

High-pressure transformation of MAPbI₃: role of the noble-gas medium

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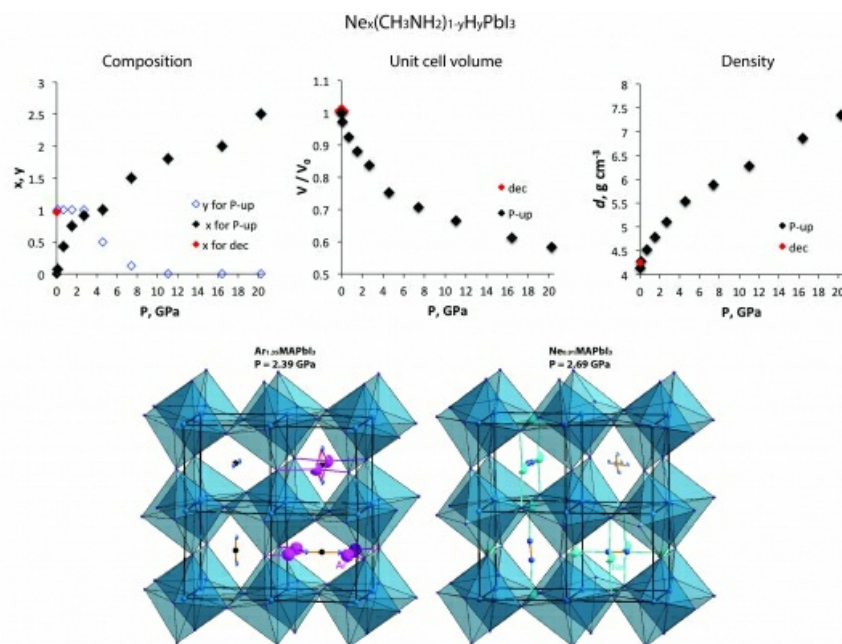
It is well known that noble gases are relatively inert which justifies their use as pressure-transmitting medium (PTM) in high-pressure (HP) studies. Recent reports [1] indicate that various noble gases taken as PTM apparently influence the outcome of structural transformations. We reach the same conclusion by a systematic study of the structural changes of methyl-ammonium lead iodide, CH₃NH₃PbI₃ (MAPbI₃), a photovoltaic perovskite [2] with pressure by choosing Ne and Ar as two PTMs. The single crystal XRD experiments were performed using synchrotron radiation at room temperature up to 20 GPa. The crystal structure of MAPbI₃ consists of a framework of corner-sharing PbI₆ octahedra and methyl-ammonium cations, CH₃NH₃⁺ (MA), which is rotating in the cuboctahedral surrounding of twelve I-atoms. Weak hydrogen bonds statistically appeared between MA and I atoms give a high flexibility to the structure, which depends, in particular, on temperature and pressure. The large structural interstices offer the possibility to host other molecules which can alter the hydrogen bonds and destabilise the structure (see e.g., the case of water molecules [3]). We found the following structural consequences of the incorporation of Ne and Ar PTM into the interstices at HP. (i) The first-order phase transition from the tetragonal phase at ambient pressure (unit cell parameters $a \approx 8.8 \text{ \AA}$, $c \approx 12.7 \text{ \AA}$) to the (pseudo)cubic HP-phase (unit cell parameter $a \approx 12.3 \text{ \AA}$) starts at pressures of about 1 and 0.1 GPa for Ar and Ne PTM, respectively. (ii) Above these pressures, a phase amorphization starts at about 1.5 GPa for Ar and 4 GPa for Ne. It is documented that a crystal of poor quality (high patchiness, inter-domain disorientation) is irreversibly amorphized, while a higher quality single crystal preserves partially a crystalline state up to 20 GPa for Ne-PTM. (iii) Ne-PTM series shows the pressure dependent incorporation of Ne and the loss of MA (see a graphic illustration). The transformation of the crystal composition can be expressed as: MAPbI₃ → Ne(x).MAPbI₃ → Ne(x).MA(1-y).H(y)PbI₃ → Ne(x).HPbI₃. The decompressed crystal shows NeMAPbI₃ composition even after four weeks upon the decompression. Ar is assimilated by the structure to form Ar_{1.4}MAPbI₃ at 2.4 GPa and a complete, irreversible amorphisation follows at about 3.5 GPa. The difference between Ne and Ar used PTM is related to the difference in their atomic radii (0.38 and 0.71 Å for Ne and Ar, respectively) and to their different ability to enter in "chemical reaction" in the restricted space between the PbI₆ octahedra.

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