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Pressure-Induced Phase Transitions and Bandgap-Tuning Effect of Methylammonium Lead Iodide Perovskite

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ABSTRACT

Pressure-induced crystallographic transitions and optical behavior of MAPbI₃ (MA=methylammonium) were investigated using in-situ synchrotron X-ray diffraction and laser-excited photoluminescence spectroscopy. We observed that the tetragonal phase that presents under ambient pressure transformed to a ReO₃-type cubic phase at 0.3 GPa, which further converted into a putative orthorhombic structure at 2.7 GPa. The sample was finally separated into crystalline and amorphous fractions beyond 4.7 GPa. During the decompression, the phase-mixed material restored the original structure in two distinct pathways depending on the peak pressures. Being monitored using a laser-excited photoluminescence technique under each applied pressure, it was determined that the bandgap reduced with an increase of the pressure till 0.3 GPa and then enlarged with an increase of the pressure up to 2.7 GPa. This work lays the foundation for understanding pressure-induced phase transitions and bandgap tuning of MAPbI₃, enriching potentially the toolkit for engineering perovskites related photovoltaic devices.

Introduction

The power conversion efficiency (PCE) of perovskite-based photovoltaic (PV) cells has a rapid increase from about 6% in 2011 to approximate 20% presently [1]. While modifying charge carrier mobility and the direct bandgap by tuning crystal chemistry can improve the PCE, extensive synthesis campaigns have revealed a limited range of materials [2]. Alternatively, pressurization is an effective and robust way to change the crystal structures and thus to guide strategies for selecting ions of appropriate size and charge by monitoring changes in PV properties [3]. The perovskite prototype has a general formula ABX_3 , creating a 3D framework with corner-sharing BX_6 octahedra in which the A component provides charge compensation (Figure 1a). The bandgaps of Pb-based MA halide perovskites, $MAPbCl_3$, $MAPbBr_3$, and $MAPbI_3$, were reported as ~ 3.1 , ~ 2.3 , and ~ 1.5 eV, respectively [4]. The appropriate bandgap for a single junction PV cell is within a range between 1.1 and 1.4 eV [5,6]. This indicates that $MAPbI_3$ could be a desirable halide perovskite material to fundamentally understand the subject. Although previous studies of pressure-induced transformation in hybrid perovskites have validated the crystallographic richness and bandgap changes [7,8], extraction of high-pressure lattice parameters, the unambiguous determination of crystal symmetry, and the refinement of atomic fractional coordinates of $MAPbI_3$ are still in need. In this paper, we discuss the phase transitions and optical properties of $MAPbI_3$ during its compression and decompression processes using in-situ synchrotron X-ray diffraction (XRD) and laser-excited photoluminescence (PL) spectroscopy techniques, which is valuable for the novel design of perovskite-based PV devices.

Figure 1. (a), $MAPbI_3$ perovskite structures (left, polyhedral model; right, schematic of 3D illustration); (b), DAC holder system with balanced screws (left, side view; right, top-down view).

Experimental details

MAPbI₃ was fabricated using a synthetic procedure reported previously [9]. In brief, polycrystalline MAPbI₃ was precipitated by cooling from 100 to 46 °C after PbI₂ and MA-I solutions were mixed in a Pyrex test tube. The PbI₂ solution was prepared by dissolving 2.50 g of lead (II) acetate (Sigma-Aldrich) in 10 mL of aqueous HI solution (57 wt%), and the MA-I solution was formed by dissolving 0.597 g of aqueous CH₃NH₂ solution (40%, Merck) in 2 mL of HI solution. Diamond Anvil Cells (DACs) with a diameter of 500 μm were aligned, assembled and pressurized before conducting in-situ synchrotron powder XRD (Figure 1b). A stainless steel gasket was pre-indented with a hole (approximate diameter: 200 μm) drilled in the center to serve as the compaction chamber to hold the sample. Ruby crystal chips were placed with the sample in the compaction chamber before sealing the DAC. The pressure was determined by ruby fluorescence under non-hydrostatic condition [10]. PL spectra and XRD patterns ($\lambda = 0.485946 \text{ \AA}$) were recorded after a loading and pressure maintaining for about 20 min in each measurement. The experiment was conducted at B1 station of Cornell High Energy Synchrotron Source (CHESS) [11].

Discussion

Structure variations

Under ambient pressure, XRD data indicate that MAPbI₃ possesses a tetragonal symmetry (*I4/mcm*, No. 140) (Figure 2a) with lattice parameters $a = 8.8648(6) \text{ \AA}$ and $c = 12.6746(8) \text{ \AA}$, which were obtained by Pawley fitting. The unit cell of the tetragonal (t) phase can be derived from the cubic aristotype (a) of perovskite structure (*Pm-3m*, No. 221) in which $a_t = a_a\sqrt{2}$ and $c_t = 2a_a$. Around 0.3 GPa, newly appeared reflection peaks around 7.1° and 8.4° indicate the evolution of a new cubic (c) bilayer ReO₃-type phase (*Im-3*, No. 204) in which $a_c = 2a_a$ [12]. Although the reflections of the cubic aristotype might substantially overlap with those of cubic supercell, no trace of such reflections was found during the compression. Beyond 0.4 GPa, the initial *I4/mcm* phase completely transformed into cubic *Im-3* polymorph with lattice parameter $a = 12.4076(8) \text{ \AA}$, whose tilt character can be identified as $a^+a^+a^+$ in Glazer notation, suggesting that the PbI₆ octahedra tilted in equal magnitude about all three axes. With a continuous compression to 2.3 GPa, the unit cell volume of the *Im-3* phase decreased and the Bragg reflection peaks broadened as a result of the applied pressure. At 2.7 GPa, there was a triple splitting on the 00l reflection around 9.5°, indicating the appearance of a new phase. Such a triple splitting could be attributed to the degeneration from cubic *Im* to orthorhombic *Immm* (No. 77) symmetry in which PbI₆ octahedra performed the $a^+b^+c^+$ tilting. Beyond 2.7 GPa, MAPbI₃ started to convert into an amorphous form and it reached a nearly complete amorphous state at 4.7 GPa, with no further change in XRD patterns up to 6.4 GPa (also refer to 2D diffraction patterns in Figure 2c). Upon a gradual pressure-release to 0.5(8) GPa, the partial amorphous phase directly converted back to the *Im-3* phase, without showing of the *Immm* polymorph which appeared during the compression process (Figure 2b, d). At 0.5(5) GPa, MAPbI₃ restored the

