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Synthesis of Novel Organic-Inorganic Self-Organized Compounds Containing Quaternary Ammonium Ions and its Structural Characterization

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Organic-inorganic layered perovskite compounds described by $(RNH_3)_2MX_4$ [R: alkyl group, M: divalent metals, X: halogen] were reported to form self-organized quantum-well structures. In this study, we aimed to synthesize novel organic-inorganic self-organized compounds with quaternary ammonium ions instead of primary alkylammonium ions. New compounds, $[(C_{12}H_{25})_2(CH_3)_2N]PbBr_2$ (DLDMPbBr) and $[(C_{12}H_{25})_2(CH_3)_2N]PbI_2$ (DLDMPbI) were synthesized, and the structural characterizations were performed on X-ray diffraction and optical measurements. The absorption peaks of these compounds showed higher photon energy than those of conventional layered perovskite compounds

with primary alkylammonium ions. This result indicated that novel quantum confinement structures were constructed with the DLDMPbBr and DLDMPbI.

Keywords Organic-inorganic hybrid; Perovskite; Quantum confinement structure; Low dimensional compounds; Excitons

INTRODUCTION

Organic-inorganic layered perovskite compounds, described by $(RNH_3)_2MX_4$ [R: alkyl group, M: divalent metals, X: halogen], self-organize quantum-well structures where MX_6 octahedra form inorganic well layers and are sandwiched between organic barrier layers. These compounds show interesting optical properties caused by the quantum confinement effect owing to the difference of the band gap energy between the inorganic well layers and organic barrier layers [1-8] . In these compounds, the dimension of the semiconductor inorganic region can be controlled by changing organic cations [9, 10]. However, there are only a few reports about layered perovskite compounds, except for primary ammonium ions as organic cations. In this study, we used quaternary ammonium ions such as dilauryldimethylammonium ion $[(C_{12}H_{25})_2(CH_3)_2N^+]$ instead of primary ammonium ions in order to synthesize novel organic-inorganic self-organized compounds. Structural characterizations and optical properties of the products were compared to those of layered perovskite compounds with alkylammonium ions.

EXPERIMENTAL

DLDMPbBr was prepared by the recrystallization from an *N*-methyl-2-pyrrolidone solution containing stoichiometric amount of $(C_{12}H_{25})_2(CH_3)_2NBr$ and $PbBr_2$. DLDMPbI was also obtained by the recrystallization from a dimethylsulfoxide (DMSO) solution of $(C_{12}H_{25})_2(CH_3)_2NI$ and PbI_2. The compositions of DLDMPbBr and DLDMPbI were estimated by elemental analyses. Spin-coated films of the compounds were prepared from the chloroform solution for DLDMPbBr and a mixed solution of acetone and DMSO for DLDMPbI, respectively. The structural characterizations of the products and spin-coated films were performed by X-ray diffraction measurements (Rigaku Rint 2000). Absorption spectra of the spin-coated films were performed on a UV-Vis spectrometer (SHIMADZU UV3100PC).

RESULTS AND DISCCUSSION

XRD patterns of DLDMPbBr and DLDMPbI powder are shown in Figure 1. These compounds exhibited a number of clear defined (00l) Brugg reflections. This result indicates that DLDMPbBr and DLDMPbI form layered structure with interlayer of 35.3 Å.

XRD patterns of DLDMPbBr and DLDMPbI spin-coated films are shown in Figure 2. The spin-coated film of DLDMPbBr showed higher order reflections based on the interlayer-spacing of 34.0 Å. DLDMPbI was also observed high order reflections of interlayer of 32.7 Å. These results suggest that the spin-coated films also have layered polycrystalline structures as well as the powder.

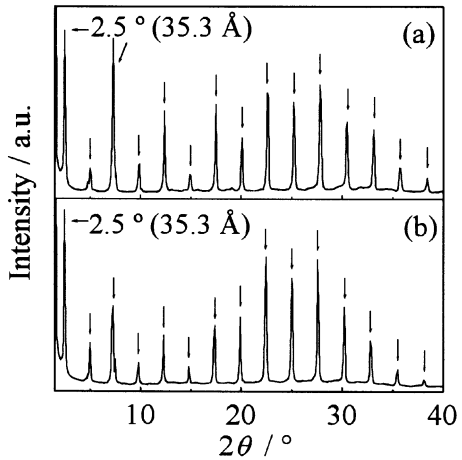

FIGURE 1 XRD patterns of DLDMPbBr(a) and DLDMPbI(b) powder.

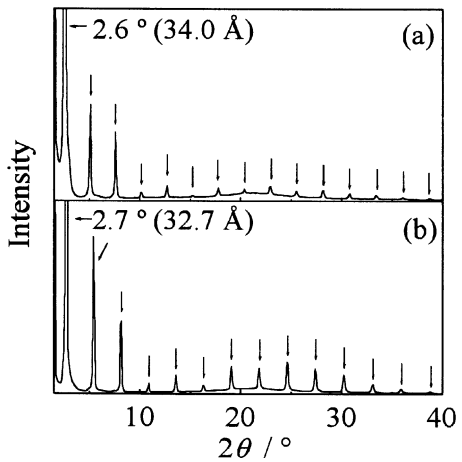

FIGURE 2 XRD patterns of DLDMPbBr(a) and DLDMPbI(b) spin-coated films.

Figure 3 shows the UV-Vis absorption spectra of DLDMPbBr DLDMPbI spin-coated films. The films showed absorption peak at around 352 nm for DLDMPbBr

and at 438 nm for DLDMPbI, respectively. These absorption peaks exhibited higher photon energy than those of conventional layered perovskite compounds with primary monoalkylammonium ions (i.e. at 396 nm for PbBr systems and at 524 nm for PbI systems) [11].

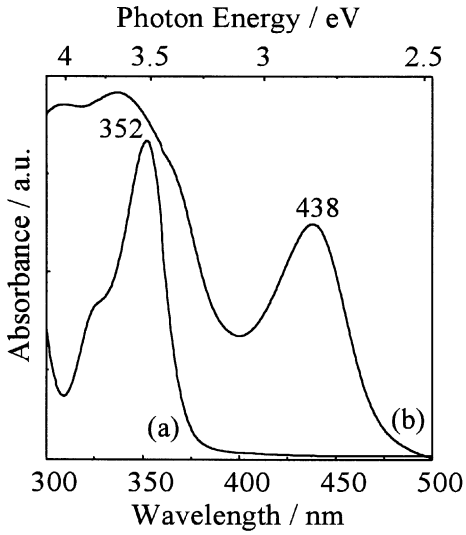

FIGURE 3 Absorption spectra of DLDMPbBr(a) and DLDMPbI(b) spin-coated films.

These results suggest that the inorganic layers of the products have different structures from conventional layered perovskite structures. The different arrangements of PbX_6 octahedra in the inorganic layers seems to cause the blue shift in the absorption spectra.

CONCLUSION

The DLDMPbBr and DLDMPbI have high regularity and peculiar layered structures that have unique optical

properties. These compounds also showed high self-organized properties and high solubilities in common organic solvents to prepare spin-coating films.

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