Structural characterization of halide perovskites by X-ray measurements and advanced analysis

DSCATM Bressanone 28-30 October 2019

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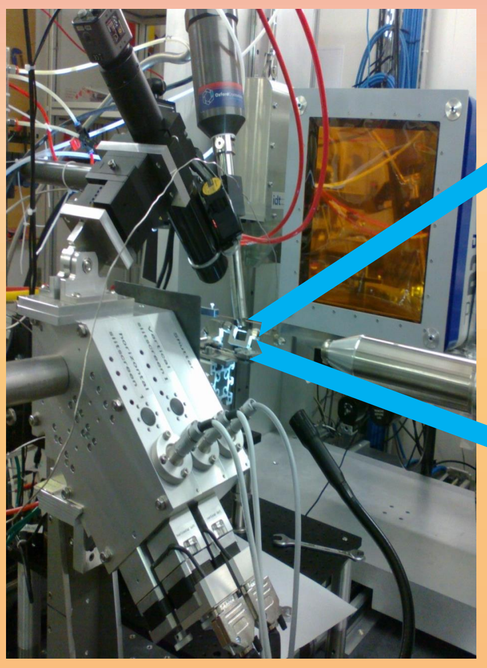
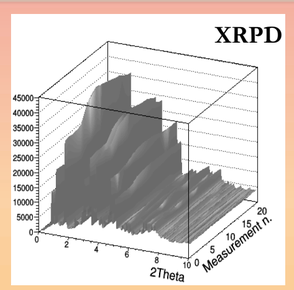
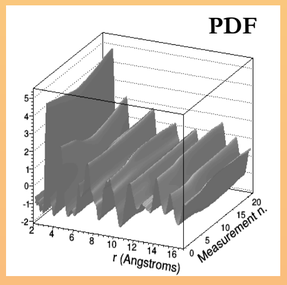
Multi-probe in situ experiments

The advent of new-generation X-ray sources as well as more sensitive and fast detectors discloses the possibility of deeper static and dynamic structural investigations. X-ray powder diffraction (XPD) and pair distribution function (PDF) measurements are sensitive to long and short-range order, which can be modelled by fitting procedures.





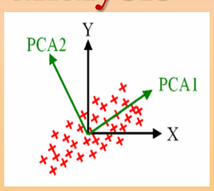
Monitor structural dynamics



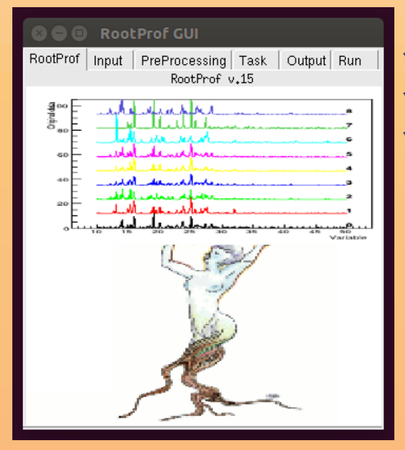
Advanced data analysis

Subtle structural changes induced in situ by varying external parameters (temperature, light) can be also detected by processing efficiently multiple measurements. In this case, the traditional approach to fit each measurement independently can be coupled with the new approach to apply multivariate methods such as Principal Component Analysis and Phase Sensitive Detection to the whole dataset [1].

Multivariate analysis



www.ba.ic.cnr.it/softwareic/rootprof

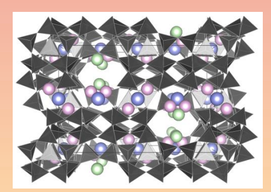


- ✓ All profiles processed at the same time
- ✓ Probe-independent processing
- ✓ Adapted variants of existing methods

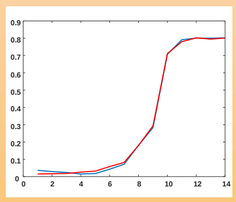
RootProf

a program for multivariate analysis of profiles [1]

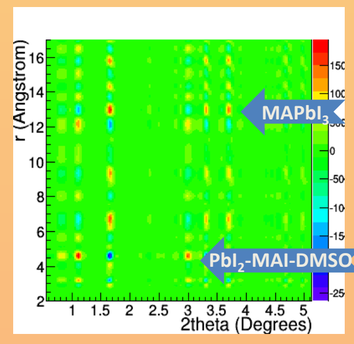
Prompt location of active atoms



Fast extraction of structural kinetics

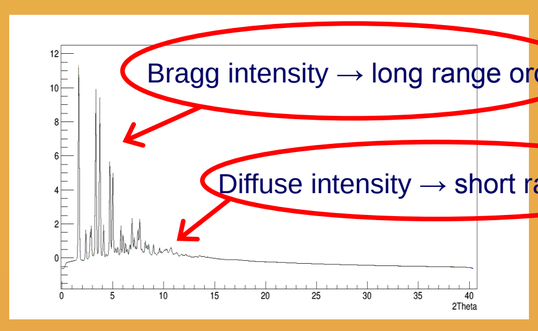


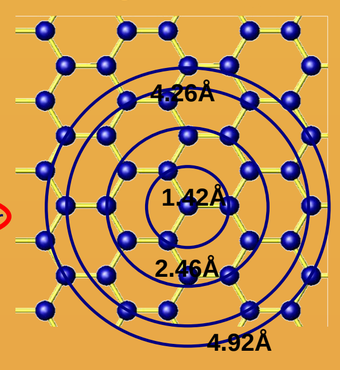
Combined information from different techniques



