Experimental report

04/10/2017

Proposal:	**5-24-575**	**Council:**	4/2016
Title:	Bulk v nano-crystalline methyl ammonium lead bromide: structural origin for the high exciton binding energy in the nano-crystalline material		
Research area:	Chemistry		

This proposal is a new proposal

Main proposer:	**Paul HENRY**
Experimental team:	Kaibo ZHENG Junsheng CHEN Paul HENRY
Local contacts:	Thomas HANSEN

Samples:	CH3NH3PbBr3_NP CH3NH3PbBr3_bulk CH3NH3PbBr3_film

Instrument	Requested days	Allocated days	From	To
D20	3	3	04/11/2016	07/11/2016

Abstract:

Organometal halide perovskite nanoparticles are brightly luminescent, due to their large exciton-binding energies. Extensive X-ray characterization studies, using synchrotron X-rays, imply that the high binding energy cannot be rationalized solely on the basis of quantum confinement. We find evidence that subtle strain-induced structural changes are behind the high binding energy in nanocrystalline (NC) materials. However, X-ray methods are not sensitive to the organic part of the NC materials. In order to establish the complete correlation between the structure and the electronic properties, we need to zoom in specifically on the organic cation, which is known to be a key player influencing both the short-range and the long-range ordering. Acquiring this structural missing link is the goal of the present proposal using NC and their bulk counterparts to probe the long-range order of the inorganic octahedral and organic units. Probing the organic cation order will give insight into the interplay with the halide framework, which influences electronic structure, and ferroelectricity implied by EXAFS, which can account for the different charge carrier dynamics of two samples.

Experimental report for proposal 5-24-575

Introduction – Organometal halide perovskite (OHLP) materials emerged a few years ago as promising materials for low-cost, high efficiency opto-electronic devices. For example, solar cells with power conversion efficiency >20% have already been demonstrated. [1-3] However, their applications in emitting devices such as light emitting diodes and lasers are still limited, due to low photon emission efficiency. Recently, several synthesis of colloidal OHLP nanoparticles (NP) (CH_3NH_3(MA)$PbBr_3$ etc.) have been reported, with superior photoluminescence quantum yield compared to the bulk materials. [4-6] Our X-ray diffraction and EXAFS data reveal considerable lattice compression and reduced intra-octahedron Pb^{2+} off-centering in the NPs compared to the microcrystals (MCs). In the MCs, the local environment of Pb can be described a distorted quasi-octahedron with two different Pb-Br2 bonding distances along the c axis and four equal Pb-Br1 distances in the ab plane. The Pb is off-centered, with a Br1-Pb-Br1 angle of 167.15(38)° in the (110) plane. In the NPs, the Br1-Pb-Br1 angle is calculated to be closer to 180°. However, the above studies could not track **directly** the contributions of methylammonium (MA) cations in the lattice, as X-ray based characterization only provides the Pb/I ordering. In fact, we have observed reduced H bonding in MA ions to halides in NPs via FTIR spectroscopy, which **indirectly** suggest significantly different cation ordering between NPs and MCs. Such differences may influence or be influenced by the distortion of the $PbBr_6$ octahedra.

Proposed aims of the experiment when submitted – Measure bulk (MC) and NP samples to study cation ordering of the MA as a function of temperature to add to our EXAFS and FTIR work. Investigate whether the orientation of the MA induces ferroelectricity, which in turn would influence the electronic structure and charge carrier dynamics. Probe the temperature dependent phase transitions for any differences induced by particle size effects.

Experiment – D20 was used initially in the high resolution set-up with a wavelength 1.87 Å (Ge115) to test the bulk and nanoparticle (NP) samples. Bulk was found to be high quality but the organic binder for the NP sample was found to dominate the diffraction signal. Therefore, we decided to remove the oleic acid binder by solvent extraction while collecting bulk data. Data were collected on the bulk sample using a ramp rate of 0.5K per minute from 10-320K. Long data sets were also collected at 10K, 140K, 150K and 165K after a phase transition incompatible with that reported in the literature was observed around 150K. After solvent extraction, the NP sample was cooled and a ramp collected from 10-320K at 0.5K per minute. Diffraction was very weak and the ramp was repeated in the high flux mode at 2.4 Å (HOPG002).

