MS13-1-15 3D ED of hybrid perovskites
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Abstract
Hybrid perovskites are a new class of materials that have raised a remarkable interest due to their promising properties for a variety of applications beyond photovoltaics. In particular, metal-halide organic-inorganic perovskites have been recognized as promising semiconductors with tunable optoelectronic properties, which make them excellent candidates for applications in chiroptics, spintronic, photodetectors, and light emitting devices. Often these structures cannot be crystallized in well-ordered and sufficiently large crystals to be studied by single crystal X-ray diffraction (XRD) and 3D electron diffraction (3D ED) becomes a valuable option. Unfortunately, they suffer from beam irradiation in part due to their intrinsic intercalated architecture of inorganic and organic layers, so that their TEM analysis is extremely challenging. Here we present two case studies of unknown metal halide perovskites whose structure is determined using 3D ED in low dose mode, avoiding excessive beam damage. The first structure is a 1D lead iodide hybrid perovskite where the inorganic part forms octahedral chains intercalated by a polycyclic aromatic hydrocarbon molecule with ethynyl pyridinium wings. The molecules are packed by π - π interaction. The inorganic part has been determined ab-initio with direct methods, while the location and the configuration of the organic molecule was derived using simulated annealing. The second type of structures are lead bromide hybrid perovskites where the organic part is made either by benzylamine (BZA) or thiophenemethylamine (TMA). These compounds crystallize in the sub-micrometre range, making standard crystallographic investigations for structure solution very difficult. Moreover, their structure analysis is complicated by twinning at the nanoscale. Also, the inorganic layer of both structures can be determined ab-initio, while the organic part cannot be found. We found that the TMA-based crystal is a 2D layered perovskite with the form TMA2PbBr4, while the BZA-based one is a 1D perovskite with the PbBr6 octahedra arranged in ribbons. We expect to locate the molecules in both cases using simulated annealing on powder XRD data. These results showcase how to implement 3D ED on complex hybrid structures, providing insight on their arrangement at the nanoscale that cannot be directly studied by X-ray diffraction analysis.