

## Hydrostatic pressure effects on structural and electronic properties of inorganic-organic quantum dot crystal $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$

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### Introduction

A series of lead-halide based inorganic-organic perovskite semiconductors forms the designed and controlled self-organized quantum structures composed of  $[\text{PbX}_6]^{+}$  (X: Cl, Br, I) octahedra, which act as multi-quantum wells, wires and dots for carriers, separated by insulating organic molecular parts. The quantum dot crystal,  $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ , is composed of isolated  $[\text{PbI}_6]^{+}$  octahedra which are bridged by methylamine ions and water molecules as a template to form a 3D superlattice structure [1], as shown in Fig. 1. In this study, we have investigated the pressure effects on the electronic and structural interactions between dots and between a dot and a methylamine molecule.

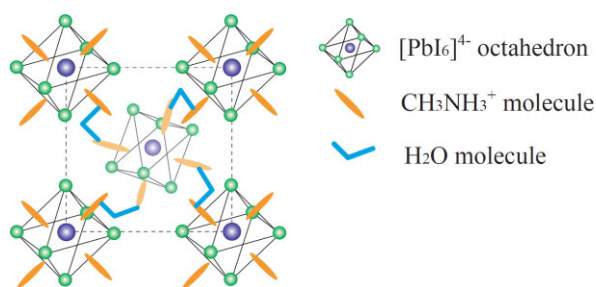


Fig. 1 Schematic view of crystal structure of  $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ .

### Experimental

Single crystals of  $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$  were grown by a solution method. We performed spectroscopic (Raman, photoluminescence (PL), optical absorption) and powder X-ray diffraction measurements under high pressure. High-pressure X-ray diffraction studies were carried out to 40 GPa at room temperature using a diamond anvil cell at the BL-18C (wavelength: 0.6198 Å) at KEK-PF. Liquid He was used as a pressure transmitting medium to ensure hydrostatic pressure.

### Results and Discussion

We observed a pressure-induced structural phase transition from a monoclinic (Phases I) to a higher-symmetric structure (Phases II) at 4.5 GPa. The cell parameters of Phase I are shown in Fig. 2. The bulk modulus of Phase I was obtained 10.2 GPa using the Birch-Murnaghan equation of state, indicating the most compressive among the series of lead-halide based inorganic-organic perovskite semiconductors, *e.g.* 14 GPa for the quantum wire crystal  $[\text{NH}_2\text{C}(\text{I})=\text{NH}_2]_3\text{PbI}_5$  and 16 GPa for the cubic perovskite  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ .

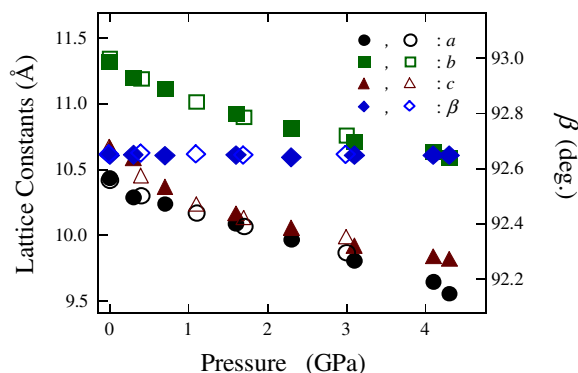


Fig. 2 Pressure dependence of cell parameters in Phase I. Open symbols for data on down-strokes.

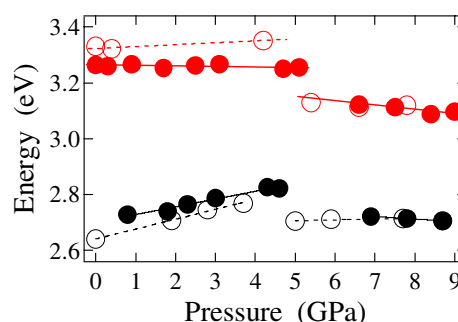


Fig. 3 Pressure dependence of peak energy of free exciton band in PL (black circles) and absorption (red circles) spectra. Open circles for data on down-strokes.

In the phase transition at 4.5 GPa, the free exciton band both in PL and absorption spectra shifts abruptly to a lower energy by 0.1 eV as shown in Fig. 3. This transition was reversible on down-strokes. The HOMO-LUMO transition energy of  $[\text{PbI}_6]^{+}$  octahedra decreased with pressure in Phase II, while it did not change with pressure in Phase I. We found that the pressure dependence of the Stokes shift of the free exciton band was different between Phase I and Phase II. We also examined non-hydrostatic pressure effects on the structural properties by using Fluorinert as a pressure medium, and found an intriguing difference between hydrostatic and non-hydrostatic compression.

### Reference

[1] R. Beverly et al., Can. J. Chem. 65, 1042 (1987).

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