Hydrothermal Synthesis and Structure of Zero-dimensional Organic–inorganic Perovskites

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A low-dimensional organic–inorganic perovskite compound, $(C_4H_8N_2H_4)_2PbBr_6 \cdot 2H_2O$, was synthesized from cyclic amines and $PbBr_2$ by using a hydrothermal reaction. The versatile optical properties caused by the quantum confinement structure were investigated.

Much attention has been recently paid to the synthesis and characterization of organic–inorganic perovskites because of their unique electronic, magnetic, and optical properties.[1–3] Layered perovskites with the general formula $(RNH_3)_2PbX_4$ (R; C_nH_{2n+1}, X; halogen) naturally form a quantum-well structure, that is, a two-dimensional structure consisting of a lead halide semiconductor sheet sandwiched between organic insulator layers. The layered structure is self-organized through the neutralization of $[PbX_6]^{4-}$ with organic ammonium in an orientation determined by the hydrogen bonds and halide ions, and by a van der Waals interaction between adjacent organic ammoniums. Since the insulating organic layers have a wide band gap, the excitons are confined in the inorganic $[PbX_6]^{4-}$ layer; these provide strong photoluminescence with high optical nonlinearity and characteristics with potential applications in optical devices.[4,5]

Another unique feature of organic–inorganic perovskites is their structural tunability, so that the relationship between structures and properties can be easily explored within a single structural family. These materials offer a diversity of possible combinations of inorganic and organic parts.[6,7] The crystallographic orientation and the spacing between the inorganic parts 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 in terms of the organic cations.

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 compounds.[8–11] The compound $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$, which is one of the 0-D materials reported, consists of isolated $[PbI_6]^{4-}$, $CH_3NH_3^+$, and H_2O molecules, but it has a weak stability against ambient atmosphere. To improve the stability of the 0-D compounds, we tried to fabricate $[PbBr_6]^{4-}$-based compounds (i.e., $(CH_3NH_3)_4PbBr_6 \cdot 2H_2O$) by a method similar to the synthetic method of $[PbI_6]^{4-}$ compounds, but with no success.

Recently, low temperature hydrothermal reactions of inorganic precursors in the presence of organic cations have proven highly productive for the synthesis of novel solid-state materials.[12,13] In this study, we attempted to fabricate novel zero-dimensional metal halide perovskites by using the hydrothermal technique. Since the dimensionality of the inorganic framework in the metal halide perovskites is readily affected by the molecular structures and interactions of organic moieties, cyclic amines were selected instead of alkylamines in this study. Cyclic amines are planar molecules, which are expected to have some influence such as strong molecular interaction and steric hindrance on the arrangement of $[PbBr_6]^{4-}$ octahedra. The preliminary optical properties afforded by the quantum confinement structures are also investigated.

The title compound $(C_4H_8N_2H_4)_2PbBr_6 \cdot 2H_2O$ was prepared by a hydrothermal reaction. After all conditions were optimized, the feed molar ratio of piperazine:HBr:$PbBr_2$ in this reaction was controlled at 7:25:1. Anhydrous piperazine (0.70 g, 7.0×10^{-3} mol) was dissolved in mixed solutions of H_2O (10 g) and 48% HBr aqueous solution (4.2 g, 2.5×10^{-2} mol).

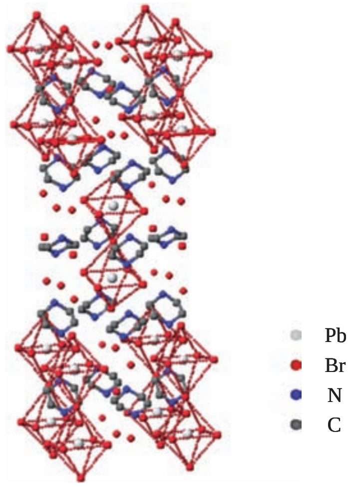

Figure 1. Structural model for the crystal of $(C_4H_8N_2H_4)_2PbBr_6 \cdot 2H_2O$.

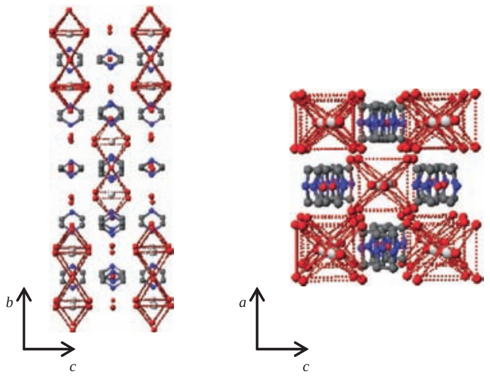

Figure 2. Detailed crystal structure for $(C_4H_8N_2H_4)_2PbBr_6 \cdot 2H_2O$.

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After adding 99.99% lead bromide (0.37 g, 1.0×10^{-3} mol), the reaction suspension was heated at 120 °C in a Teflon-lined autoclave for 6 h. Colorless granular crystals were obtained by slow cooling from 120 °C to room temperature. The composition of the obtained crystal was identified by elemental analysis.; Anal. for $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$. Calcd.: C 10.7; H 3.11; N 6.23%. Found: C 10.7; H 3.08; N 6.22%.

