Experimental report

26/03/2022

Proposal: 5-14-269 **Council:** 10/2019

Title: Unraveling the Disorder-Function Relationship in Organic-Inorganic Metal Halide Perovskites via Elastic Neutron Diffuse Scattering

Research area: Materials

This proposal is a new proposal

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Samples: CD3ND3PbBr3

Instrument	Requested days	Allocated days	From	To
D10	8	4	15/03/2021	19/03/2021

Abstract:

We propose to characterize nanoscale structural defects in perovskite photovoltaic materials with the goal of gaining a fundamental understanding of how these defects affect optoelectronic properties. Unlike traditional semiconductors for photovoltaics which require a nearly perfect crystal structure, high-efficiency hybrid organic-inorganic metal halide perovskite semiconductors contain a high density of intrinsic static and dynamic defects. Local lattice distortions and structural heterogeneities which result from these defects interact with photo-induced excitations and govern ion migration. As a result, structural defects can be both beneficial and detrimental to the functionality and stability of hybrid perovskites; a full understanding of the relationship between defects and optoelectronic properties is lacking. In this proposal, we will utilize elastic neutron diffuse scattering techniques to characterize structural defects and ultimately connect the associated lattice distortions with optoelectronic properties of hybrid perovskite photovoltaics.

Report on: Unraveling the Disorder-Function Relationship in Organic-Inorganic Metal Halide Perovskites via Elastic Neutron Diffuse Scattering

Experimenters: Nicholas Weadock, Hans-Georg Steinrück

Hybrid organic-inorganic metal halide perovskites (HOIP) have recently been the subject of intense research due to their high efficiency as solar absorbers and ease of fabrication. Contrary to traditional semiconductor solar absorbers such as Si and GaAs, HOIP single crystals and/or thin films are solution processed and contain a high number of structural defects and disorder, which may be intrinsic.

Continued improvement of the efficiency and stability of HOIP-based solar cells requires a fundamental understanding of the relationship between structural defects and optoelectronic properties. [1] Defect types include Schottky and Frenkel defects, and lattice distortions generated by accumulated charges and impurities. [2] These defects provide pathways for degradation *via* ion migration and/or photo-induced phase transitions. The nature and quantity of these defects are not well understood, even in single crystals. Therefore, further studies are warranted to understand the relationship between disorder and optoelectronic properties. [3]

We proposed to characterize intrinsic structural defects in MAPB via elastic neutron diffuse scattering (NDS) of single crystals. MAPB is a thermodynamically stable model system from which other HOIPs are derived, providing a baseline with which to relate local disorder to optoelectronic properties. [4] Specifically, we aim to characterize the type and number of point defects and associated lattice distortions. Furthermore, the effects of preparation method on defect character will be investigated by measuring samples prepared with inverse temperature- and antisolvent-induced crystallization. [3] NDS measurements about several Bragg peaks will be performed on fully deuterated single crystals (few mm's per side) fabricated by our collaborators in the Karunadasa group at Stanford University. The Karunadasa group has experience in fabricating d-HOIPs, having previously prepared d-MAPI for our neutron scattering experiments. [5]

Our experiment was performed on D10, the single-crystal diffractometer using the triple-axis energy analyzer to minimize thermal diffuse scattering contributions. A neutron wavelength of 1.53Å was used for these measurements. Full reciprocal space maps about the 400 and 440 Bragg peaks were found to be not feasible due to time constraints. Instead, we measured transverse scans across the 400 and 440 Bragg peaks at 250 and 285 K, and additional longitudinal scans for the 400 peak. The resolution in the longitudinal *l* direction at the 440 peak is poor, giving a broad Bragg peak.

Figure 1 plots the transverse and longitudinal scans for the 400 peak at 250 K. Static defects introduce additional scattering intensity away from the Bragg peak that falls of as Δq^{-2}. We plot $I(\Delta q^{-2})$ as a guide to the eye in Fig. 1c,d, and observe that the intensity variation indeed matches will with the expected dependence. However, the same dependence occurs for thermal diffuse scattering, which can be removed by examining the scattering intensity at several temperatures. No significant differences were observed between 250 and 285 K, suggesting a minimal contribution from thermal diffuse scattering. However, the change in temperature is relatively small in this case.

