Available online at www.sciencedirect.com

ScienceDirect

Solid State Sciences 9 (2007) 855−861

www.elsevier.com/locate/ssscie

Synthesis, structure and optical properties of different dimensional organic−inorganic perovskites

Yinyan Li [a,b], Guoli Zheng [a,b], Cuikun Lin [a,b], Jun Lin [a,*]

[a] Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,
5625 Renmin Street, Changchun 130022, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

Received 11 March 2007; received in revised form 14 June 2007; accepted 26 June 2007
Available online 1 July 2007

Abstract

By varying the substituent position of aminomethyl on pyridine ring in acid solution, different dimensional lead bromide frameworks ranging from zero-dimension and one-dimension to two-dimension were obtained. 2-(Aminomethyl)pyridine (2-AMP) or 3-(aminomethyl)pyridine (3-AMP) and $PbBr_2$ construct hybrid perovskites, of which $(H_2$2-AMP$)PbBr_4$ (**1**) exhibits two-dimensional perovskite sheets with special hydrogen bonds and $(H_2$3-AMP$)_2PbBr_6$ (**2**) shows an uncommon zero-dimensional inorganic framework with isolated octahedra. The characteristic exciton peaks in absorption spectra are located at 431 nm for compound **1** and at 428 nm for compound **2**. $(H_2$4-AMP$)PbBr_4$ (**3**) with one-dimensional zigzag edge-sharing octahedral $PbBr_4^{2-}$chains can be obtained using 4-(aminomethyl)pyridine (4-AMP) as organic component under the same experimental conditions as those for 2-AMP and 3-AMP.

Keywords: Perovskite; Zero-dimensional; Exciton

1. Introduction

Recently, more and more attention has been paid to the organic−inorganic hybrids. Various organic ions and molecules can be inserted into the interlayer space of inorganic layered structures to form intercalation compounds. In these materials, inorganic sheets and layers of the organic molecules or ions are interstratified at a molecular level [1]. Hybrid perovskites with organic−inorganic layer alternated structures have been widely studied due to their structure flexibility and potentially useful magnetic, electrical and optical properties [2]. This kind of material, generally expressed as $(R\text{-}NH_3)_2\text{-}MX_4$ or $(NH_3\text{-}R\text{-}NH_3)MX_4$ (where, R = organic group, M = divalent metal, and X = halogen), consists of an extended network of corner-sharing metal halide octahedra, alternating with a bilayer or monolayer organic moiety.

Optical properties of the group 14 (IVA) metal organic−inorganic perovskites have been the focus of considerable recent attention as a result of the strong room temperature exciton emission. In addition to tailing the position of the optical features by making substitutions on the metal or halogen sites, control over the specific structure of the metal halide sheets through the appropriate choice of the organic cations should also provide a means for influencing the optical properties. An extensive work has been devoted to optical properties based on haloplumbate layered perovskites [3].

An important feature of organic−inorganic perovskite is their structural tunability. Some structural differences are observed if the counter ions of the inorganic parts are monoprotonated or diprotonated amines. The crystallographic

---

* Corresponding author. Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China. Tel.: +86 431 85262031; fax: +86 431 5698041.

E-mail address: jlin@ciac.jl.cn (J. Lin).

1293-2558/$ - see front matter © 2007 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2007.06.011

orientation and the thickness of the perovskite sheets can be varied by choosing appropriate organic cations. In other words, inorganic units can be self-organized into low-dimensional crystals, where they form zero-(0-D), one-(1-D), two-(2-D), and three-dimensional (3-D) networks according to the organic cations. The effective dimensionality of the extended inorganic anion has a significant impact on the physical properties of the hybrid perovskite [4].

Due to the structure flexibility of the hybrid perovskite, choosing different organoammoniums to stabilize different orientation or dimension perovskite sheets is an interesting area to explore relationship between structures and properties within a single structure family. Although 3-D and 2-D compounds consisting of metal halide perovskites have been extensively studied, there are few reports dealing with the 1-D and 0-D materials [4]. The compound $(CH_3NH_3)_4PbI_6\cdot 2H_2O$, which is one of the reported haloplumbates-based 0-D materials, consists of isolated $[PbI_6]^{4-}$, $CH_3NH_3^+$, and H_2O [5]. Recently, the transformation of a 2-D perovskite structure to expanded 2-D and finally to a 0-D hexanuclear cadmium chloride cluster has been reported by varying the size of substituents on the associated counter ions [6].

