

Self-Organization of PbBr-Based Layer Perovskite Organic/Inorganic Superlattice Materials through Intercalating Organic Ammonium Molecule into PbBr₂

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Oriented thin films of PbBr-based layer perovskites having an organic/inorganic superlattice structure were successfully prepared through intercalation of alkylammonium bromides ($C_nH_{2n+1}NH_3Br$; $n \geq 2$) into lead bromide PbBr₂ thin films. Vacuum-deposited PbBr₂ films (20 nm thick) on fused quartz substrates were exposed to alkyl ammonium bromides vaporized by heating at a base pressure of about 10^{-5} torr. The exposed films exhibited a strong exciton absorption around 3.1 eV, which is characteristic of the PbBr-based layer perovskites. The appearance of the exciton absorption indicates the formation of PbBr-based layer perovskite structure through the intercalation of alkylammonium bromide molecules into the PbBr₂ films. Further, the X-ray diffraction profiles of the films demonstrated that their layer structure is oriented parallel to the film plane; only peaks corresponding to (00n) plane of the PbBr-based layered perovskites were observed in the intercalated films, where the c axis is in the stacking direction of their layer structure.

Key words: layer perovskite, self-organization, superlattice, organic-inorganic composite, intercalation, thin film

1. INTRODUCTION

Lead halide layer perovskites, which are expressed by the chemical formulae $(RNH_3)_2PbX_4$: RNH_3^+ ; organic ammonium molecular cation and X; halogen, are a family of self-organized low-dimensional semiconductor materials. The layer perovskites naturally form a superlattice structure where a lead halide semiconductor layer and an organic ammonium layer are alternately piled up at the monolayer level (Fig.1).¹⁻⁴ Owing to their low-dimensionalized semiconductor structure, they form a stable exciton with a large binding energy of several hundred meV and exhibit interesting optical properties due to the stable exciton: sharp and intense exciton emission, biexciton lasing, efficient nonlinear optical effect and electroluminescence due to the exciton, and so on.⁵⁻⁸

Crystal sample of the layer perovskites is usually prepared by the solvent evaporation from organic solutions in which stoichiometric amounts of lead halide and organic ammonium halide are dissolved because the perovskites are thermally unstable and not applicable to the crystal growth technique in melt phase. The solvent-evaporation technique results in very small size crystals (typically several square millimeter platelet crystal with a few tens micrometer thickness). Such small crystals are not preferable for practical device application. Accordingly, the alternative way to apply the layer perovskite to practical devices is to employ them in film morphology.

In this work, we found that oriented thin films of PbBr-based layer perovskites were formed in a self-organizing manner through the intercalation of alkylammonium molecules into PbBr₂ films. The new preparation technique is expected to provide a

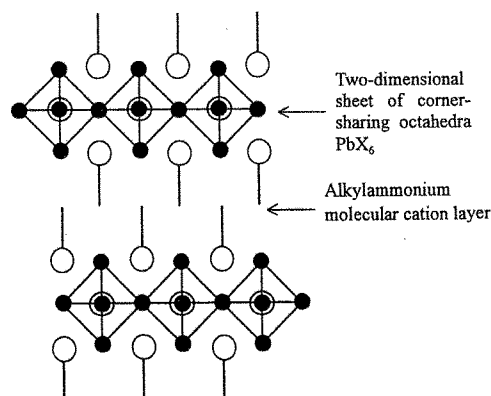


Fig.1. Schematic Structure of PbBr-based layer perovskite having a superlattice structure where a semiconductor layer of corner sharing octahedra PbX₆ is sandwiched with a dielectric layer of alkylammonium cation $C_nH_{2n+1}NH_3^+$.

promising approach to apply the layer perovskites to practical optical devices. Here, we report the preparation of PbBr-based layer perovskite thin films through intercalating organic ammonium bromide into PbBr₂ film in vapor phase, and their orientational structure and optical properties.

2. EXPERIMENTAL

In this work, we employed five alkylammonium bromides ($C_nH_{2n+1}NH_3Br$) methylammonium bromide ($n=1$), ethylammonium bromide ($n=2$), propylammonium bromide ($n=3$), butylammonium bromide ($n=4$) and hexylammonium bromide ($n=6$).

Lead bromide PbBr₂ thin films (20 nm thick) were vacuum-deposited on fused quartz substrates at about 10⁻⁵ torr. For the intercalation of alkylammonium bromide, then, the films were exposed to alkylammonium bromide vaporized by heating at a base pressure of about 10⁻⁵ torr without exposure to the air.

Absorption spectra and X-ray diffraction profiles of the intercalated films were measured with a UV-VIS spectrophotometer (Shimadzu UV-2400PC) and an X-ray diffractometer (Rigaku RINT1000).