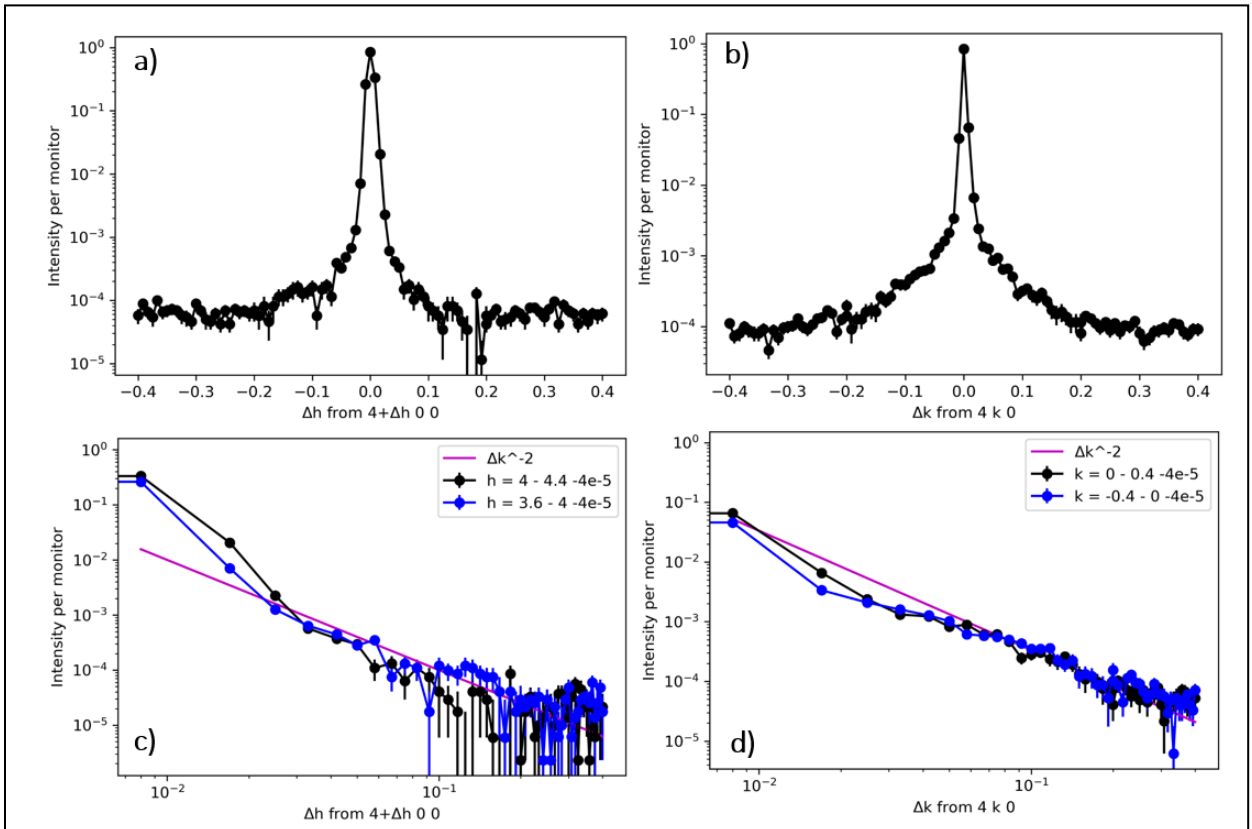

Figure 1: Transverse (a,c) and longitudinal (b,d) elastic Q-scans of the (400) Bragg peak in cubic MAPB at 250 K. Log-log plots in c), d), show that the intensity variation goes as Δq^{-2}, as expected for static and thermal diffuse scattering contributions. A small inflection in d) around $\Delta k = 0.04$ may indicate the presence of additional intensity arising from static diffuse scattering from defects.

The next steps in our analysis involve an accurate determination of the background contributions and consideration of the energy and Q resolution contributions to the scattering intensity. Given the limited range of temperatures and Bragg peaks examined, however, we anticipate that additional beamtime will be necessary to obtain an accurate picture of the defect structure in MAPB.

[1] D. A. Egger, A. Bera, D. Cahen, G. Hodes, T. Kirchartz, L. Kronik, R. Lovrincic, A. M. Rappe, D. R. Reichman, and O. Yaffe, *What Remains Unexplained about the Properties of Halide Perovskites?*, Advanced Materials **30**, 1800691 (2018).

[2] D. J. Slotcavage, H. I. Karunadasa, and M. D. McGehee, *Light-Induced Phase Segregation in Halide-Perovskite Absorbers*, ACS Energy Lett. **1**, 1199 (2016).

[3] Y. Dang, D. Ju, L. Wang, and X. Tao, *Recent Progress in the Synthesis of Hybrid Halide Perovskite Single Crystals*, CrystEngComm **18**, 4476 (2016).

[4] E. Zimmermann, K. K. Wong, M. Müller, H. Hu, P. Ehrenreich, M. Kohlstädt, U. Würfel, S. Mastroianni, G. Mathiazhagan, A. Hinsch, T. P. Gujar, M. Thelakkat, T. Pfadler, and L. Schmidt-Mende, *Characterization of Perovskite Solar Cells: Towards a Reliable Measurement Protocol*, APL Materials **4**, 091901 (2016).

[5] A. Gold-Parker, P. M. Gehring, J. M. Skelton, I. C. Smith, D. Parshall, J. M. Frost, H. I. Karunadasa, A. Walsh, and M. F. Toney, *Acoustic Phonon Lifetimes Limit Thermal Transport in Methylammonium Lead Iodide*, PNAS **115**, 11905 (2018).