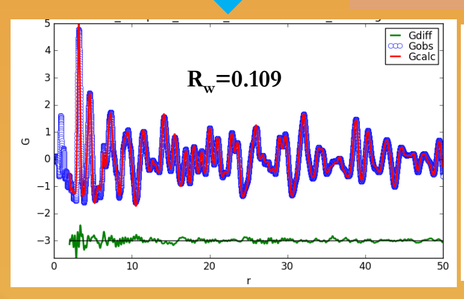
Pair distribution function

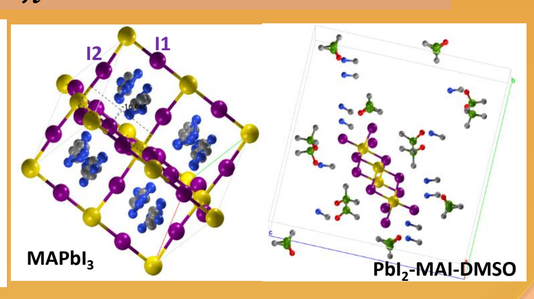
gives the probability of finding an atom at a distance "r" from a given atom





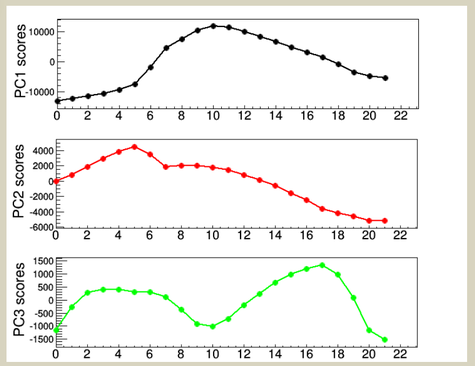
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$





Principal Component Analysis

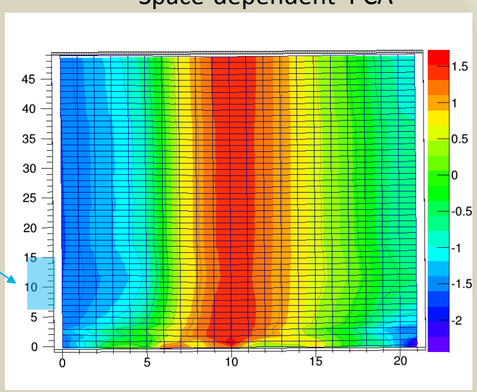
Scores



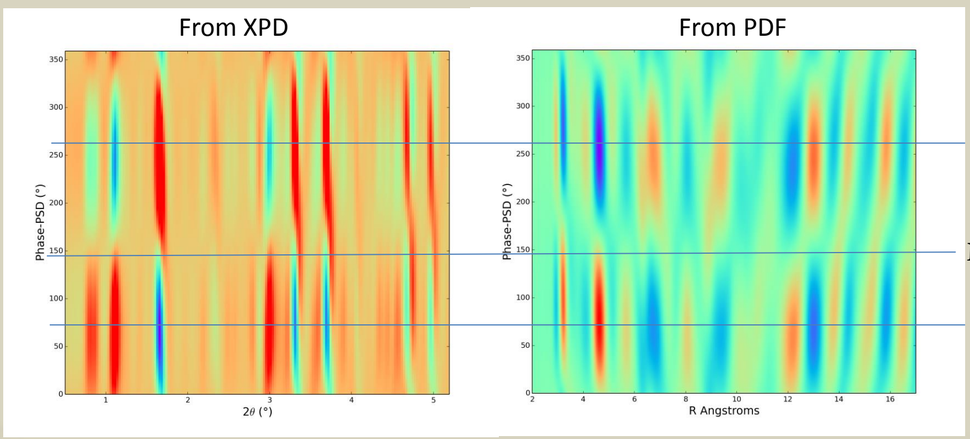
Anomalous contribution from nearest inter-octahedral ditstances

Local disorder from misaligned octahedra [2]

