Emission Enhancement and Bandgap Reduction of a Two-Dimensional Mixed Cation Lead Halide Perovskite under High Pressure

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Experimental Section

**Materials.** Lead oxide (PbO, 99.9%), methylamine hydrochloride (CH$_3$NH$_3$Cl, 99%), guanidine hydrochloride (C(NH$_2$)$_3$Cl, ≥98%), hydriodic acid (HI, 57 wt % in H$_2$O) hypophosphorous acid (H$_3$PO$_2$, 50 wt % in H$_2$O), Potassium bromide (KBr, 99.99%) and silicone oil (10 cst) were used as received from Aldrich without further purification. PbO (2232 mg, 10 mmol) was dissolved in a mixture of 20.0 mL of aqueous HI and 1.7 mL of aqueous H$_3$PO$_2$ by heating to boiling under constant magnetic stirring for at least 15 min. To the hot bright yellow solution were added solids CH$_3$NH$_3$Cl (675 mg, 10 mmol) and C(NH$_2$)$_3$Cl (478 mg, 5 mmol), and the reaction was kept under constant heating until all the reactants dissolved. The stirring was then discontinued, and the hot supersaturated solution was slowly quenched to room temperature, upon which the precipitation of dark red crystals (C(NH$_2$)$_3$)(CH$_3$NH$_3$)$_2$Pb$_2$I$_7$ commenced. The crystals were allowed to settle for further 2 hours, before the crystals were isolated by suction filtration and thoroughly dried at 60 °C in a vacuum oven. Consider that the samples are air-sensitive and the grinding and sample loading processes were carefully conducted in a N$_2$-filled glovebox.

**High-Pressure Generation:** High-pressure experiments were performed with a symmetric diamond anvil cell (DAC) with a pair of IIa-type ultralow fluorescence diamonds with a culet size of 400 μm. A T301 steel gasket was made from a 250 μm thick piece preindented to 40 μm. Then, a center hole with a diameter of 150 μm was drilled as the sample chamber for loading the samples. Typically, the prepared (C(NH$_2$)$_3$)(CH$_3$NH$_3$)$_2$Pb$_2$I$_7$ were enclosed in the gasket hole together with a ruby ball for determining the actual pressure through the standard ruby fluorescent technique. In high-pressure optical absorption, PL and XRD experiments were carried out with silicone oil as the pressure-transmitting medium (PTM); The ruby lines were found to be sharp and well-separated to
the highest pressure in our studies. All of the measurements were performed at room temperature.

**In-situ synchrotron high pressure powder X-ray diffraction:** In-situ synchrotron high pressure powder XRD experiments was carried out at BL15U1, Shanghai Synchrotron Radiation Facility (SSRF), China. Monochromatic X-ray with wavelength of 0.6199 Å was employed and the incident X-ray beam was focused to 10 μm × 15 μm spot. XRD patterns was collected with a MAR-165 CCD detector with an average acquisition time of 30s for each pressure and then were integrated on the basis of the FIT2D program, yielding 1D intensity versus diffraction angle 2-theta patterns. Materials Studio with the reflex module was also used to create the initial structures and visualize the results.

**In-situ high pressure optical absorbance, photoluminescence(PL) and infrared(IR) Measurements:** In-situ high pressure absorption and PL micrographs of the samples were obtained using a camera (Canon Eos 5D mark II) equipped on a microscope (Ecilipse TI-U, Nikon). The camera can record the photographs under the same conditions including exposure time and intensity. Absorption spectra were measured in the exciton absorption band region using a Deuterium-Halogen light source, and the excitation source, a 355 nm line of a UV DPSS laser with the power of 10 mW was used for PL measurements. High pressure PL and absorption spectra were performed using a fiber spectrometer (QE65000, Ocean Optics). In situ high pressure IR measurements were conducted using a Nicolet iN10 FT-IR micro-spectrometer.
Figure S1. (a) The evolution of PL intensity as a function of pressure. (b) PL shift as a function of pressure.
Figure S2. Tauc plots and extrapolated bandgaps of (GA)(MA)$_2$Pb$_2$I$_7$ under compression. Bandgaps obtained at 1 atm (a), 1.3 GPa (b), 4.0 GPa (c), 25.1 GPa.
Figure S3. Pressure dependent mid-infrared spectra of (GA)(MA)$_2$Pb$_2$I$_7$ up to 25 GPa
Figure S4. Tauc plots and extrapolated bandgaps of (GA)(MA)$_2$Pb$_2$I$_7$ under decompression. Bandgaps obtained at 1 atm (a), 0.6 GPa (b), 2.1 GPa (c), 5.3 GPa (d), 10.0 GPa (e) and 20.3 GPa (f).
**Figure S5.** XRD patterns for the (GA)(MA)$_2$Pb$_2$I$_7$ perovskite with decreasing pressure.