Experimental report

25/09/2022

Proposal: **7-03-190** **Council:** 10/2019

Title: Diffusional organic cation dynamics in 2D hybrid inorganic-organic perovskites

Research area: Materials

This proposal is a new proposal

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Samples: DEC2GeI4 and DEC2PbI4, DEC = decylammonium = CH3(CH2)9N

Instrument	Requested days	Allocated days	From	To
IN1 LAG	1	1	21/08/2020	22/08/2020
IN16B Si 111 BATS	4	4	25/02/2021	01/03/2021
IN5	3	3	14/08/2020	17/08/2020

Abstract:

This proposal concerns the investigation of the localised diffusional dynamics of organic molecular cations in two selected two-dimensional (2D) hybrid inorganic-organic perovskites by quasielastic neutron scattering. We propose to use both IN16b and IN5, which will provide complementary information in terms of the time-scales probed. The overall aim of the proposal is to provide a detailed description of the organic cation dynamics over a wide temperature range in these type of materials, and to understand the impact of this on the materials' optoelectronic properties.

Diffusional organic cation dynamics in 2D hybrid inorganic-organic perovskites (Exp. 7-03-190)

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1 Introduction

Hybrid organic-inorganic perovskites (HOIPs) are known as ”easy-to-make” materials that are characterized by useful optoelectronic properties, such as, e.g., a bandgap o $1.5 - 2$ eV, low exciton binding energy and long carrier diffusion lengths, which make them highly suitable for application in solar cells [1, 2]. The prototypical HOIP is methylammonium lead iodide ($CH_3NH_3PbI_3$), which features a power conversion efficiency as high as 20%, but a poor long-term stability of the material towards humidity and heat limits its potential for application in practical solar-cell devices [3]. Two-dimensional (2D) hybrid perovskites, of general formula R_2BX_4, where R is an organic cation, B is a metal (e.g. Pb) and X is a halide atom (e.g. I or Br), which are featured by a layered structure of single inorganic sheets sandwiched between organic molecular cations, are found to be much more stable than their 3D counterparts [4]. However, currently available 2D materials are characterized by a too large electronic band gap for efficient solar absorption ($2 - 3$ eV) and too high exciton binding energy (several 100 meV) with typically short carrier diffusion lengths, making them unsuitable for use in solar cells. With the aim to benefit both from the nearly perfect optoelectronic properties of 3D perovskites and from the large stability towards heat and humidity of 2D perovskites, recent efforts are directed towards the investigation of 2D/3D perovskite blends.

A contemporary challenge with respect to HOIPs generally, is to understand the impact of the organic cation dynamics on the materials' optoelectronic properties. Because of the large amount of hydrogen (H) in the organic molecules, their dynamics can be advantageously studied with quasielastic neutron scattering (QENS). For the case of 3D HOIPs, several previous QENS studies have probe the local dynamics of the organic cation inside the perovskite structure [5, 6]. As a primary example, for $CH_3NH_3PbI_3$ it was shown that the rotation of the whole dipolar molecule becomes activated in the tetragonal phase, and that this is correlated with a sharp increase in the dielectric function of the material, which, in turn, may lower the exciton binding energy [6]. For the case of 2D perovskites, however, the knowledge on the dynamical properties of organic cations in these materials are much less. With the rapidly increasing interest in 2D and 2D/3D materials, information of the local dynamics of the organic cations, and its possible influence on the materials' optoelectronic properties (in terms of electronic structure, exciton properties, dynamic disorder etc.), is much sought after.

2 Experimental details

In this experiment, we have studied the organic cation dynamics in the 2D halide perovskites BA_2PbI_4, PEA_2PbI_4, and $DAMI_4$ (M = Pb, Ge) (BA = butylammonium, PEA = phenethylammonium, and DA = decylammonium) using QENS. Powder samples of BA_2PbI_4 and PEA_2PbI_4 (IN5 and IN1) and $DAMI_4$ (M = Pb, Ge) (IN16B), were held inside standard cylindrical aluminium sample holders for all measurements.