For comparison, crystal samples of PbBr₂-based layer perovskites with an alkylammonium molecular cation as an organic layer were prepared with solvent-evaporation of the acetone solution in which stoichiometric amounts of lead bromide PbBr₂ and alkylammonium bromide were dissolved, and their X-ray diffraction profiles were measured.

3. RESULTS AND DISCUSSION

Figure 2 shows absorption spectra of vacuum-deposited PbBr₂ films after exposure to vaporized alkylammonium bromide. Before the exposure, PbBr₂ film was pale yellow and transparent; its absorption band was observed around 3.88 eV, which corresponds well to the exciton band of PbBr₂ crystal.⁹ By exposing the PbBr₂ films to vaporized alkylammonium bromides, color and absorption spectra of the films were drastically changed. When we employed methylammonium bromide, PbBr₂ films were changed orange in color after the exposure. The exposed films exhibit a step-shaped absorption around 2.3 eV which is in good agreement with the band gap of a cubic perovskite (CH₃NH₃)PbBr₃.¹⁰ This result apparently

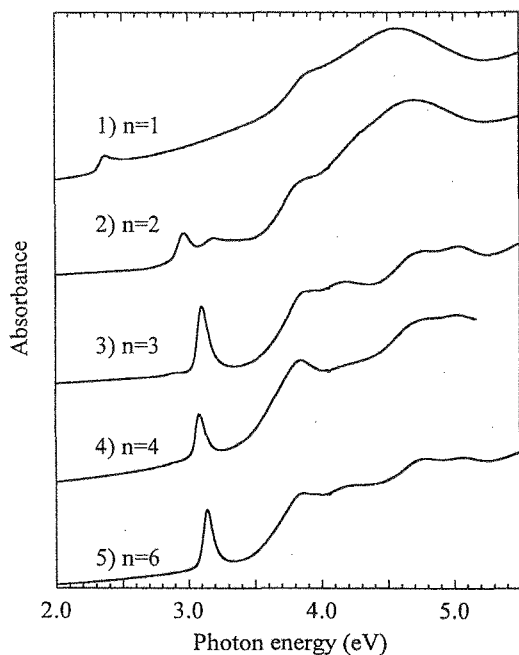


Fig.2 Absorption spectra of PbBr₂ films exposed to vaporized alkylammonium bromide (C_nH_{2n+1}NH₃Br).

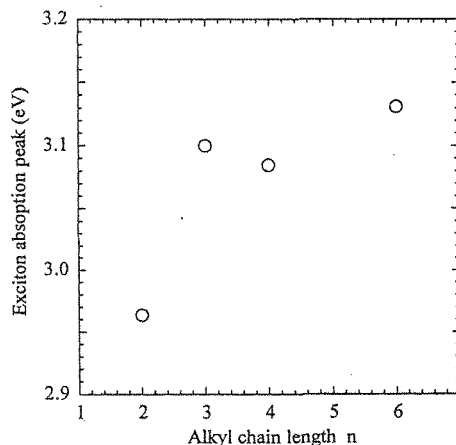


Fig.3 Dependency of exciton absorption peaks of PbBr₂ films exposed to vaporized alkyl ammonium bromide (C_nH_{2n+1}NH₃Br) on alkyl chain length n.

demonstrates that the cubic perovskite structure of (CH₃NH₃)PbBr₃ was formed by the exposure of PbBr₂ film to vaporized methylammonium bromide.

When we employed alkylammonium bromides (C_nH_{2n+1}NH₃Br; n ≥ 2), PbBr₂ films were found to be converted to PbBr₂-based layer perovskite films with high degree of layer structure orientation. In PbBr₂ films exposed to vapor of ethylammonium bromide, propylammonium bromide, butylammonium bromide and hexylammonium bromide, sharp and strong absorption due to exciton is observed around 3.1 eV, which is characteristic of PbBr₂-based layer perovskite (curves 2, 3, 4, and 5 in Fig.2).¹¹ The appearance of the exciton absorption clearly demonstrates the formation of layer perovskite structure in PbBr₂ films by the exposure.

Additionally, the exciton band is red-shifted with decreasing alkyl chain length of the ammonium bromides; the exciton absorption is peaking at 2.96 eV (n=2), 3.10 eV (n=3), 3.08 eV (n=4) and 3.13 eV (n=6), as shown in Fig.3. The red-shift of the exciton band is most likely to originate from reduction in effective quantum confinement due to partial penetration of the exciton wave-function into the narrow barrier layer of ammonium molecules with short alkyl chain.

