Low-Dose 4D-STEM Investigations of the Octahedral Network Structure in Formamidinium Lead Bromide Nanocrystals

Nadine Schrenker[1,2], Mr. Tom Braeckevelt[3], Mrs. Annick De Backer[1,2], Mr. Nikolaos Livakas[4], Mr. Chu-Ping Yu[1,2], Mr. Thomas Friedrich[1,2], Mr. Daen Jannis[1,2], Mr. Armand Béché[1,2], Mr. Maarten Roeffaers[5], Mr. Johan Hofkens[6], Mr. Johan Verbeeck[1,2], Mr. Liberato Manna[4], Mrs. Veronique Van Speybroeck[3], Mrs. Sandra Van Aert[1,2], Mrs. Sara Bals[1,2]
[1]Electron Microscopy for Materials Science (EMAT), University of Antwerp, Antwerp, Belgium, [2]NANOlab Center of Excellence, University of Antwerp, Antwerp, Belgium, [3]Center for Molecular Modeling, Ghent University, Belgium, [4]Department of Nanochemistry, Istituto Italiano di Tecnologia (IIT), Genova, Italy, [5]cMACS, Department of Microbial and Molecular Systems, KU Leuven, Leuven, Belgium, [6]Department of Chemistry, KU Leuven, Leuven, Belgium

Background incl. aims
Hybrid organic-inorganic metal halide perovskites have shown great potential as semiconductors for new optoelectronic devices, such as photovoltaics, light-emitting diodes, and X-ray detectors. Their outstanding optoelectronic properties, including a tunable bandgap, high charge carrier mobility, high photoluminescence quantum yield, and low recombination rate of photogenerated carriers, have contributed to their rapid development.(Dey et al. 2021) The structure of metal halide perovskites (MHP) is described by the chemical formula ABX3, where A is a monovalent organic cation (e.g. formamidinium (FA+) [CH(NH2)2+] or methylammonium (MA+) [CH3NH3+]) or a metal cation (e.g. Cs+), B is a divalent metal cation (typically Pb2+or Sn2+), and X is a halide anion (X = Cl-, Br-, I-). The perovskite structure consists of [BX6]4-octahedra that are connected through the corner halides. The octahedral network structure is closely linked with the polymorphic nature of MHPs, which is of great importance since phase instability is still one of the major roadblocks for long-term applications of MHPs. Only the “black” phase demonstrates photoactive properties, which dramatically decrease once the MHPs convert to the “yellow” phase. From the high-symmetry cubic phase, the transition to the lower symmetry phases can be described by rotation or shearing of the octahedra. It is crucial to understand the role of the octahedral network to unravel the structure-property connection and correlate it to transformations during degradation. Transmission electron microscopy (TEM) is an excellent method for investigating the local structure of nanocrystals (NCs), even down to the atomic level. Nevertheless, when applied to MHPs, their sensitivity to the electron beam is highly challenging. Irradiation with the electron beam easily causes degradation of the MHP NCs with PbX2 and Pb as resulting products.

Methods
In this study we utilize four dimensional scanning transmission electron microscopy (4D-STEM) to obtain phase contrast image reconstructions to investigate the local structure of colloidal FAPbBr3 NCs, which were synthesized following a hot injection method. Phase contrast imaging is beneficial for materials in which both heavy and light elements are simultaneously present, such as organic cations and lead in perovskites. Moreover, 4D-STEM is superior with respect to information-richness and dose-efficiency as compared to high-angle annular dark-field (HAADF) STEM, where only electrons scattered to relatively high angles are used. The 4D-STEM datasets were acquired with a custom-made Timepix3 detector, which is an event driven hybrid pixelated direct electron detector. To retrieve the phase information from the recorded 4D datacube, we applied a recently developed convolutional neural network (CNN).(Friedrich et al. 2023) The CNN was trained based on a large synthetic dataset, using atomic structures extracted from the materials project database. Moreover, to analyze the local structure we fitted the shape of the projected

atomic columns. For this purpose, a parametric model was used which consists of a sum of two-dimensional elliptical Gaussians, each centered on the atomic column positions. Additionally, the experimental STEM results were compared with a series of molecular dynamics (MD) simulations at constant temperature and pressure, which were performed using a machine learning potential trained on underlying Density Functional Theory energies and forces.

Results

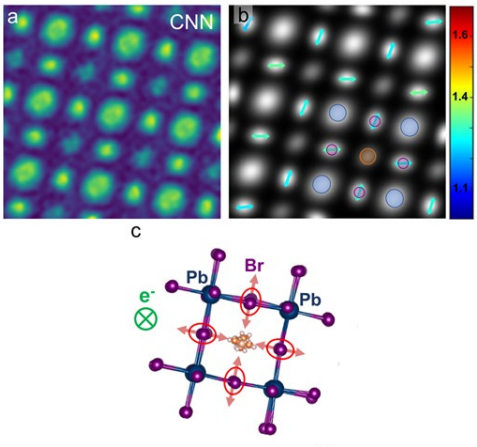
The high dose efficiency of the CNN reconstruction enables to study these beam-sensitive NCs with an electron dose that is sufficiently low to avoid the formation of Pb-rich clusters due to electron beam irradiation while maintaining a high signal-to-noise ratio. It is noteworthy that at a total electron dose below 50 e-/A2, all atomic columns, including the light formamidinium cations and Br anions can be clearly detected in the CNN reconstructions (see panel (a) in Figure 1). Moreover, a close inspection of the projected Br columns revealed deviations from perfect round projections. A possible reason are alternations in the position of the Br atoms along the viewing direction. The ellipticity ratio for the projected Br atomic columns was obtained by fitting elliptical Gaussians. In panel (b) the arrows illustrate the ellipticity ratio of the projected Br atomic columns and the overlay represents the different atomic columns ((Br = purple, Pb-Br = blue, FA = orange). This indicates that the Br atoms have a small flexibility in the octahedral network structure and can be displaced perpendicular to the Pb-Br-Pb bond, which is schematically illustrated by the red arrows in panel (c) in Figure 1. Furthermore, the performed MD simulations confirmed the displacement of the Br atomic columns. This observation is also in good agreement with previous synchrotron XRD measurements of FAPbBr3 NC, where the measured Pb-Br-Pb bond angles deviate up to 15 ° from the ideal 180 ° angle due to local disorder caused by displacement of Br anions.(Yazdani et al. 2023)

Conclusion

Thus, our approach via low-dose phase image reconstructions enables to study the local octahedral network structure of perovskites and could be transferred to in situ experiments in the future to investigate degradation mechanisms under environmental triggers.

.

Graphic:



Keywords:

perovskite, 4D-STEM, phase contrast imaging

Reference:

1. Dey, A. et al. ACS Nano 15, 10775–10981 (2021).
2. Friedrich, T., Yu, C.-P., Verbeeck, J. & Van Aert, S. Microscopy and Microanalysis 29, 395–407 (2023).
3. Yazdani, N. et al. Nature Physics 2023 1–7 (2023)