Basic Research

Imaging Atomic Structure of Hybrid Perovskite $CH_3NH_3PbI_3$

Hybrid organic-inorganic perovskites (HOIPs) have attracted great research interest as promising materials for the next generation photovoltaic energy harvesting, electro-optic detection, and all-optical conversion. Their remarkable charge-transport and absorption properties are underpinned by hybrid perovskite atomic structures.

Understanding the atomic structure and structural instability of organic-inorganic hybrid perovskites is the key to appreciate their remarkable photoelectric properties and understand failure mechanism.

However, atomic imaging of OIHPs by electron microscopy is challenging due to the extreme beam sensitivity. So far, the damage-free pristine structure of $CH_3NH_3PbI_3$ ($MAPbI_3$) has never been captured at the atomic scale.

Recently, Dr. WANG Xiao's group at the Shenzhen Institute of Advanced Technology (SIAT) of the Chinese Academy of Sciences collaborated with Dr. ZHAO Jinjin, Dr. LI Jiangyu and Dr. GAO Peng's team from Shijiazhuang Tiedao University, Southern University of Science and Technology and Peking University respectively, adopted low-dose imaging by direct-detection electron-counting camera, successfully imaged the atomic structure of perovskite $MAPbI_3$ and discovered the degradation pathway of $MAPbI_3$ in detail.

Their study was published in *Nature Communications*.

The researchers investigated the atomic structure

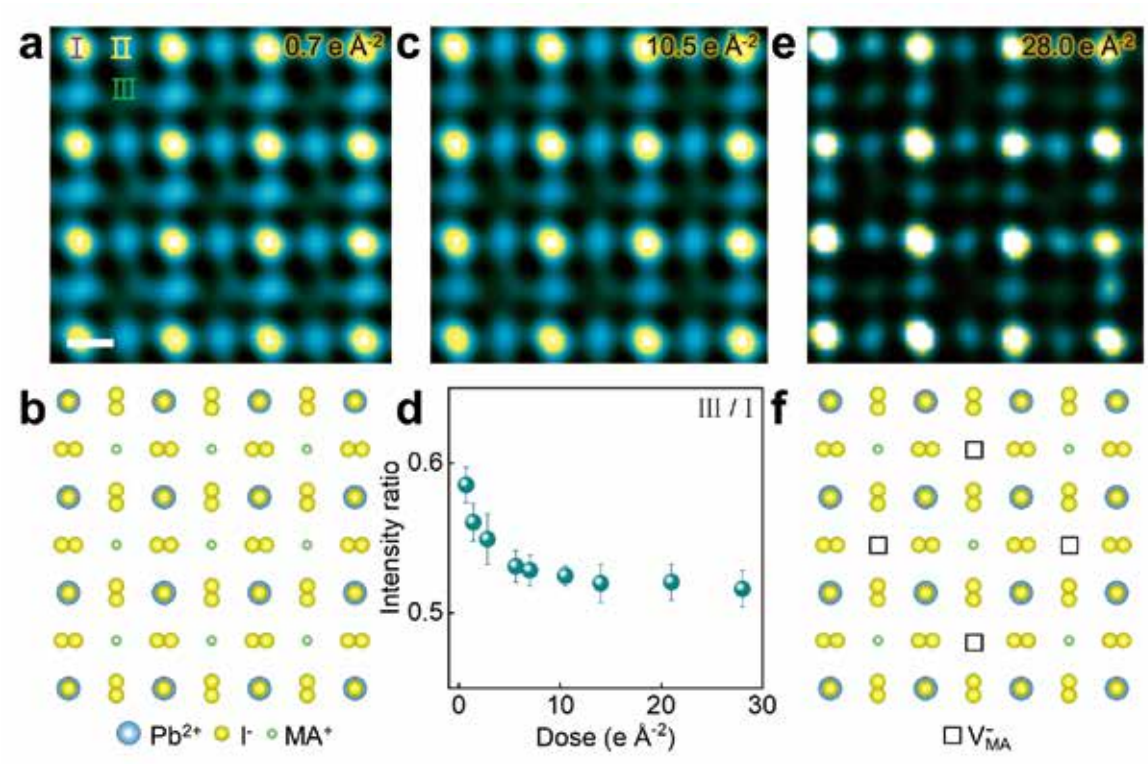

Fig. 1 Atomic-imaging of the loss of MA^+ and intermediate phase. (Image by SIAT)

