Experimental report

30/06/2023

Proposal: **7-01-571** **Council:** 10/2022

Title: The harder & heavier, the better: isotope effects, distortion pathways & stability enhancement in MAPbI3under high pressure

Research area: Materials

This proposal is a continuation of 7-04-177

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Samples: CH3ND3PbI3
CH3NH3PBI3

Instrument	Requested days	Allocated days	From	To
IN1 LAG	3	3	25/05/2023	28/05/2023

Abstract:

Following our pilot study on the vibrational dynamics of hydrogenous MAPbI3 across variable pressure-temperature conditions and recent on-site technical developments by Ivanov et al. we request the set of measurements on IN1-LAGRANGE using an improved compact high-pressure setup. The experiment is aimed at exploring the high-pressure boundaries of the low-temperature phase of hydrogenous (CH3NH3PbI3) and deuterated (CH3ND3PbI3) specimens. The present work is motivated by the pronounced isotope effects recently reported for deuterated species, resulting in colossal stability enhancement and the modulation of charge-carrier lifetimes upon pressurization. These effects are of direct relevance to the processing of these materials, as part of wider efforts aimed at developing structurally and operationally stable solar-cell devices. The proposed experiment on IN1-LAGRANGE will shed light on hitherto-unexplored mechanisms behind stabilization thanks to superb access to the librational dynamics of methylammonium cations in MAPbI3 in the spectral range below 40 meV.

The harder & heavier, the better: isotope effects, distortion pathways & stability enhancement in $MAPbI_3$ under high pressure

I. EXPERIMENTAL PLAN

Hybrid Organic-Inorganic Perovskites (HOIPs) have evolved from being considered a class of exotic materials to a promising platform for next-generation photovoltaic materials. However, even though the efficiencies of HOIPs-based devices continue to rise exponentially, their structural instability continues to limit the expansion of this technology.

The atomic mechanisms resulting in the degradation of HOIPs remain unsolved. In the case of the paradigmatic HOIP, methylammonium lead iodide ($MAPbI_3$), dielectric spectroscopy studies fall short of reaching the boundary between the ordered, low-temperature phase and the amorphous phase after pressurization [1].

In this experiment, we first obtained a reference spectrum of $MAPbI_3$ at ambient-pressure on IN1-LAGRANGE, and then explored the destabilization regime beyond 10 kbar of the low-temperature phase of $MAPbI_3$ using the available high-pressure cell described elsewere [2].

II. RESULTS AND DISCUSSION

Table I summarizes the experimental output. The INS spectra of $MAPbI_3$ under pressure are presented in Figure 1. We were successful in separating the signals from the sample and the high-pressure cell with the Si_{111} and Si_{311} configurations. This made it possible to measure the inelastic spectrum of $MAPbI_3$ over the relevant energy-transfer regime at pressures as high as 15 kbar. The INS spectrum of the low-temperature phase of this perovskite was comprehensively interpreted in our previous works with the aid of first-principles calculations [3, 4]. Pressurization induces a spectral red shift (2 meV) of the τ(C-N) mode and the librations ca. 13 and 16 meV. As pressure is increased, a pronounced "melting" of the spectral features can be seen up to 500 meV, specially in the range provided by the silicon reflections. The signal from the τ(C-N) mode red-shifts about 6 meV with respect to ambient pressure.

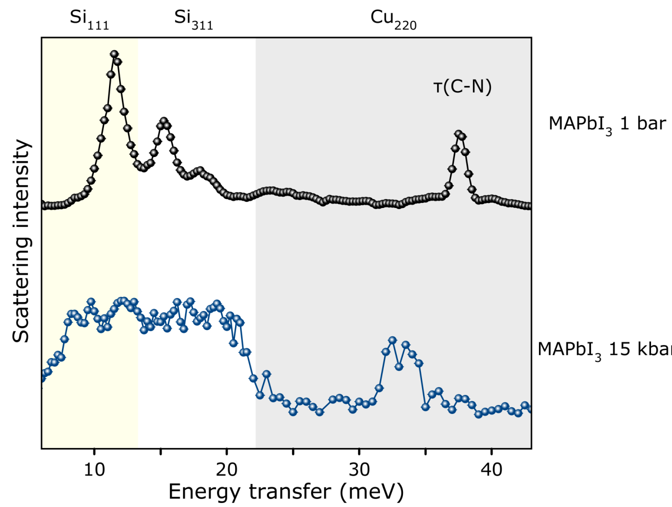

FIG. 1: Evolution with increasing pressure of the INS spectra of $MAPbI_3$ measured at 40 K on LAGRANGE.

We also measured the hydrogenated and partially-deuterated perovskite precursors, MAI and MAI-d_3, to explore isotope effects in HOIPs. A preliminary analysis of these data confirms that deuteration severly affects the potential-energy landscape on both methyl and amine ends of the organic cation. These measurements are summarized in the Table below.

TABLE I: Summary of the high-pressure measurements conducted on IN1-LAGRANGE during this experiment on $MAPbI_3$, MAI and MAI-d_3. Std refers to a standard alloy cell and HP to the one designed for high-pressure experiments.

Sample	Temperature	Cell	Pressure	Energy range
$MAPbI_3$	40 K	Std	1 bar	5 – 50 meV
$MAPbI_3$	40 K	HP	10 kbar	5 – 50 meV
$MAPbI_3$	40 K	HP	12.5 kbar	5 – 50 meV
$MAPbI_3$	40 K	HP	15 kbar	5 – 500 meV
MAI	10 K	Std	1 bar	5 – 500 meV
MAI-d_3	10 K	Std	1 bar	5 – 500 meV

[1] K. Gesi, *Ferroelectrics*, 1997, **203**, 249–268.

[2] A. Ivanov, R. Sadykov and M. Jiménez-Ruiz, 2018, Proceedings of the Molecular Spectroscopy Science Meeting MSSM2018, Rutherford Appleton Laboratory Technical Report RAL TR–2018–014 (Chilton, 2018). Weblink: epubs.stfc.ac.uk/work/40650049.

[3] K. Druzbicki, R. S. Pinna, S. Rudić, M. Jura, G. Gorini and F. Fernandez-Alonso, *J. Phys. Chem. Lett.*, 2016, **7**, 4701–4709.

[4] K. Drużbicki, R. Lavén, J. Armstrong, L. Malavasi, F. Fernandez-Alonso and M. Karlsson, *The Journal of Physical Chemistry Letters*, 2021, **12**, 3503–3508.