Experimental report

14/02/2017

Proposal: 7-02-169 **Council:** 10/2016

Title: Low frequency lattice excitations in hybrid perovskites for photovoltaic

Research area: Physics

This proposal is a new proposal

Main proposer: Philippe BOURGES

Experimental team: Afonso DA CUNHA FERREIRA
Jacky EVEN
Philippe BOURGES
Antoine LETOUBLON

Local contacts: Stephane RAYMOND

Samples: CH3NH3PbBr3
HC(NH2)2PbI3

Instrument	Requested days	Allocated days	From	To
IN12	10	5	26/01/2017	31/01/2017

Abstract:

This proposal wish to study the lattice excitations in lead-halide based hybrid organic perovskites. Recently, these compounds of general formula MPbX3 (where M is organic molecule and X an halogne atom) have conducted to a scientific breakthrough in the quest for low-cost solar cells, with record efficiencies up to 20%. We want to adress the questions of the role of low energy excications for understanding of underlying mechanisms related to transport properties. The low energy excitations corresponds to two aspects (certainly coupled): the low energy phonons related PbX3 octahedra and the relaxation dynsmics of the organic molecule. These compounds exhbit a complex sequence of phase transitions which involve the dynamical disorder of the organic cations. High quality single crystals of sufficient mass to measure phonons has been grown at the university of Rennes. We wish to study two systems: MAPbBr3 (MA=methylammonium (MCH3NH3)), and FAPbI3 FA=formamidinium (HC(NH2)2) . We request 10 days on IN12.

Subject: Structural and dynamic properties of hybrid perovskites for photovoltaic applications.

Proposal: 7-01-169

Team: Afonso Da Cunha Ferreira (LLB and INSA Rennes), Philippe Bourges (LLB), Antoine LéToublon (INSA Rennes), Jacky even (INSA Rennes).

Our project focuses mainly on better studying the dynamic and structural properties of hybrid perovskites (i.e. low-frequency phonons and relaxation molecular dynamics) [1]. This work is part of PhD projet of Afonso Ferreira from LLB-Saclay and FOTON-Rennes. Recently, the three-dimensional hybrid perovskites have conducted to a scientific breakthrough in the quest for low-cost solar cells, with record efficiencies up to 20%. Currently, lead-halide materials of general formulae $MPbX_3$ (X=halogen, I, Br, Cl; M=methylammonium ($MA=MCH_3NH_3$), or M=formamidinium ($FA = HC(NH_2)_2$) are the most popular.

Recent papers show the importance of low energy phonons for the photo-conversion process [2,3]. An efficient hot-phonon bottleneck is reported that slows down the cooling of hot carriers by three to four orders of magnitude compared to standard semiconductors. This has been shown using ultrafast optical characterization and first-principle calculations in four kinds of lead-halide perovskites [3]. That reveals a stronger phonon bottleneck effect in hybrid perovskites than in their inorganic counterparts. The up-conversion of low-energy phonons is proposed to be responsible for the bottleneck effect. The presence of organic cations introduces overlapping phonon branches and facilitates the up-transition of low-energy modes. The blocking of phonon propagation associated with an ultralow thermal conductivity of the material also increases the overall up-conversion efficiency. This allows long-lived hot carriers in these materials.

Using triple-axis spectrometers at LLB, we have recently measured acoustic and low-energy optical phonons for three different perovskite systems: MAPbBr3, MAPbI3 and FAPbBr3. In MAPbBr3, combining inelastic neutron scattering (INS) with Raman and Brillouin scattering (BS), as well as ultrasonic (US) measurements [4,5], we were able to provide a detailed analysis of low energy structural excitations, including the determination of sound velocities and elastic constants.

In our experiment (7-01-169) on IN12 at ILL (22^{nd}-27^{th} January 2017), we have been studying the acoustic phonon branches of the formamidinium-based iodine hybrid perovskites, $FAPbI_3$. The experiment on that system was particularly challenging as the interesting phase (called α-phase) which exhibits photovoltaic properties is metastable. After a few days, the sample evolves into a yellow phase (called δ-phase) which presents no particular physical interest. Hopefully, the α-phase can be restored upon heating for a short period of time. That procedure was achieved in small single crystals [6]. However, on large single crystals, only part of the sample is restored in a single grain and most of the sample remained as a powder sample. Therefore, we had to align on a single grain (amy about 10% o fthe total volume) to observe acoustic phonons.

Nevertheless, we could measure dispersing acoustic phonons in that system by performing constant energy scans up to 1.2 meV only: two symmetric modes are observed on top of a large background (see figure a)). The counting time for the figure is 20mn/point. The high background is coming from quasi-elastic signal from hydrogen atoms excitations of the FA molecule. It is almost independent of the sample orientations. This way we could separate both the dispersing and symmetric phonons mode from the quasi-elastic background. We were able to obtain clear phonon

acoustic modes for certain reciprocal space positions and calculate the respective associated sound velocities (an example of which can be seen in the figure b)). . Sound velocities have been estimated in most directions at room temperature. The detailed analysis of the data should be done and we should be able to extract the 3 elastic constants of the cubic phase: the longitudinal compression (Young's modulus) C_{11}, the transverse expansion C_{12} and the shear modulus C_{44}.