Initial results – In Figure 1, the bulk sample shows the expected low T orthorhombic phase (<150K *Pnma*), the tetragonal phase (157<T<237K *I4/mcm*) and a cubic phase above 237K (*Pm3m)*, which agree with the literature. [7] However, the phase in the region 150<T<157K, previously reported as tetragonal, is incompatible with this assignment. The long data sets at 10K, 140K and 165K were found to be compatible with published literature and, despite the high level of incoherent scattering, we were able to assign the MA orientation in both the orthorhombic and tetragonal phases, supporting high resolution work using single crystal X-ray diffraction on the iodide analogue. [8] Two possibilities were investigated for the phase stable from 150-157K. The first was a preferred MA disordering such that the tetragonal a-axis in the *I4/mcm* phase, where the MA is pseudo 8-fold disordered around a mirror plane, allowed preferential disorder such that a long-short axis pair was formed in an orthorhombic unit cell. The second possibility was an incommensurate modulated phase, also a result of MA disorder. However, due to the limited Q-range available (Q_{max} = 6 $Å^{-1}$) we were unable to find a suitable model for either case. The low signal:background ratio as a result of using hydrogenous samples prevented further in-depth structural analysis.

The primary aim of the experiment was to compare phase behaviour of bulk and NP samples and it was necessary to use hydrogenated samples, as deuteration of the NP synthesis route was economically unfeasible. The NP sample showed that the MA ordering at low temperature was completely suppressed, with a probable phase transition around 240K. Full structural analysis was not possible for the NPs due to the poor signal:noise quality but the phases were assigned as cubic at high temperature and tetragonal below 240K. Therefore, the conclusion was that the strain induced effects of particle size reduction were significant in this material, particularly at low temperature. We were unable to answer the local environment questions with this experiment.