Space-dependent PCA



Phase Sensitive Detection

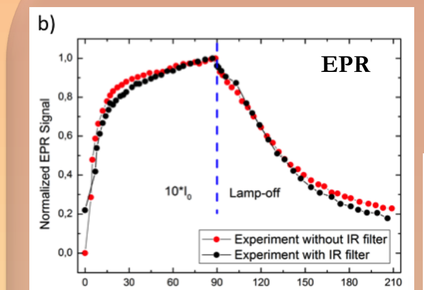


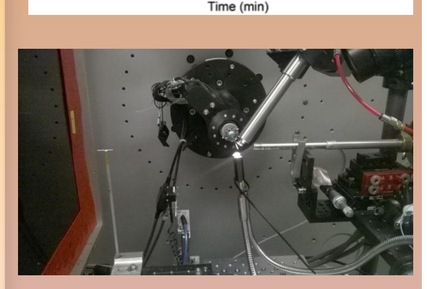
$MAPbI_3$ cubic

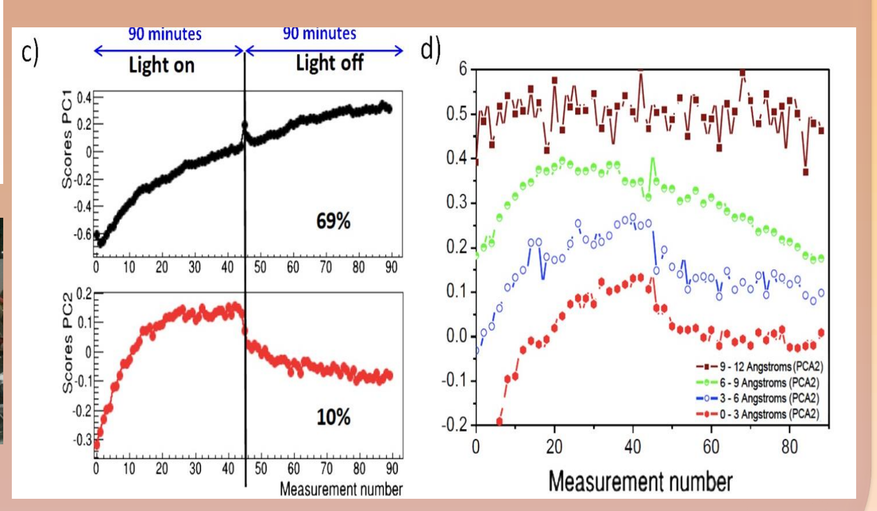
$MAPbI_3$ tetragonal

PbI_2-MAI-DMSO

Reversible generation of paramagnetic Pb_3^+ defects in $MAPbI_3$ perovskite under illumination, induced by the presence of Pb-O defects that may trap photogenerated holes [3]

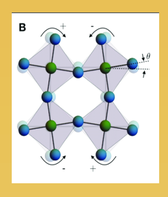


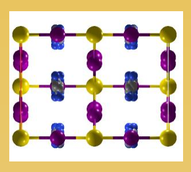




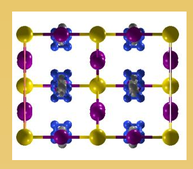
Higher light-induced effect for the shorter interatomic distances (R<3 Å), consistent with the range of Pb-O distances (2.25 Å)

Validation by fitting individual profiles with the tetragonal $MAPbI_3$ crystal structure

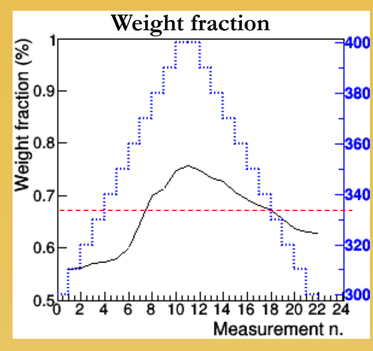




300K



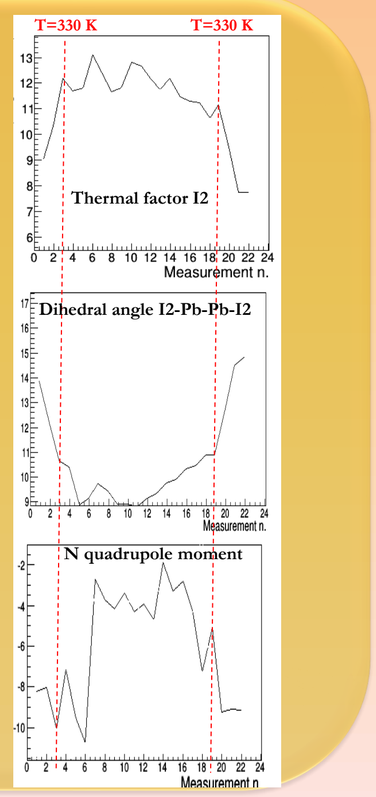
400K



Phase-transition order parameters:

$$Q_N = Z\left[3\sigma_z^2 - \left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right)\right]$$

Shape parameter describing the orientation distribution of the MA molecule



[1] R. Caliandro, B.D. Belviso, J. Appl. Cryst. 2014, 47, 1087–1096.
[2] R. Caliandro, D. Altamura, B.D. Belviso, A. Rizzo, S. Masi, C. Giannini, J. Appl. Cryst. 2019, 52, 1104–1118.
[3] S. Colella, M. Todaro, S. Masi, A. Listorti, D. Altamura, R. Caliandro, C. Giannini, E. Carignani, M. Geppi, D. Meggiolaro, G. Buscarino, F. De Angelis, and A. Rizzo ACS Energy Letters 2018, 3 1840–1847.