

## The role of the organic cation in acoustic phonons and hot carrier properties of lead bromide perovskites

Milos Dubajic<sup>1</sup>, Irina Kabakova<sup>2</sup>, Michael P. Nielsen<sup>1</sup>, Andreas Pusch<sup>1</sup>, Marco Fronzi<sup>2</sup>, Mike Ford<sup>2</sup>, Xuguang Jia<sup>3</sup>, Nicholas J. Ekins-Daukes<sup>1</sup>, Stephen Bremner<sup>1</sup>, Gavin Conibeer<sup>1</sup>

<sup>1</sup> School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, 2052 Sydney, Australia

<sup>2</sup> School of Mathematical and Physical Sciences, University Technology Sydney, 2007 Sydney, Australia

<sup>3</sup> Collaborative Innovation Center of Photovoltaic Science and Engineering (CICPSE), Changzhou University, Jiangsu, China

Hybrid perovskites have shown impressive photovoltaic device performances due to long electronic carrier diffusion lengths, low exciton binding energy, high absorption coefficient and low thermal conductivity [1]. Additionally, their solution processability keeps fabrication costs low and makes them attractive for incorporation into 3<sup>rd</sup> generation photovoltaics devices. One specific property that those materials possess, inhibited carrier thermalization with the lattice, is crucial for the implementation of the Hot Carrier Solar Cell, a device that is predicted to bring conversion efficiency up to 86% under maximum concentration [2]. However, the slow carrier cooling rates in hybrid organic-inorganic perovskites, an order of magnitude lower than in bulk III-V [3,4,5], cannot be described with previous theoretical approaches (like hot phonon bottleneck effect and carrier screening) used for the explanation of the hot electron phenomena in III-V materials. The reason lies in the fundamental microstructural differences between those two materials, where perovskites are extraordinary due to their highly anharmonic, soft and dynamically disordered lattice.

Thus, in this work we directly probe lattice dynamics of hybrid organic inorganic single crystal perovskites by Brillouin Spectroscopy. This spectroscopic technique is highly sensitive to low energy acoustic phonons (in the GHz frequency,  $\mu\text{eV}$  energy range) near the Brillouin zone centre. As perovskites exhibit phase transitions upon temperature change, we perform temperature dependent scans and can resolve transverse and longitudinal acoustic phonon linewidths and frequencies in cubic, tetragonal, and orthorhombic phase. Since phonon linewidth is inversely proportional to phonon lifetime, this can reveal the nature of electron-phonon and phonon-phonon interaction, which are both highly relevant for a better understanding of electron relaxation processes in these materials.

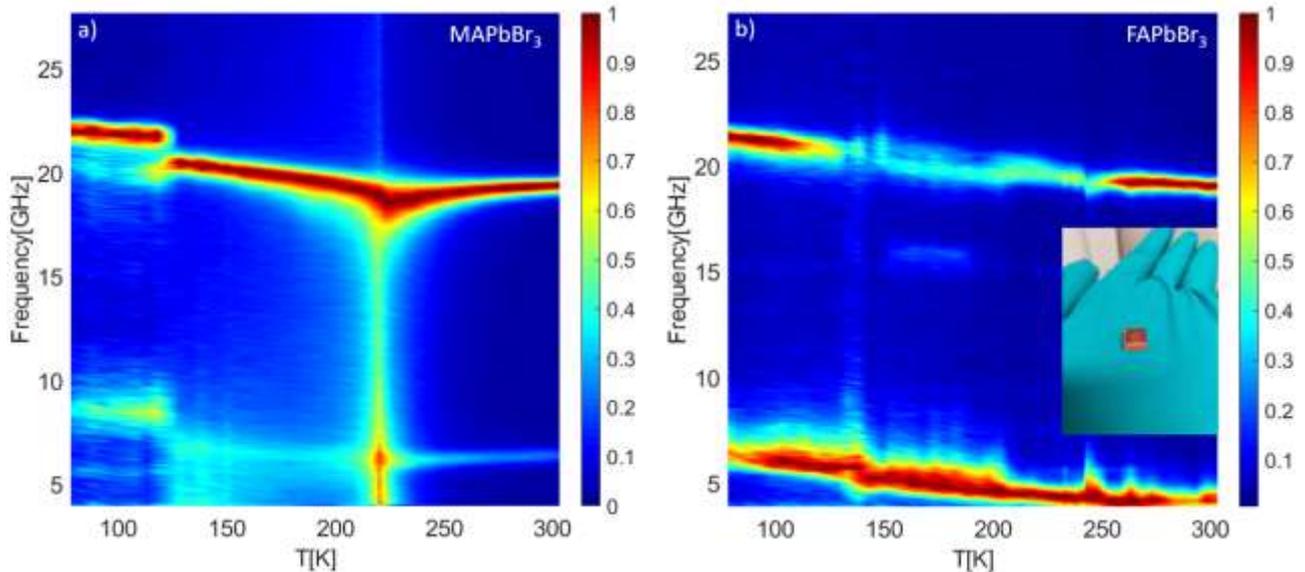
In order to systematically and consistently study the role of phonon dynamics on the hot carriers relaxation mechanisms two single crystals, methylammonium lead bromide (MAPbBr<sub>3</sub>) and formamidinium lead bromide (FAPbBr<sub>3</sub>), materials with similar electronic but different phononic structures were chosen. They chemically differ only in the A site cation, one of which is methylammonium (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) with the other being formamidinium (CH<sub>5</sub>N<sub>2</sub><sup>+</sup>). Thus, we can identify what influence the organic cation has on the carrier relaxation dynamics and describe a new mechanism, not present in III-Vs, but potentially characteristic for hybrid perovskites.