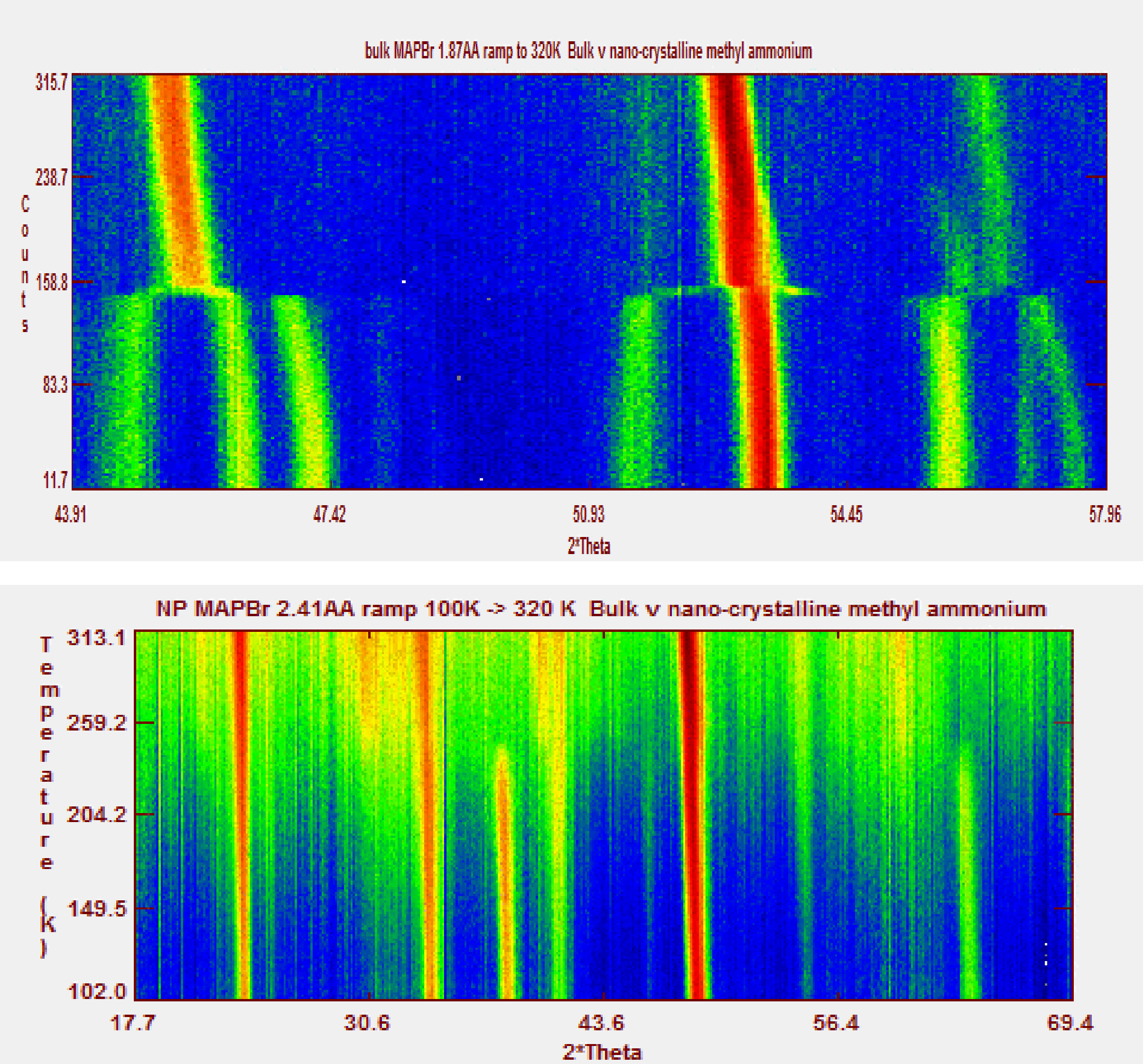

Figure 1 (upper) bulk MAPBr over the temperature range 10-320K. (lower) NP MAPBr over a similar temperature range. Note the different wavelengths for the two data collections so the scattering angles cannot be directly compared.

Current status – We plan to submit a proposal to ISIS in the next round (Oct 2017) to look at a fully deuterated MC MAPBr sample as a function of temperature, using the total scattering method, to investigate the local structure directly. If this is successful we will look to optimise a strategy to synthesise deuterated NPs to perform a parallel study. The ILL data from D20 will be used in this proposal, particularly to justify study of the structure of the phase stable from 150-157K which we were unable to solve with the limited Q-range available on a monochromatic instrument. The data from this experiment will form part of a manuscript describing particle size effects in MAPBr, likely 3-6 months after a successful ISIS experiment.

References

[1] Kim, H.-S.; Lee, C.-R.; Im, J.-H.; et al. *Sci. Rep.* **2012**, *2*, 591.
[2] Etgar, L.; Gao, P.; Xue, Z. *J. Am. Chem. Soc.* **2012**, *134*, 17396–17399.
[3] Zhou, H.; Chen, Q.; Li, G.et al. *Science* **2014**, *345*, 542–546.
[4] Schmidt, L.; Pertegas, A.; Gonzalez-Carrero, S.et al. *J. Am. Chem. Soc.* **2014**, *136*, 850–853.
[5] Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.et al. *Nat. Nanotechnol.* **2014**, *9*, 687–692.
[6] Xing, G.; Mathews, N.; Lim, S. S. S. et al. *Nat. Mater.* **2014**, *13*, 476–480.
[7] Swainson, I.P.; Hammond, R.P.; Soulliere, C. et al. *J. Solid State Chem.* **2003**, *176*, 97-104.
[8] Ren, Y.; Oswald, I.W.H.; Wang, X. et al. *Cryst. Growth Des.* **2016**, *16*, 2945-2951.