The measurements on IN5 were performed using two different incident neutron wavelengths of 5 Å and 2.5 Å. For 5 Å neutrons, an energy resolution of 0.1 meV and accessible q-range of $\sim 0.2 - 2$ Å^{-1} at the elastic line were obtained.

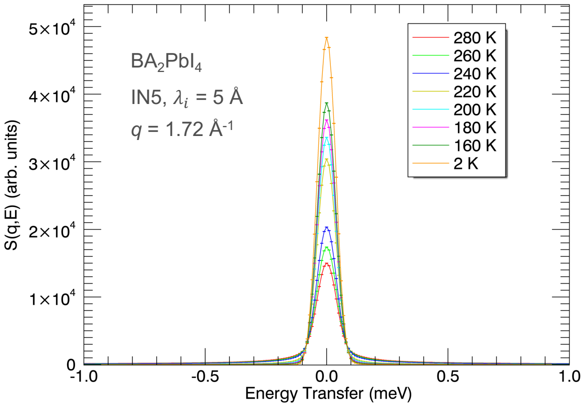

Figure 1: Quasielastic lineshape for BA_2PbI_4 measured at IN5 using 5 Å wavelenght neutrons

For 2.5 Å neutrons the respective values were 0.62 meV and $\sim 0.4 - 4$ Å^{-1}. Standard corrections were applied to the time-of-flight data with the LAMP software [7] and included normalization to a vanadium standard, background subtraction, and correction for the energy-dependent efficiency of the detectors. A measurement of the sample at 2 K was used as a resolution function in the fitting of the quasielastic lineshape. QENS measurements were performed at about 10 different temperatures in the range $(50-370$ K) for each sample, in order to cover the dynamics in all crystallographic phases.

At IN1-LAGRANGE INS measurements were performed at base temperature of 10 K. We used a combination of monochromator crystals (Si(111), Si(311), and Cu(220)) in order to cover a wide range of incident neutron energies (E_i) in the range $0-500$ meV. The corresponding energy resolutions were about 0.8 meV for Si(111) (covering $E_i = 4.5 - 20$ meV) and Si(311) (covering $E_i = 16.5 - 60$ meV), and about 0.8% of E_i for Cu(220) (covering $E_i = 26 - 500$ meV). The final neutron energy was fixed to $E_f = 4.5$ meV and was selected by the PG(002) analyzer. Standard data reduction were performed within the LAMP software [7].

The measurements at IN16B were performed in the backscattering and time-of-flight spectrometer (BATS) set-up using the Si(111) analyzers. This set-up yielded an energy resolution and accessible energy transfer (E) range was about $\sim 1.5 - 8\mu$eV and $\sim -130 - 180$ μeV, respectively. The accessible momentum transfer (q) range was about $0.2 - 1.8$ Å^{-1} at the elastic line. In addition, measurements were performed with a shifted energy transfer window, in order to extend the energy transfer range on the neutron energy gain side to -350 μeV. A measurement of the sample at 2 K was used as a resolution function in the fitting of the quasielastic lineshape.

Short scans were performed upon cooling from 350 K to 2 K, in order to monitor the elastic and inelastic intensities as a function of temperature, to gain information on in which temperature range the dynamics are accessible to the here probed timescales. This was followed by QENS measurements at about 10 different temperatures in the range $(150 - 370$ K) for each sample.

3 Results and discussion

The following section showcase some of the results which we obtained at IN5 for the sample BA_2PbI_4. Figure 1 shows the quasielastic lineshape of BA_2PbI_4 as a function of temperature. As can be seen, there is a quasielastic signal starting from about 150 K, and which grows intensity with increasing temperature. Upon passing through the phase transition at around 230 K, there is a sudden large increase in the quasielastic signal, indicating that there are further dynamical relaxational processes which become activated in the high-temperature phase. This is also consistent with the temperature response of the generalized density of states (GDOS), which is shown in Fig. 2 (a). At low temperature, the GDOS show several sharp peaks in the energy range $10 - 50$ meV, which corresponds to librations of the organic cations, in combination with vibrations of the inorganic lead iodide framework. In the high temperature phase, these peaks becomes severely broadened, and there is further a significant increase in low-energy modes (< 10 meV), which most likely is due to the activation of organic cation rotations.