In addition to Brillouin Spectroscopy which is used to assess phonon properties we perform power dependent Continuous Wave Photoluminescence (CWPL) in the same temperature range to identify if carriers at elevated temperatures are present in the different crystal phases and test if a correlation exists with the phonon properties measured by Brillouin Spectroscopy at the same conditions.

To understand the dependence of phonon properties on the phases of the perovskite material as well as the organic cation, we performed temperature dependent Brillouin spectroscopy of MAPbBr<sub>3</sub> (see Figure 1a) and FAPbBr<sub>3</sub> (see Figure 1b).

Shown in Figure 1, two bright regions from 5 GHz to 10 GHz and from 20 GHz to 25 GHz exist which represent Longitudinal Acoustic (LA) and Transverse Acoustic (TA) phonons, respectively. By

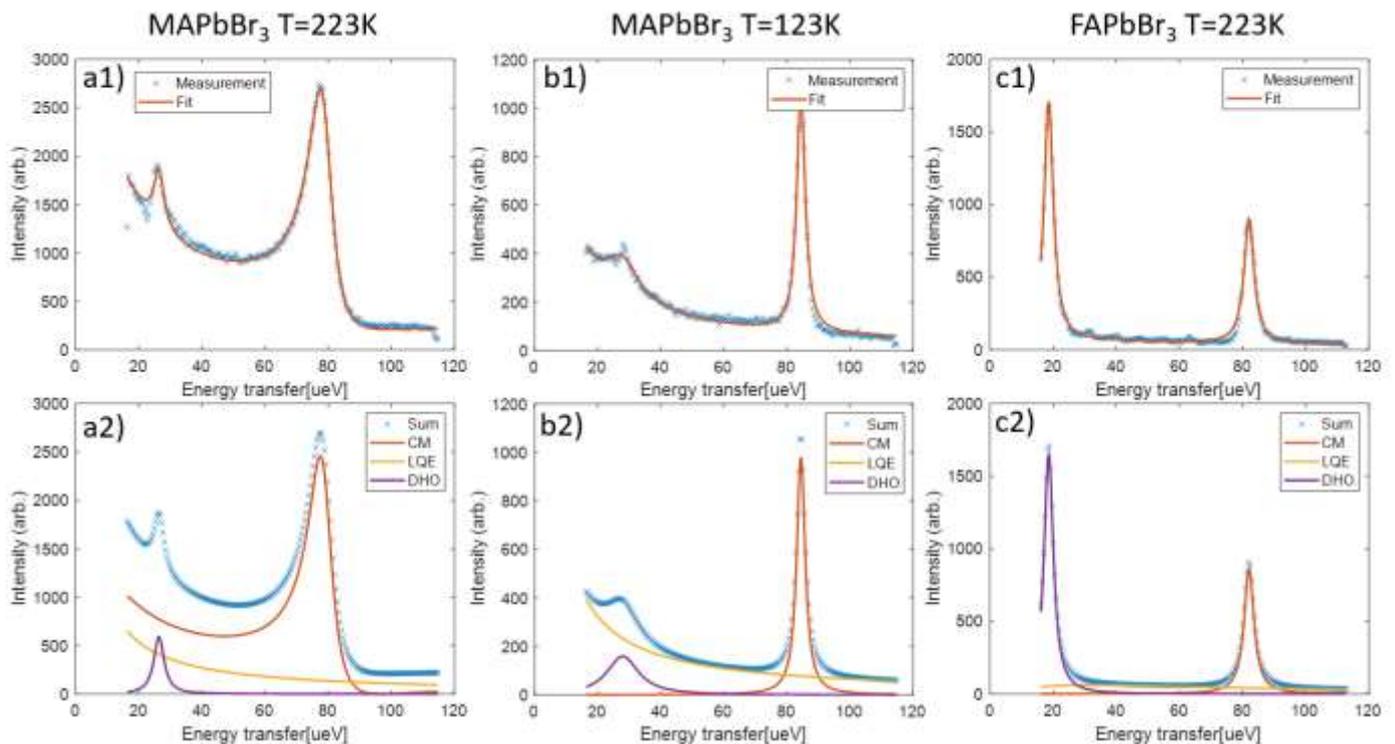
tracking the phonon evolution with temperature it is evident that discontinuous and asymmetrical shapes are present for MAPbBr<sub>3</sub> near 130K and 225K (temperatures that correspond to the phase transition temperatures for both crystals), whereas FAPbBr<sub>3</sub> exhibits continuous transitions for both LA and TA towards higher phonon frequencies (phonon hardening) with decreasing temperature.