I4/mcm phase, which demonstrates a reversibility of the structure conversion under varied pressures (Figure 2d).

Figure 2. Integrated XRD patterns of MAPbI₃ during (a), compression; (b), decompression runs; and its 2D patterns during (c), compression; and (d), decompression runs.

In order to determine the influence of the maximum compression pressure (peak-pressure) on the phase transitions and microstructural evolution during the decompression process, a series of *in-situ* XRD measurements were conducted with different peak-pressures. For example, when 3.5 GPa was chosen as the highest pressure, the *Immm* polymorph recovered at 2.8 GPa during a decompression. However, such a phase wasn't observed if the peak-pressure was increased to 6.4 GPa. Followed by the recovery of *Immm* phase, MAPbI₃ continued to convert back to the *Im-3* phase when the pressure was reduced to 0.9 GPa. These two different phase transition pathways confirmed that the resultant structures of MAPbI₃ in a decompression process closely depend on the peak-pressure reached in the compression process. The fact that the *Immm* phase was absent in a decompression process when the peak-pressure reached 6.4 GPa indicates that *Immm* phase could be a metastable structure, compared with cubic *Im-3* and tetragonal *I4/mcm* phase which was restored reversibly as long as the applied peak-pressure does not exceed 8.0 GPa.

Optical properties

The bandgap values during a compression process were calculated using *in-situ* pressure-PL spectra of MAPbI₃ (Figure 3a, b). Typically, this method slightly overestimates the bandgap values in comparison with those determined by Tauc plot using absorption data [13]. Under ambient pressure, the peak wavelength of the PL spectrum was located at 764 nm, which was equivalent to a bandgap of 1.62 eV. As the pressure reached 0.3 GPa, the PL central peak showed a red-shift, suggesting a pressure-induced reduction of the bandgap when it transformed from tetragonal *I4/mcm* phase to cubic *Im-3* supercell. From 0.41 GPa to 1.95 GPa, the PL central peaks show a gradual blue-shift, which could be a result of the increasing tilting angle of PbI₆ octahedra in the *Im-3* supercells. Above 2.0 GPa, the PL band weakened drastically, making the central peak indistinguishable. At 2.7 GPa, the PL peak completely vanished as the *Im-3* phase fully transferred to the *Immm* polymorph. The value of peak-pressure also imposed an impaction on the PL behavior. When 6.4 GPa was applied as the peak-pressure, the PL was absent during the whole decompression process down to ambient pressure. In contrast to the maximum pressure of 6.4 GPa, with 3.5 GPa as the peak-pressure, a weak PL band appeared at 1.7 GPa during the decompression process when the *Im-3* polymorph started to restore. Such a difference in PL observation confirms that the generation of PL is closely associated with the perovskite structure. Consequently, the pressure-induced structure transformation from *I4/mcm* phase (ambient pressure) to *Im-3* supercell (<0.4 GPa) could serve as an effective platform to reduce the bandgap energy. Based on the variation of the bandgap as a function of the pressure, we suggest that a relatively low-pressure manipulation on MAPbI₃ could be promising to extend the absorption range over the long wavelength region, which is extremely intriguing for future PV device improvement.

Figure 3. (a), Room temperature photoluminescence spectra of MAPbI₃; (b), Calculated bandgap as a function of compression pressure.

Conclusions

This study shows the pressure-induced bandgap tuning effect of MAPbI₃ using *in-situ* synchrotron XRD and laser-excited PL techniques. Upon compression, MAPbI₃ underwent a series of phase transitions from tetragonal phase (*I4/mcm*) under ambient pressure to a suggested orthorhombic structure (*Immm*), through an intermediate ReO₃-type cubic supercell (*Im-3*), and eventually started amorphization. During the decompression process, MAPbI₃ restored original tetragonal polymorph through different phase transition pathways, depending on the peak-pressure loaded in the compression processes. PL study showed that the transition from *I4/mcm* to *Im-3* symmetry resulted in a bandgap narrowing, whereas the transition from *Im-3* to *Immm* symmetry led to a bandgap broadening. These findings reveal the flexibility in adjusting and achieving desired structures and bandgap values of MAPbI₃ by applying an external pressure. Moreover, this combined chemical–pressure strategy may provide a valuable platform where a design of new perovskites for photovoltaic applications could be realized.

Acknowledgments

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