two series of <110>-oriented hybrid perovskites were reported.[4,5] Mitzi et al. reported the first series of layered, SnI_2-based, <110>-oriented perovskites, which were constructed by using mixed ligands of methylammonium and iodoformamidinium cations. Different-dimensional inorganic sheets were obtained by modulating different proportions of the two ligands, which caused the series of materials to undergo semiconductor–metal transition.[4] We obtained a $PbBr_2$-based <110>-oriented perovskite with special optical properties stabilized by a single ligand of *N*-(3-aminopropyl)imidazole.[5] The <110>-oriented hybrid perovskite constructed by using a single ligand has superiority to that constructed from mixed ligands. For example, the single-ligand perovskite is easy to synthesize and flexible to process into thin films for photoelectric applications by simple methods. So it is of great interest and importance to construct new <110>-oriented perovskite materials by using a single ligand.

In this paper, we choose 2-(aminoethyl)isothiourea as an organic ligand to construct a $PbBr_2$-based perovskite. 2-(aminoethyl)isothiourea (shown in Scheme 1) has two types of organic amine groups on its two ends: a primary amine and a formamidine. This type of configuration of the organic ligand provides the possibility of constructing special hybrid perovskites. By using this ligand, an unusual, contorted, <110>-oriented hybrid perovskite, $C_3H_{11}SN_3PbBr_4$ (**1**), is obtained.



Scheme 1. Structure of the organic ligand 2-(aminoethyl)isothiourea.

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Result and Discussion

Crystal Structure

The title compound crystallizes in a monoclinic crystal system of space group $P2_1/c$. Figure 1 shows the crystal packing structure of compound **1** viewed along the (001) and (010) directions, which highlight the <110> direction of the hybrid perovskite. The whole framework is made up of <110>-oriented perovskite-type inorganic sheets alternating with layers of organic dications. In the common <100>-oriented layered hybrid perovskite structure, octahedra of the inorganic sheets share opposite corners in one direction. However, in the <110>-oriented hybrid perovskite compound **1**, octahedra of the inorganic sheets share opposite corners along the *c* axis and neighboring corners along the *b* axis. By sharing both neighboring corners of two Br4 atoms (along the *b* axis) and opposite corners of Br2 atoms (along *c* axis), the PbBr6 octahedra line up to form a zigzag <110>-oriented hybrid perovskite (Figure 1a). Compared with other reported <110>-oriented hybrid perovskites, compound **1** has a contorted inorganic framework, which is determined by the particular organic ligand used. The first <110>-oriented perovskite, $[NH_2C(I)=NH_2]_2(CH_3NH_3)_2Sn_2I_8$,[4a] has a very regular inorganic sheet. The bridging angles Sn–I–Sn are close to 180° probably because of the flexibility of the mixed organic ligands. The other <110>-oriented perovskite stabilized by a single ligand, *N*-(3-aminopropyl)imidazole, has a slightly distorted perovskite sheet with bridging angles of 162.68 and 171.85°.[5] In compound **1**, however, one of the bridging angles (Pb–Br4–Pb) greatly deviates from 180° [144.23(2)°], and this brings about a contorted perovskite sheet in the structure of this compound.

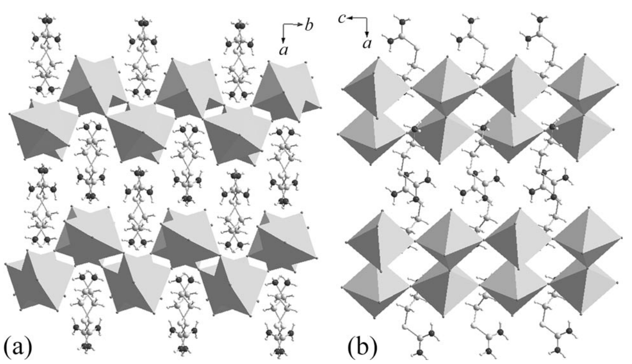

Figure 1. Crystal packing structure of <110>-oriented compound **1** viewed along the *c* axis (a) and the *b* axis (b).