**Figure 1. 2D Brillouin Spectroscopy Scans: x axis-lattice temperature; y axis-acoustic phonon frequency; z axis- normalized (0,1) counts; a) MAPbBr<sub>3</sub> and b) FAPbBr<sub>3</sub> single crystals, inset- photo of the measured FAPbBr<sub>3</sub> crystal.**

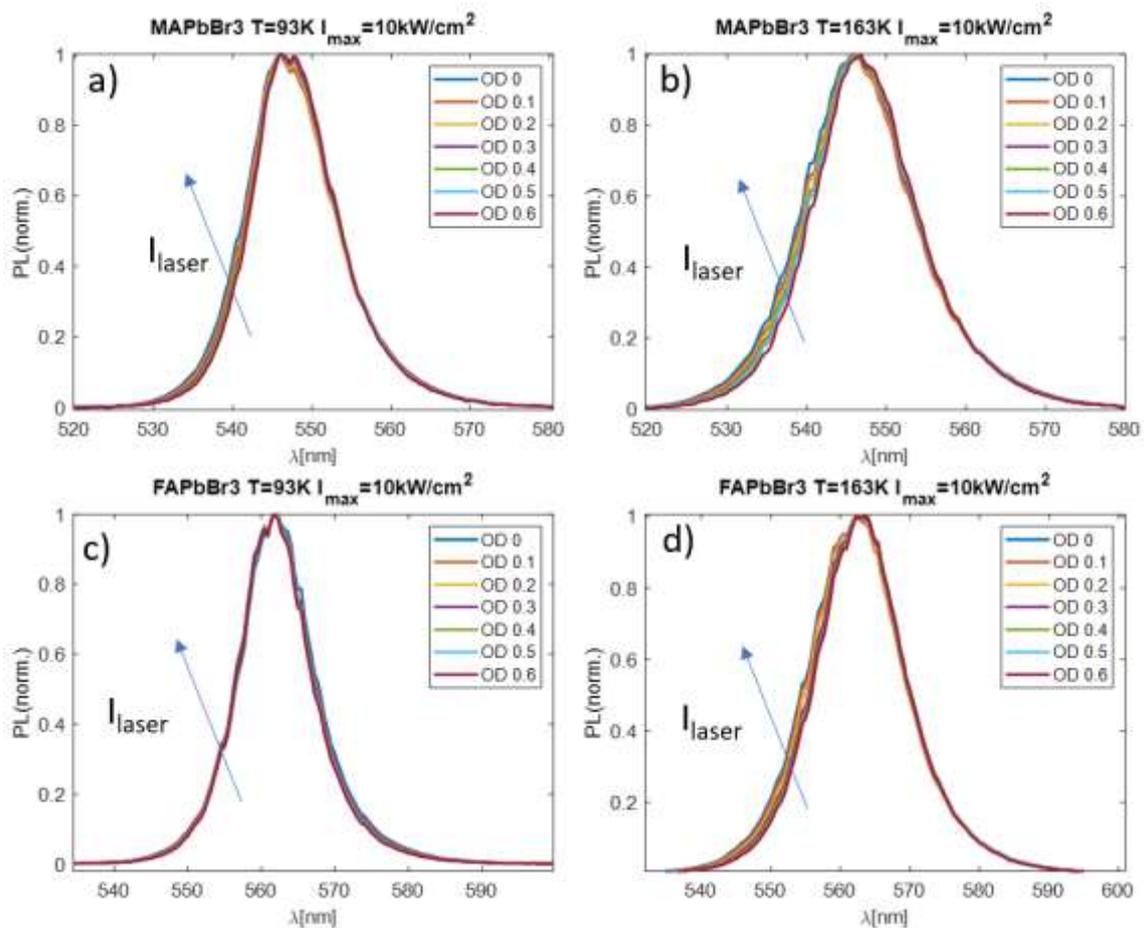
The first question that arises is what the origin of the spectral features in Figure 1 is and why they are so different for the two crystal types. We explain this by the coupling of the MA site cation rotational modes with the LA phonons in the case of MAPbBr<sub>3</sub>. Various experimental studies [6] identified that in cubic ( $T > 237\text{K}$ ) and tetragonal ( $150\text{K} < T < 237\text{K}$ ) phases two different rotational modes exist. However, once the crystal undergoes the orthorhombic transition ( $T < 150\text{K}$ ) the slow rotational mode is suppressed due to different crystal symmetry, leaving only the fast one present. Thus, we propose a model of coupled MA slow rotational mode and LA phonon in MAPbBr<sub>3</sub> which describes the asymmetric LA spectral shape up to 150K in Figure 1a. Measured Brillouin spectra alongside with fits are presented in the Figure 2.