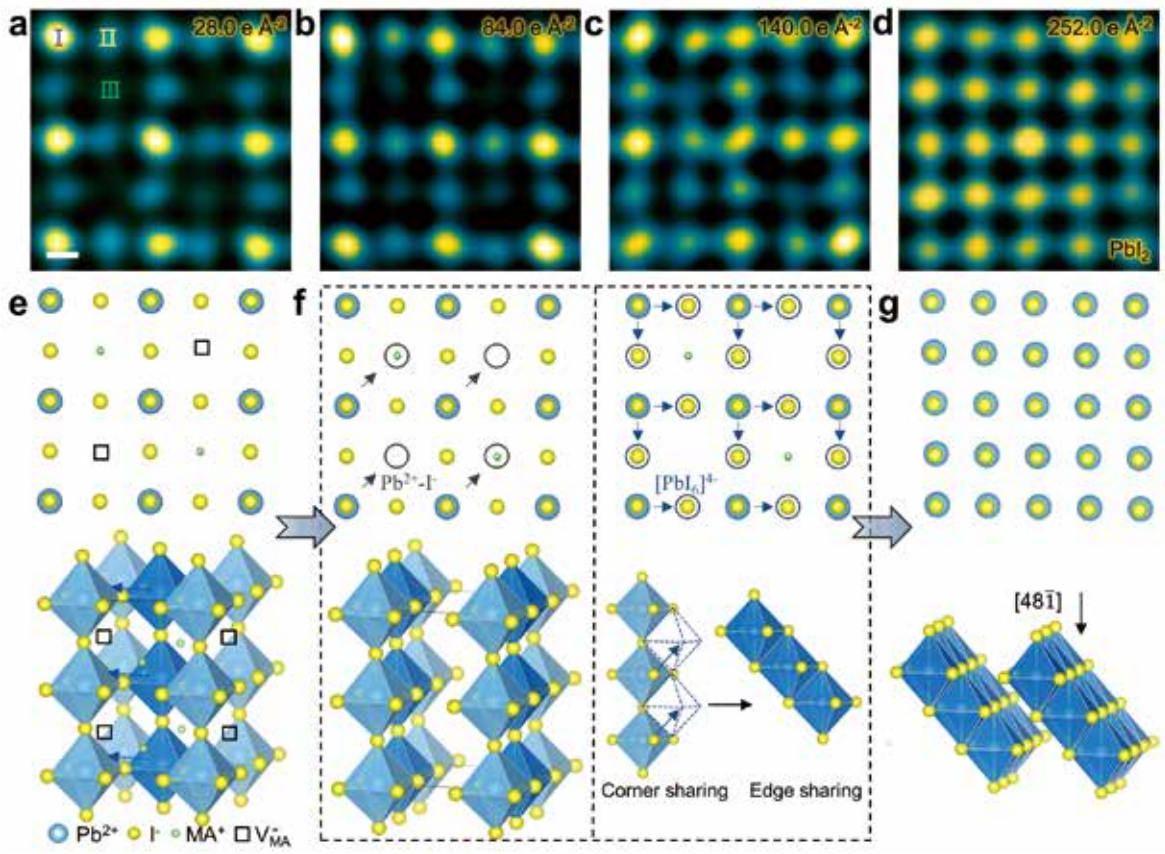

Fig. 2 Atomic-scale imaging of the decomposition pathway. (Image by SIAT)

via an imaging technique using a negative value of the spherical-aberration coefficient. As the dose increased, the intensity of MA^+ was decreased with the formation of V_{MA}^-. At a certain dose, the intensity kept constant, indicating a relatively stable intermediate phase, $MA_{0.5}PbI_3$, which was verified by further TEM analysis and molecular dynamic simulation.

Consistent with the CL measurement, DFT calculations showed that the bandgap will increase as the MA vacancy's density increases, which provided a potentially new strategy to tune the bandgap in constructing tandem solar cell and facilitated multiwave electroluminescence emission, adjusting various color luminescence under increasing bias voltage. With the discovery of the intermediate, the researcher further investigated the atomic-scale decomposition pathway of $MAPbI_3$. At the first stage, the V_{MA}^- formed and the intermediate phase $MA_{0.5}PbI_3$ emerged. Consequent diffusion of Pb^{2+} and I^- into V_{MA}^- and the $[PbI_6]^{4-}$ octahedron slipping from corner sharing to edge sharing makes the structure gradually evolve to PbI_2.

This work can be used to guide the future TEM characterizations, enrich the understanding of the degradation mechanism and optimization strategies, and provide atomic-scale insights into understanding its fundamental properties.

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Reference
S. Chen, C. Wu, B. Han, Z. Liu, Z. Mi, W. Hao, . . . P. Gao, (2021) Atomic-scale imaging of $CH_3NH_3PbI_3$ structure and its decomposition pathway. *Nature Communications* 12, 5516. doi: 10.1038/s41467-021-25832-9.