Figure 4 a) shows the X-ray diffraction profiles of the PbBr₂ films exposed to vaporized alkylammonium bromides. For comparison, X-ray diffraction profiles of powdered crystal samples of PbBr₂-based perovskites with alkylammonium molecular cations as an organic layer are also shown in Fig.4 b). Only (00n) peaks are observed in the film samples, while the crystal samples exhibit a diffraction peak corresponding to the (100) or the (010) peak around a 2 theta of 15 degrees in addition to the (00n) peaks, where the c axis is in the stacking direction of their layer structure. The layer spacing values *d* of the exposed films calculated from the diffraction peaks are in good agreement with those of the crystal samples; the *d* values of the film samples

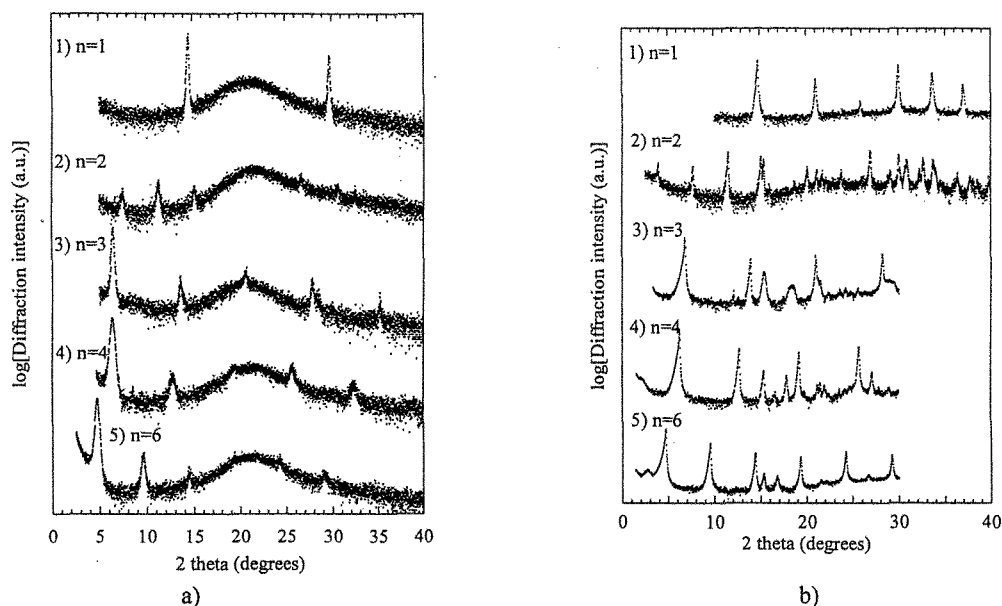


Fig.4. a) Xray diffraction profiles of PbBr_2 films exposed to vaporized alkylammonium bromide ($\text{C}_n\text{H}_{2n+1}\text{NH}_3\text{Br}$). b) Xray diffraction profiles of powdered crystals of PbBr -based layer perovskite with alkylammonium molecular cations as an organic layer.

are 0.61 (0.60) nm for $n=1$, 1.18 (1.15) nm for $n=2$, 1.36 (1.29) nm for $n=3$, 1.39 (1.41) nm for $n=4$ and 1.86 (1.88) nm for $n=6$, where numerals in parentheses denote the d values of the crystal samples. Besides supporting that layer perovskite structure is surely formed in the exposed films, the results demonstrates that the layer structure is highly oriented parallel to the film plane.

It is well known that lead halides form a layer structure with van der Waals gap, and that organic molecules are easily intercalated into the van der Waals gap.¹² In the formation process of the layer perovskite structure by exposing PbBr_2 film to vaporized alkylammonium bromide, accordingly, the intercalation of alkylammonium bromide molecules into the van der Waals gap of the PbBr_2 films is assumed to occur at the first step. Then, the layer structure of PbBr_2 is supposed to be converted to the layer perovskite structure by the solid state reaction between PbBr_2 and the intercalated alkylammonium bromide molecules. To reveal the formation process of the layer perovskite structure, the in situ evaluation of structural change of PbBr_2 film during the intercalation by the using RHEED measurement is now in progress.

4. SUMMARY

In this study, we demonstrated that oriented films of PbBr -based layer perovskites having a superlattice structure where a semiconductor layer of corner sharing octahedra PbX_6 is sandwiched with a dielectric layer of alkylammonium cation $\text{C}_n\text{H}_{2n+1}\text{NH}_3^+$ are successfully formed through intercalating organic ammonium bromide into PbBr_2 film in vapor phase.

To date, only simple spin-coating technique using conventional organic solvent such as acetone and dimethylformamide has been applicable to the preparation of good quality thin films of the layered

perovskites. In comparison with the spin-coating technique, the intercalation technique is advantageous to the construction of layer perovskite films with precisely controlled film thickness and film structure. For example, layer perovskite films with controlled domain size and orientation is expected to be prepared through control of the film structure of lead halide using the epitaxial growth technique followed by the intercalation of organic ammonium halide. We believe that this new preparation technique of layer perovskite thin films contributes much to the development of organic/inorganic superlattice materials based on layer perovskites and their practical application.

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