In this paper we reported new organoammoniums which stabilize different dimensions of $PbBr_4^{2-}$-based hybrid perovskite in hydrobromic acid solution at room temperature. The amines we chose here are 2-(aminomethyl)pyridine (2-AMP), 3-(aminomethyl)pyridine (3-AMP) and 4-(aminomethyl)pyridine (4-AMP). They are all aminomethylpyridines except different substituent position of aminomethyl. The reason we chose these amines comes from two considerations: first, the aminomethylpyridines has both a primary amine and a pyridine which may be used to construct distorted perovskite structure; second, it is possible to study if the different position of the aminomethyl on the pyridine ring would bring about different inorganic framework due to the difference in hydrogen bond position. Finally, the three ammoniums construct different dimensional $PbBr_2$ frameworks on the same conditions. The compound **1** $[(H_22\text{-AMP})PbBr_4]$ which coordinates 2-AMP and $PbBr_2$ in acid solution has common two-dimensional perovskite sheets with special hydrogen bonds. While the compound **2** $(H_23\text{-AMP})_2PbBr_6$ which combines 3-AMP and $PbBr_2$ shows an uncommon zero-dimensional inorganic network with isolated octahedrons. Optical properties of the new hybrid materials have been studied, which show that the exciton peak of the $PbBr_4^{2-}$-based perovskites in absorption spectra is 431 nm for compound **1** and 428 nm for compound **2**. The similar type of amine 4-AMP was also used to obtain an unusual zigzag edge-shared octahedral chains of $PbBr_2$.

2. Experiment section

2.1. Materials and synthesis

$PbBr_2$ (99.99%, Aldrich), 2-(aminomethyl)pyridine(99%, Alfa Aesar), 3-(aminomethyl)pyridine (99%, Alfa Aesar) and 4-(aminomethyl)pyridine (97%, Alfa Aesar) were used without further purification. Hydrobromic acid (40%) was used as received from Beijing Chemical Industry Co., Ltd. The title compounds were prepared by reacting lead halide and amine in hydrobromic acid, as shown in Scheme 1.

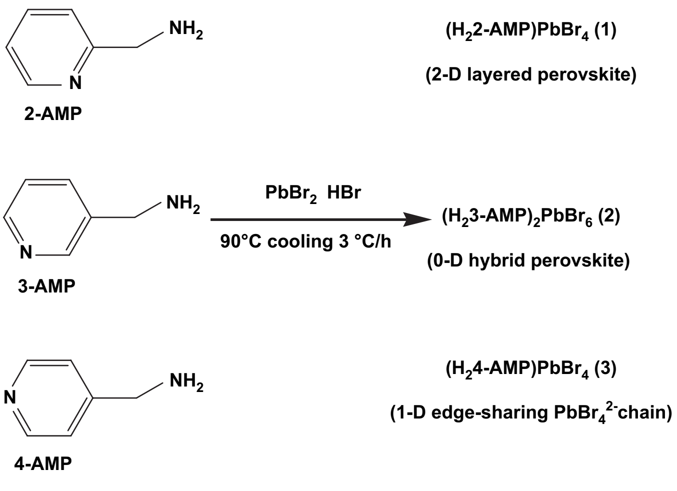
Compound **1**: equimolar amounts of $PbBr_2$ (0.367 g 0.1 mmol) and 2-(aminomethyl)pyridine (0.108 g 0.1 mmol) were added to 10 mL hydrobromic acid (40%), and the mixture was heated to 90 °C by refluxing, then slowly cooled (3 °C/h) to room temperature in N_2 atmosphere with the formation of colorless crystal of $(C_6H_{10}N_2)PbBr_4$ (**1**) (yield: 43.3%). IR (cm^{-1} KBr): ν (NH_3^+): 3248, 3081, 3035, 2819, 2756; ν (pyridinium): 1567, 1543, 1485, 1469; δ (NH_3^+): 1620, 1629; δ (Ar–H): 766. Elemental analysis: Calcd for $C_6H_{10}N_2PbBr_4$: C, 11.31%; H, 1.58%; N, 4.40%. Found: C, 11.40%; H, 1.65%; N, 4.48%.

Compound **2**: similar method to that for compound **1** was used to synthesize $(C_6H_{10}N_2)_2PbBr_6$ (**2**) (yield: 34.5%). IR (cm^{-1} KBr): ν (NH_3^+): 3104, 3074, 3053, 2997, 2549; ν (pyridinium): 1576, 1584, 1474, 1455; δ (NH_3^+): 1631; δ (Ar–H): 814, 799, 781, 679. Elemental analysis: Calcd for $C_6H_{10}N_2PbBr_4$: C, 11.31%; H, 1.58%; N, 4.40%. Found: C, 11.26%; H, 1.53%; N, 4.35%.

Compound **3**: similar method to that for compound **1** was used to synthesize $(C_6H_{10}N_2)PbBr_4$ (**3**) (yield: 40.7%). IR (cm^{-1} KBr): ν (NH_3^+): 3190, 3132, 3065, 2927; ν (pyridinium): 1590, 1554, 1509, 1495, 1475; δ (NH_3^+): 1635; δ (Ar-H): 862. Elemental analysis: Calcd for $C_6H_{10}N_2PbBr_4$: C, 11.31%; H, 1.58%; N, 4.40%. Found: C, 11.35%; H, 1.63%; N, 4.51%.

2.2. Characterization

Diffraction intensities were collected on a Rigaku RAXIS-RAPID image plate diffractometer using the ω-scan technique with Mo Kα radiation ($\lambda = 0.71069$ Å). Absorption corrections were applied using the multiscan technique [7a]. The structures were solved by direct methods using SHELXS-97 [7b] and refined by means of full-matrix least-squares techniques using the SHELXL-97 program [7c] as implemented in WINGX [7d]. Non-hydrogen atoms were refined



Scheme 1. The synthetic process of compounds **1**, **2**, and **3**.