The coupled mode is modelled using equations from [7] which represent non-linear mixing of the damped harmonic oscillator (phonon) and relaxational (quasi-elastic) susceptibilities. It can be clearly shown from the equations that the extent of coupling determines the low energy side spectral asymmetry. That can be seen in Figure 2 a2) where the spectrum measured at the border of the tetragonal-cubic phase transition ( $T = 223\text{K}$ ) fits to a asymmetric Lorentzian line centred at  $80 \mu\text{eV}$  (red line, CM in the legend) with the highest coupling constant. Once the crystal reaches the orthorhombic phase, the slow rotational mode of MA is suppressed, the phonon lineshape becomes symmetric (Figure 2. b) and no coupling between the remaining fast rotational mode and LA phonon is observed. When the MA cation is replaced with the FA cation, symmetric shapes are observed at each temperature (Figure 1 b), which indicates that no coupling is present in the case of FAPbBr<sub>3</sub>.



**Figure 2. Brillouin Spectroscopy scans with fits: x axis-phonon energy; y axis- Brillouin Spectroscopy counts; a1) Experimental values and fit, a2) Decomposition of the modelled spectrum to a contributions from Coupled Mode (CM), Large Quasi-Elastic (LQE) and Damped Harmonic Oscillator (DHO) spectral lines for MAPbBr<sub>3</sub> at T=223K; b1) and b2) for MAPbBr<sub>3</sub> at T=123K; c1) and c2) for FAPbBr<sub>3</sub> at T=223K.**

Clearly, the organic cation influences the acoustic phonon properties of hybrid perovskites, but will that reflect on the carrier relaxation dynamics and if so, is there any correlation? Power dependent CWPL measurements were carried out with the aim to answer this question (see Figure 3). Qualitatively, to determine whether hot carrier population is present, the high energy side of the PL spectrum (low wavelength) needs to be observed. Following the generalized Planck's radiation law equation, it can be shown that the broadening of the high energy side is related to the elevated carrier temperature. We see that the high energy tail broadens with increasing laser photon flux, for all cases except for c) depicting results for FaPbBr<sub>3</sub> at T=93K, meaning that hot carriers are present in both orthorhombic and tetragonal phase in MAPbBr<sub>3</sub> whereas no hot carrier population is detected in the low temperature orthorhombic phase of the FAPbBr<sub>3</sub>. This is a rather unusual result as it is well established in III-Vs that hot carrier lifetime extends as electron-phonon scattering is suppressed, with decreasing temperature due to low phonon population at low temperatures. By performing qualitative analysis of the CWPL spectrum carrier temperatures will be obtained which will shed more light on the potential correlation between Brillouin spectra and hot carrier temperatures. Furthermore, by performing density functional theory calculations we aim to reveal the origin behind different phonon properties in MA and FA cation perovskites.



**Figure 3** Power dependent CWPL spectrum of two crystals: x axis-emitted photon wavelength; y axis- normalized PL intensity; legend- laser intensity was attenuated from  $I_{\max}$  using optical density (OD) filters from OD 0 to OD 0.6.

## References

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