The organic ligand influences the arrangement of the inorganic sheet through both hydrogen bonding and steric hindrance. Figure 2 shows the crystal structure of compound **1** showing the hydrogen bonds. 2-(Aminoethyl)-isothiourea has primary ammonium and formamidinium groups on two ends of one ligand, which has a similar effect as the two ligands (methylammonium and iodoformamidinium) in Mitzi's work.[4] Hydrogen atoms on both the primary ammonium (N1) and the formamidinium (N2, N3) groups extend to the inorganic sheets and form hydrogen bonds with the Br atoms. The formamidinium group approaches the top of the zigzag <110>-oriented inorganic sheet. The hydrogen atom attached to one of the nitrogen atoms of the amidocyanogen, N2, forms a hydrogen bond with terminal bromine Br1, while that on the other nitrogen atom of the amidocyanogen, N3, forms a hydrogen bond with terminal bromine Br3 in the adjacent zigzag sheet (Figure 2). The formamidinium group therefore extends between neighboring inorganic sheets along the *a* axis, and the N2–C3–N3 angle of formamidium stretches to 120.6(5)°. The primary ammonium nitrogen atom, N1, extends to the valley of the zigzag sheet. Three N–H···Br hydrogen bonds form between hydrogen atoms on amidocyanogen (N1) and two bridging bromine atoms (Br4) and one terminal bromine (Br3) of the PbBr6 octahedra, which provide a "bridging halogen configuration" similar to that in the common <100>-oriented hybrid perovskites.[1a] All of the hydrogen bond lengths range from 2.554 to 2.751 Å and bond angles range from 134.109 to 171.200°, which indicate stronger hydrogen bonds in the compound. In addition, the interactions between sulfur and bromine atoms cannot be ignored. The distance between S and Br3 is 3.510 Å (shown in Figure 2), which is less than the sum of van der Waals radii. This is a very short distance, indicative of an enhanced interaction between the organic and inorganic components. A sulfur-based ammonium cation has already been incorporated in halogenometallate salts by Mercier,[6] in which the sulfur atom plays an important structural role. The sulfur atom of the organic ligand in compound **1** contributes to the stabilization of the perovskite layers as well as their distortion.

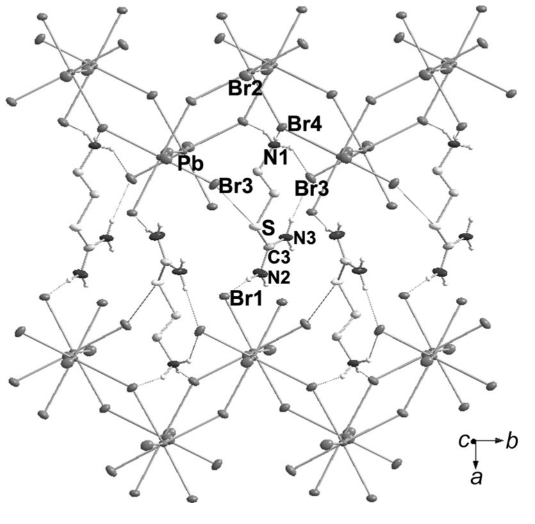

Figure 2. Structure of compound **1** showing the hydrogen bonds.

The special configuration of the organic ligand and the hydrogen bonds make the <110>-oriented inorganic sheet more contorted, and the PbBr6 octahedron is also more distorted than those previously reported.[5] The bridging angle Pb–Br4–Pb is 144.23(2)°, which deviates greatly from a straight angle, indicating the largely contorted inorganic sheets in the *ab* plane. The other bridging angle Pb–Br2–Pb along the *c* axis is 170.54(2)°, suggesting a slight corrugation in this direction. The octahedra in compound **1** are more distorted: they have Br–Pb–Br bond angles varying from 81.958(15) to 95.124(15)° and Pb–Br bond lengths varying from 2.8440(6) to 3.1569(6) Å (Table 1). The rather strong tilt of the equatorial $PbBr_2$ plane can be easily visualized in Figure 1. The tilt in these polyhedra is mainly due to the cooperation of the formamidium and primary ammonium cations in the ligand as well as the important interactions between the sulfur atoms of the ligand and the bromine atoms of the inorganic layer, as mentioned above. Both ammonium heads trend to form hydrogen bonds with appropriate bromine atoms. The formamidium moiety, which has one carbon fragment bearing two ammonium parts can provide flexible hydrogen bonds, whilst the primary ammonium moiety on the other end is suitable for fixing the layered perovskite sheet. When formamidium cooperates with methylammonium in one ligand, hydrogen bonds of the latter stabilize the perovskite sheets, while those of the former extend to two adjacent perovskite sheets due to their flexibility. These interactions between the organic ligand and the inorganic layer result in the formation of the novel contorted <110>-oriented hybrid perovskite.

Table 1. Selected bond lengths [Å] and angles [°] for **1** (symmetry transformations used to generate equivalent atoms: #1: *x*, –*y* + 1/2, *z* + 1/2; #2: –*x*, *y* – 1/2, –*z* + 1/2; #3: *x*, –*y* + 1/2, *z* – 1/2; #4: –*x*, *y* + 1/2, –*z* + 1/2).

