

*Local structure of lead halide perovskites for photovoltaic applications*Jiaxun Liu¹, Anthony Phillips¹, Martin Dove¹¹School Of Physics And Astronomy, Queen Mary University Of London, London, United Kingdom

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Fabricating high-efficiency, low-cost and long-term stability solar cells is of significant importance to solve energy problems. Recently, hybrid inorganic–organic lead halide perovskites, with the general formula of ABX_3 ($A = CH_3NH_3^+$; $B = Pb^{2+}$; $X = I^-$, Br^-), have become promising for easy fabrication and high efficiency. The power conversion efficiency of devices based on such perovskite material has been substantially increased from 3.8% in 2009 to 22.1% in 2016 [1]. The high symmetry of the parent perovskite structure ABX_3 can be reduced by orientational disorder of methylammonium (MA) cations, rotation and distortion of BX_6 octahedra. Since this disorder appears to be fundamental to the improved properties of these devices, understanding the crystal structures and phase transitions of perovskite materials can aid in enhancing performance of perovskite materials.

Here, we combine neutron total scattering with Reverse Monte Carlo (RMC) modelling to investigate the rotational disorder of the MA cations. As the name implies, total scattering is a combination of the Bragg and diffuse scattering over all scattered energies. This gives the local instantaneous atomic structure, rather than the average long-range structure given by Bragg scattering. This local view is critical to understanding the effects of disorder in these materials. The RMC simulation method produces a three-dimensional configuration consistent with all experimental structural data [2]. The starting configuration stems from a supercell with the atoms in their ideal average positions determined by Rietveld refinement. In each move, a random atom within the configuration is chosen and moved a small amount; moves are accepted or rejected probabilistically using the Metropolis algorithm.

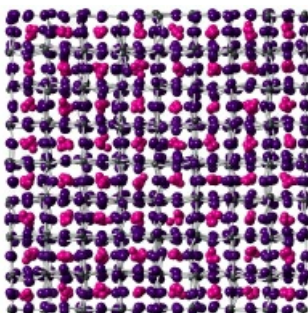
Since the positions of hydrogen atoms are vital to understanding the energetics of the MA cations, we have prepared a fully deuterated $MAPbI_3$ sample. We have collected total neutron scattering measurements in the three reported phases: the highly-disordered cubic phase ($Pm\bar{3}m$) above 327 K, the intermediate tetragonal phase ($I4/mcm$) with some disorder, and the fully-ordered orthorhombic phase ($Pnma$) below 165 K. For comparison, we have also studied the inorganic analogue $CsPbI_3$ to give information on the effect of different cations within the perovskite structure, and hence to understand this family's structural flexibility.

The resultant RMC configurations at high temperature indicate that the cubic frameworks are considerably distorted. By comparing the original configuration with RMC configuration in terms of each polyhedron, we obtain the fraction of three types of distortion including PbI_6 rotations, Pb-I bond stretching and I-Pb-I bending. [3]. Unique and high-quality structural information is extracted from RMC and total scattering to better understand the mechanism of perovskite materials. By comparing the behaviour of hybrid organic-inorganic and purely inorganic perovskites, we are able to elucidate the relationships between the structural disorder in these materials and their optoelectronic properties, leading towards the goal of rational design of new photovoltaics.

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[2] Keen, T. et al. (2005). *J. Phys.: Condens. Matter* 17 S15–S22.

[3] Hui, T. et al. (2005). *J. Phys.: Condens. Matter* 17, S111.



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