The crystal structure was determined by crystallographic X-ray measurements.[14] The data were collected at a temperature of 23 ± 1 °C using the ω-scan technique to a maximum 2θ of 55.0°. Figures 1 and 2 show the crystallographic X-ray measurement results for $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$. The room temperature orthorhombic phase adopts the *Pnnm* space group with lattice constants of $a = 8.5$, $b = 26.5$ and $c = 9.8$ Å. The crystal consists of edge-sharing dimeric $[PbBr_6]^{4-}$ units ($[Pb_2Br_{11}]^{7-}$) surrounded by piperazinium cations and water molecules with the shortest N···O distance of 2.8 Å. This indicates that two hydrogen sites of piperazinium cation can coordinate water molecules, resulting in the formation of isolated $[Pb_2Br_{11}]^{7-}$ units, which have an intermediate dimensionality of 0-D and 1-D.

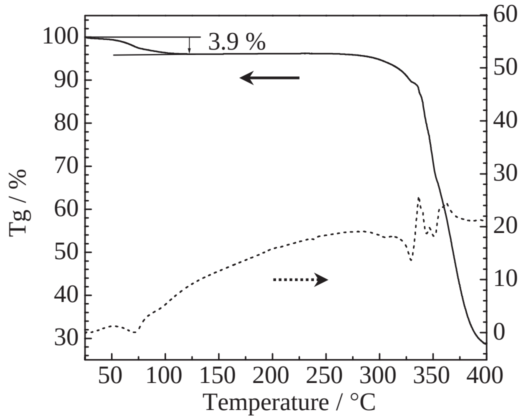

Figure 3. TG-DTA scan for a $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$ powder sample.

Figure 3 shows the thermogravimetric and differential thermal analysis (TG–DTA) data of the obtained $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$ crystal in nitrogen atmosphere. The weight of the sample begins to decrease from 50 °C. Approximately 3.9% weight loss was observed upon heating up to 100 °C. This is in good agreement with the expected weight change for the complete loss of water molecules from the crystal (4.0%), indicating that the binding interaction of water in the crystal is relatively low. The residual $(C_4H_8N_2H_4)_2PbBr_6$ crystal was stable up to 300 °C and was more stable than the conventional layered perovskite compounds.[3]

The diffuse reflection spectrum of the $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$ crystal is shown in Figure 4. The absorption spectrum of a two-dimensional compound, $(C_6H_{13}NH_3)_2PbBr_4$, was also shown as a comparison. The quasi-0-D compound exhibited a strong absorption at 312 nm with a small shoulder on the low energy side. This absorption peak and the shoulder are assigned to the excitons from the $[PbBr_6]^{4-}$ 0-D dot and dimeric $[PbBr_6]^{4-}$ octahedral, respectively. As the dimensionality of $[PbBr_6]^{4-}$ units changes, the lowest exciton energy shifts to higher energy, which is mainly ascribed to the quantum confinement effect.

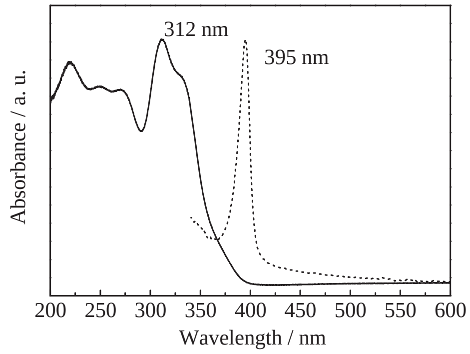

Figure 4. Diffuse reflection spectrum of $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$ powder sample (straight line). Absorption spectrum of $(C_6H_{13}NH_3)_2PbBr_4$ spin-coated film was displayed as a comparison (dashed line).

Through the systematic control of synthesis conditions, it was possible to control the structures of the metal halide perovskites. Crystals with different features such as whisker-like (piperazine:HBr:$PbBr_2$ = 1:2:1), needle-like (1:4.8:1), and granular crystals (6:18:1 or 7:25:1), were obtained by changing the feed ratio of piperazine:HBr:$PbBr_2$. In addition, another novel crystal, $(CH_3C_4H_7N_2H_2)_2Pb_2Br_6{\cdot}H_2O$, was obtained by the hydrothermal reaction from 2-methylpiperazine. Although the crystal structure of $(CH_3C_4H_7N_2H_2)_2Pb_2Br_6{\cdot}H_2O$ has not yet been accurately determined, a novel quasi-0-D structure will probably be obtained, because of the observation of the characteristic absorption peak at 308 nm.

In conclusion, the new synthetic technique for 0-D organic–inorganic perovskites, which has rarely been found can be developed utilizing the hydrothermal technique from cyclic amines. We will extend our work and obtain more effective systems, which will be reported elsewhere.

References and Notes

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14 A single crystal of $(C_4H_8N_2H_4)_2PbBr_6{\cdot}2H_2O$ having approximate dimensions of $0.3 \times 0.3 \times 0.2$ mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo Kα radiation. *Crystal data*: MW: 899.96, $a = 8.8006(8)$, $b = 8.626(1)$, $c = 16.735(1)$ Å, $\beta = 98.673(3)°$, $V = 1255.8(2)$ Å^3, space group = $P2_1/a$ (#14), $Z = 4$; $D_{\text{calcd}} = 2.632$ g/cm^3, μ(Mo Kα) = 116.65 cm^{-1}, $\lambda = 0.71069$ Å, $2\theta_{\max} = 55.0°$; total data collected = 11191, reflections observed = 2569 ($I > 2.00\sigma(I)$, $2\theta < 54.96°$); 115 variables; $R = 0.067$, $R_w = 0.087$.

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