The different types of rotational modes of the BA cations were determined by analyzing the elastic incoherent structure factor (EISF). Figure 2 (b) shows the EISF of BA_2PbI_4, extracted from fitting the QENS data, in the two different crystallographic phases. As can be seen, in the low temperature phase at 200 K, the organic cation dynamics can be solely ascribed to three-fold (C_3) rotations of the methyl and ammonia groups. Upon passing the phase transition, there is a significant drop in the EISF (increase in quasielastic intensity), meaning that there are more dynamical processes in the observed time window. This additional dynamics can be modelled using an additional rotational mode of the BA cation. In particular, the data is in good agreement with a model considering, in addition to the C_3 rotations of the methyl/ammonia groups, an additional C_2 rotation of the CH_2NH_3 part of the BA cation. In addition, to describe the data even better we include also a faster librational mode of the CH_2 parts which is modelled as a quasi dumbell with a short jump distance [8]. In addition, our study showed that the organic cation dynamics in PEA_2PbI_4 (not shown in this report) is much more restricted due to the stronger inter-molecular interactions. In PEA_2PbI_4, only the C_3 rotations of the ammonia groups is active from $100 - 370$ K.

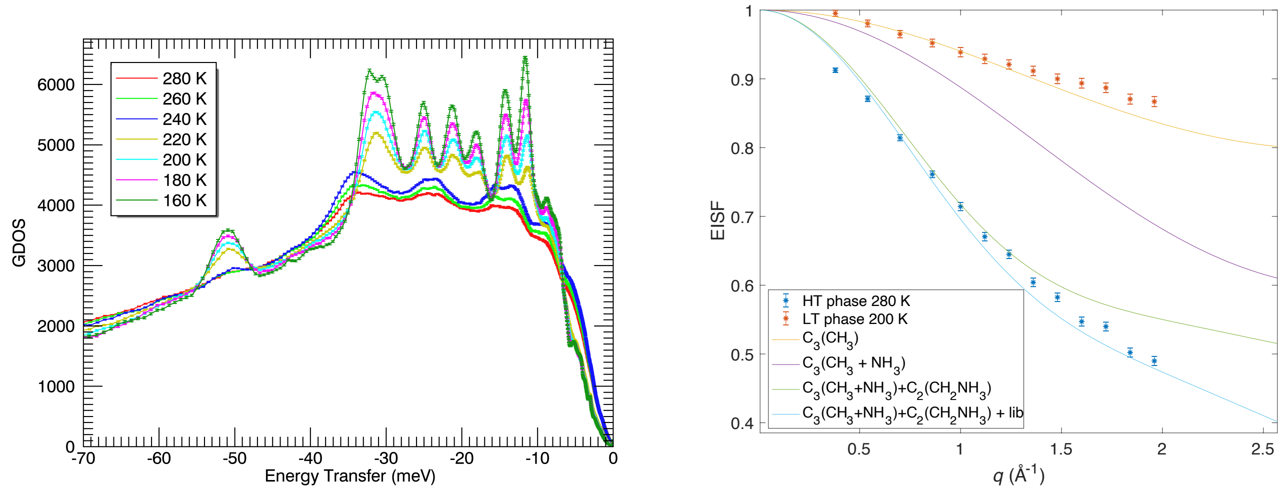

Figure 2: (Left panel) GDOS of BA_2PbI_4 as a function of temperature. (Right panel) EISF extracted from the QENS fits of BA_2PbI_4, in the high temperature (HT, 280 K) and low temperature (LT, 200 K) phases.

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