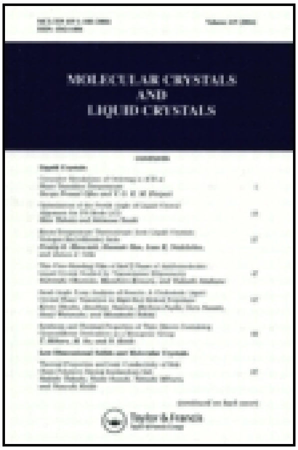

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PbBr-Based Layered Perovskite Organic-Inorganic Superlattice with Photochromic Chromophore-Linked Ammonium Molecules as an Organic Layer

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PbBr-Based Layered Perovskite Organic-Inorganic Superlattice with Photochromic Chromophore-Linked Ammonium Molecules as an Organic Layer

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Oriented films of novel organic-inorganic layered perovskites, which have a superlattice structure consisting of a PbBr-based semiconductor layer and a photochromic ammonium layer, were formed in a self-organizing manner by spin-coating from the solutions of $PbBr_2$ and an ammonium bromide linked with a photochromic chromophore such as salicylidenaniline and stylbene.

Keywords: layered perovskite; superlattice; photochromism; organic-inorganic composite

INTRODUCTION

Lead halide-based layered perovskite $(RNH_3)_2PbX_4$ self-organizes a superlattice structure consisting of a lead halide (PbX_4) semiconductor layer and an organic ammonium (RNH_3) layer. Owing to their low-dimensional semiconductor structure, they form a stable exciton with a large binding energy,[1)] and exhibit attractive optical properties due to the exciton such as efficient exciton emission, optical nonlinearity and so on.[1-3)]

In addition to their low-dimensional semiconductor nature, their self-organization is attractive from the standpoint of material design in organic-inorganic surperlattices. By using organic ammonium molecules with a functional group such as π-conjugated chromophore as an organic layer, for example, a variety of superlattice materials combined with functional organic layer and low-dimensional semiconductor are expected to be provided.[4)]

Incorporation of photochromic chromophore into the organic layer in the perovskites is an attractive way to develop new organic-inorganic superlattice materials with photoactive functionality. For example, changes in physical properties of ammonium layer by photochromic reaction are expected to modulate electronic properties of inorganic semiconductor layer. In this work, we succeeded in preparing oriented thin films of PbBr-based layered perovskites having a layer of organic ammonium molecules linked with photochromic chromophore.

EXPERIMENTAL

Molecular structures of photochromic organic ammonium bromides containing salicylideneaniline and stylbene chromophores (**1** and **2**) were used as an organic layer (Fig. 1). Stoichiometric amounts of lead bromide $PbBr_2$ and the ammonium bromide were dissolved in DMSO. Then, thin films of the PbBr-based layered perovskite with photochromic ammonium molecules as an organic layer were prepared on fused quartz substrates by spin-coating from the DMSO solutions.

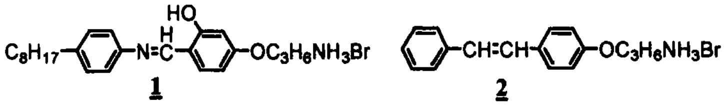

FIGURE 1 Molecular structures of photochromic chromophore-linked ammonium bromides

RESULT AND DISCUSSIONS

Figure 2 shows absorption spectrum of film spin-coated from the mixed solution of $PbBr_2$ and salicylideneaniline-linked ammonium bromide 1. The absorption spectrum of a spin-coated film of 1 are also shown in the same figure. In the absorption spectrum of the spin-coated film from the mixed solution, strong exciton absorption is observed around 390 nm, which is characteristic of PbBr-based layered perovskites. Appearance of the exciton absorption demonstrates the formation of PbBr-based layered perovskites structure in the spin-coated films. In addition to the exciton peak, two peaks due to salicylideneaniline chromophore are observed at 305 nm and 350 nm while the peaks locate at 295 nm and 340 nm in the spin-coated film of 1 (dotted line in Fig.2). The spectral features reveal that PbBr-based layered perovskite structure with salicylideneaniline-linked ammonium layer is surely formed in the spin-coated film from the mixed solution.

Figure 3 shows absorption spectra of spin-coated films from the mixed solution of $PbBr_2$ and 2 and the solution of 2. Besides the absorption due to stylbene chromophore at 275 nm, sharp exciton absorption is observed at 390 nm in the spin-coated film from the mixed solution, demonstrating formation of PbBr-based layered perovskite structure with stylbene chromophore in organic layer.

Figure 4 shows X-ray diffraction profiles of the spin-coated films of the layered perovskites with photochromic chromophore and powder sample of $PbBr_2$. In the profiles of the spin-coated film, only

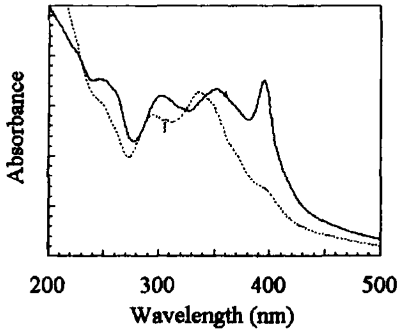

FIGURE 2 Absorption spectra of spin-coated films from mixed solution of $PbBr_2$ and 1 (solid line) and solution of 1 (dotted line).

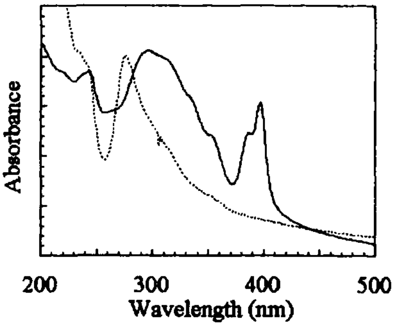

FIGURE 3 Absorption spectra of spin-coated films from mixed solution of $PbBr_2$ and 2 (solid line) and solution of 2 (dotted line).

diffraction peaks corresponding to layer structure of the perovskites, (00n) peaks, are observed while no diffraction peaks due to $PbBr_2$ are observed. In addition to supporting the formation of layered perovskite structure, the profiles clearly demonstrate that the layer structure is oriented parallel to the film plane.[4,5] From the diffraction peaks, values of interlayer spacing of the perovskites containing 1 and 2 were calculated to be 2.0 nm and 2.9 nm, respectively.

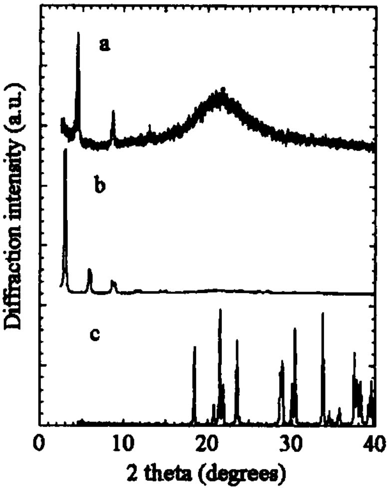

FIGURE 4 X-ray diffraction profiles of spin-coated films from mixed solutions of $PbBr_2$ and 1 (a) and $PbBr_2$ and 2 (b), and powder sample of $PbBr_2$ (c).

CONCLUSION

Oriented thin films of novel organic-inorganic layered perovskites with photochromic ammonium layer, were successfully prepared by the simple spin-coating from the solutions of stoichiometric amounts of $PbBr_2$ and an ammonium bromide linked with photochromic chromophore such as salicylideneaniline and stylbene.

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