Therefore, we have now determined the acoustic phonons in 4 different compounds $MAPbBr_3$, $FAPbBr_3$ bromides and their iodine counterparts $MAPbI_3$ and $FAPbI_3$ in their high temperature cubic phase. A comparison of the deduced elastic constants in the 4 compounds will be completed soon.

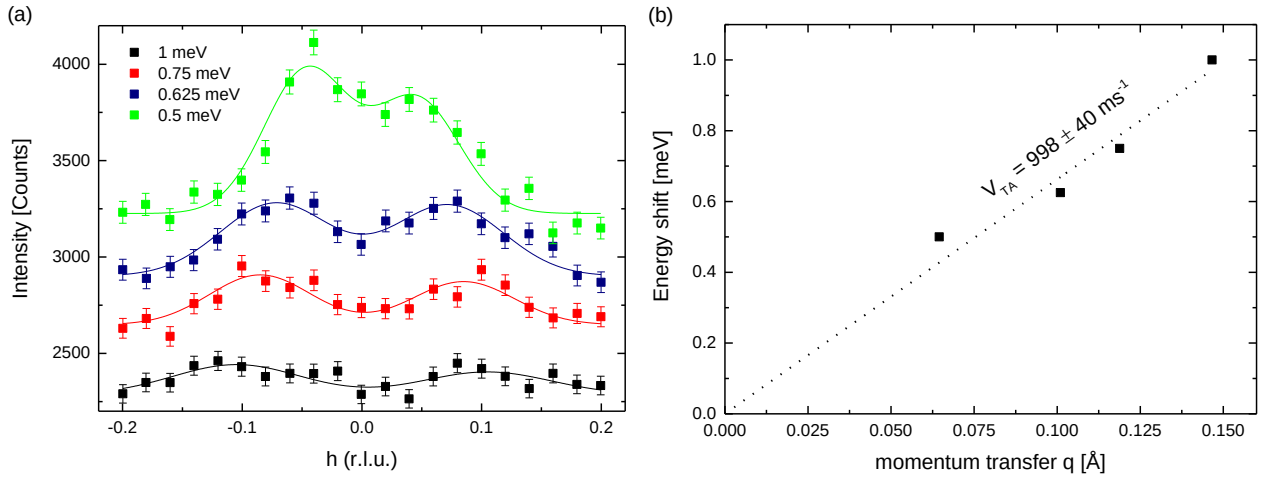

Figure 1. (a) Transverse acoustic (TA) phonon spectra measured by inelastic neutron scattering in the cubic phase of FAPbI3 (α-FAPbI3, room temperature) for different energy values at the (002) Bragg peak, 2along the [110] direction (i.e. Q = (h h 2)). (b) Dispersion curve of the TA phonons (Figure 2a) close to the (002) Bragg peak. The slope corresponds to the sound velocity for the TA phonon branch of α-FAPbI3.

However, we could not study the acoustic phonon temperature dependences due to a lack of time. Furthermore, it has been reported that these perovskite systems undergo phase transitions at low temperatures when the dynamical disorder of the organic cations are frozen [1]. It may also play an important role for the phonon bottleneck effect mentioned above. From a theoretical point of view, the pseudo-cubic phase is a reference for many effects, such as strain and phase transitions. Symmetry analysis and Landau theory has been performed [1] to address questions related to phase transitions: is there a coupled order parameter? What is the nature/role of the cation's dynamics in the phase transitions? These questions have still to be addressed.

References:

[1] J. Even, M. Carignano and C. Katan, Nanoscale, (2016),8, 6222-6236.

[2] Ye Yang, et al, Nature Photonics, 10, 53–59 (2016)

[3] Jianfeng Yang, et al, "Acoustic-optical phonon up-conversion and hot-phonon bottleneck in lead-halide perovskites", Nature Communications, DOI: 10.1038/ncomms14120

[4] J. Even, S. Paofai, Ph. Bourges, A. Létoublon, S. Cordier, O. Durand, & . Katan SPIE 9743, Physics, Simulation, and Photonic Engineering of Photovoltaic Devices V, 97430M (14 March 2016)

[5] A. Létoublon, S. Paofai, B. Rufflé, Ph. Bourges, B. Hehlen, Th. Michel, C. Ecolivet, O. Durand, S. Cordier, C. Katan and J Even, 7 (19), pp 3776–3784 J. Phys. Chem. Lett. (2016) DOI: 10.1021/acs.jpclett.6b01709

[6] Ayan A. Zhumekenov, , et al, ACS Energy Lett, 1, 32−37 (2016).