Pb–Br(3)	2.8440(6)	Pb–Br(1)	2.9657(6)
Pb–Br(2)	3.0010(5)	Pb–Br(2)#1	3.0357(5)
Pb–Br(4)#2	3.1569(6)	Br(2)–Pb#3	3.0357(5)
Br(1)–Pb–Br(2)	95.124(15)	Br(3)–Pb–Br(2)#1	87.138(16)
Br(1)–Pb–Br(2)#1	91.822(15)	Br(2)#1-Pb–Br(4)	84.612(15)
Br(1)–Pb–Br(4)#2	89.093(16)	Br(2)–Pb–Br(4)#2	81.958(15)
Br(4)–Pb–Br(4)#2	92.715(9)	Pb–Br(2)–Pb#3	170.54(2)
Pb–Br(4)–Pb#4	144.23(2)	N(3)–C(3)–N(2)	120.6(5)

Optical Properties

The key aspect of perovskite materials containing group IVA metals is that they exhibit sharp room-temperature photoluminescence resonances arising from an exciton state associated with the semiconducting inorganic sheets.[7] The optical spectra of a crystallized film of compound **1** were recorded at room temperature. A description of the thin-film deposition, film image (Figure S1), and XRD pattern (Figure S2) are given in the Supporting Information. Figure 3 shows its photoluminescence excitation and emission spectra. The excitation band at 360 nm and the narrow emission peak at 402 nm are the typical excitonic absorption and emission arising from two-dimensional $PbBr_4^{2-}$ layers in hybrid perovskites, respectively. Relative to the previously reported $PbBr_2$-based, <110>-oriented perovskite (with excitonic absorption at 398 nm and emission at 424 nm),[5] compound **1** shows a slight blueshift. The band structure of compound **1** was calculated by using the CASTEP code based on DFT. The calculated results are given in Figures S3 and S4.

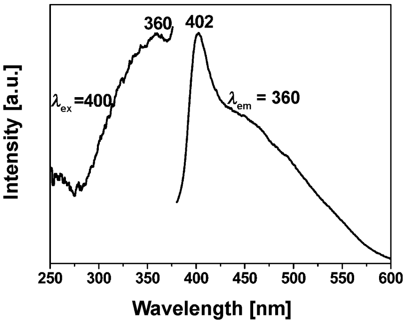

Figure 3. Photoluminescence excitation (left) and emission (right) spectra of compound **1**.

Conclusions

A new contorted, <110>-oriented hybrid perovskite was obtained by using an appropriate organic ligand, 2-(aminoethyl)isothiourea. The new compound provides an example for the synthesis of new <110>-oriented hybrid perovskite materials by selecting an appropriate organic ligand. Choosing other new organic ligands to construct hybrid perovskites with novel structures is work that is still in progress.

Experimental Section

Materials: $PbBr_2$ (99.99%, Aldrich) and 2-(aminoethyl)isothiourea (98%, Alfa Aesar) were used without further purification. Hydrobromic acid (40%) from Beijing Chemical Industry Co., Ltd. was used as received.

Compound 1: An equimolar mixture of $PbBr_2$ (0.367g 0.1 mmol) and 2-(aminoethyl)isothiourea (0.157g 0.1 mmol) in hydrobromic acid (10 mL, 40%) was heated to 80 °C for two hours, and a clear solution was obtained. The solution was then cooled to room temperature. After concentration at room temperature for about one month, colorless crystals of $C_3H_{11}SN_3PbBr_4$ (**1**) were obtained. IR (KBr): $\nu(NH_3^+)$: 3300, 3114; ν(pyridinium): 1578, 1533, 1471; $\delta(NH_3^+)$: 1650, 1643, 1622; δ(Ar–H): 764, 738, 690 cm^{-1}. $C_3H_{11}Br_4N_3PbS$ (648.02): calcd. C 5.56, H 1.17, N 6.48; found C 5.72, H 1.36, N 6.29. Crystal data of compound **1** are shown in Table 2.

Table 2. Crystal data and structure refinement for **1**.

Formula	$C_3H_{11}SN_3PbBr_4$	Volume [Å^3]	1362.06(16)
Weight	648.04	*Z*	4
Wavelength [Å]	0.71073	$F_{(000)}$	1152
Crystal system	monoclinic	Reflections collected	7354
Space group	$P2_1/c$	Goodness-of-fit on F^2	1.021
a [Å]	13.2976(9)	*R* indices	$R_1 = 0.0264$,
b [Å]	8.5472(6)	$[I > 2\sigma(I)]$	$wR_2 = 0.065$
c [Å]	11.9843(8)	*R* indices	$R_1 = 0.0303$,
β [°]	90.439(1)	(all data)	$wR_2 = 0.0671$

Characterization

Diffraction intensities were collected on a Rigaku RAXIS-RAPID image plate diffractometer by using the ω-scan technique with Mo-K_α radiation (λ = 0.71069 Å). Absorption corrections were applied with the multiscan technique.[8a] The structures were solved by direct methods with SHELXS-97[8b] and refined by means of full-matrix least-squares techniques with the SHELXL-97 program,[8c] as implemented in WINGX.[8d] Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms attached to carbon atoms were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed, with anomalous dispersion corrections incorporated therein.[8e] FT-IR spectra were measured with a Perkin–Elmer 580B infrared spectrophotometer by using KBr pellets. Elemental analysis was carried out with a Vario EL instrument.

CCDC-661736 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Description of thin-film deposition, film image, XRD pattern, and calculated band structure (CASTEP code) of compound **1**.

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