The Effect of Ionic Composition on Acoustic Phonon Speeds in Hybrid Perovskites

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The effect of ionic composition on acoustic phonon speeds in hybrid perovskites from Brillouin spectroscopy and density functional theory

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Faculty of Chemistry Materials and Interfaces | מכון ויצמן למדע WEIZMANN INSTITUTE OF SCIENCE

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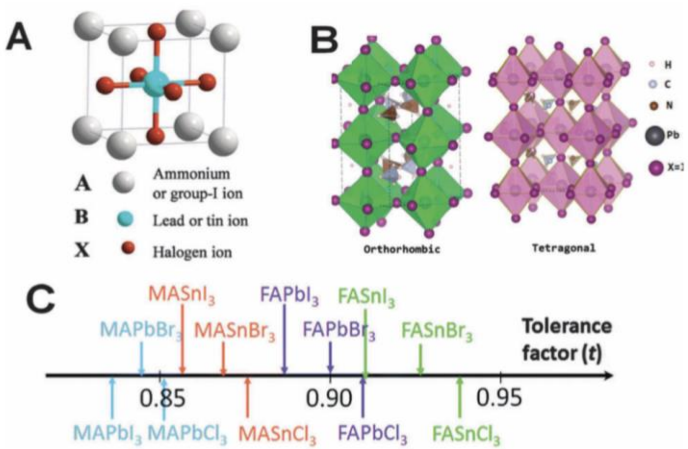
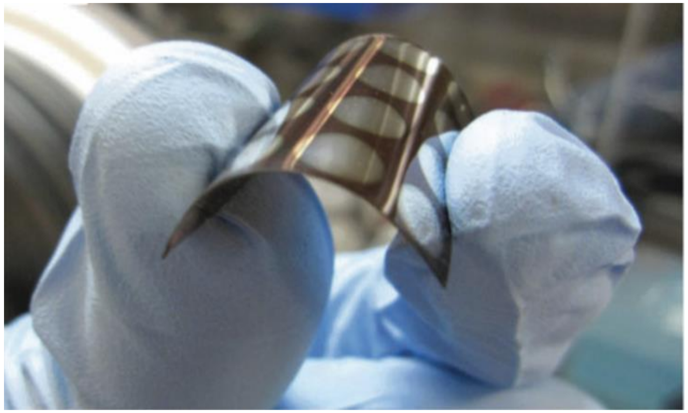
ESPCI PARIS | PSL

Φ(R) Department of Physics University of Regensburg

Motivation

Hybrid organic-inorganic perovskites





HOIP applications:

- Solar energy, LEDs, lasers;
- HOIP solar cell efficiency >20%;
- Low cost fabrication;
- Deposition on corrugated/flexible/structured surfaces;

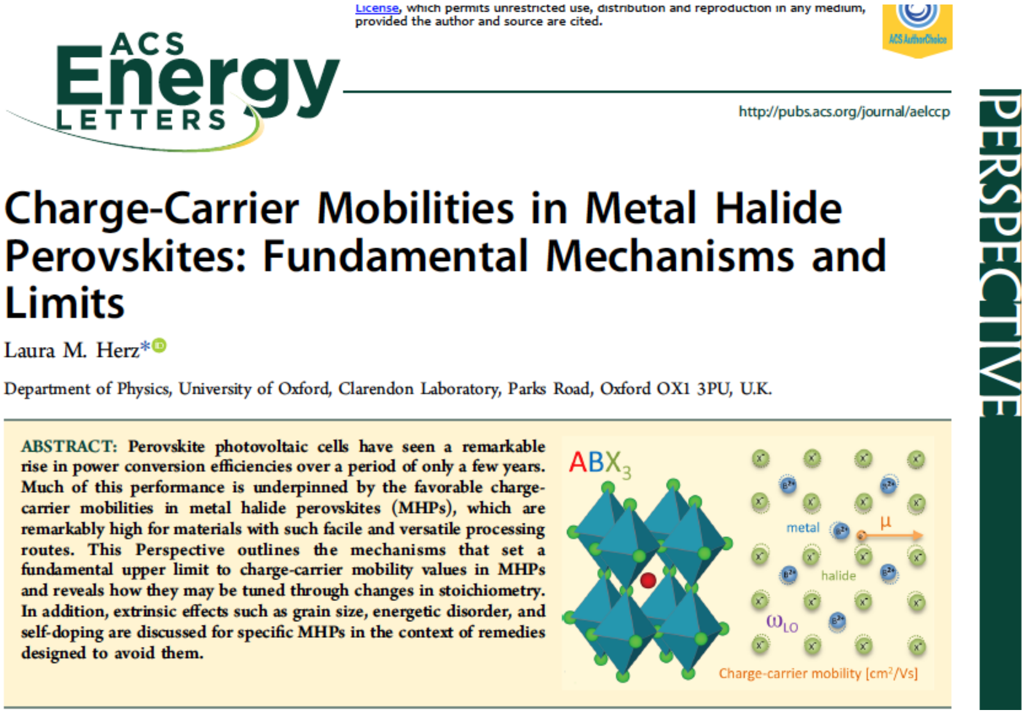
Open questions:

- Mechanical and chemical stability;
- Temperature-related structural changes;
- Role of phonons in the charge-carrier scattering;
- Tailoring electric and mechanical properties by ionic composition.

Zhao&Zhu "Organic-inorganic hybrid lead halide perovskites for optoelectronic and electronic applications," Chem. Soc. Rev. 45, 655 (2016).

Motivation

Ionic composition and charge mobility



ACS Energy Letters

http://pubs.acs.org/journal/aelccp

PERSPECTIVE

Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits

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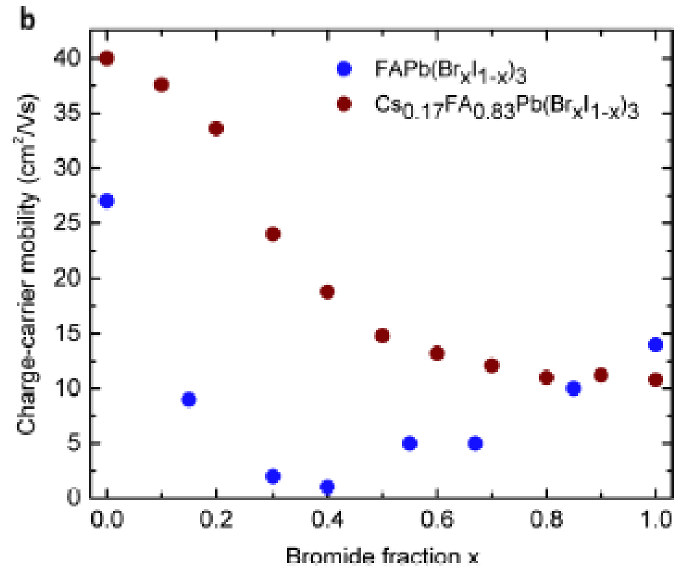
ABSTRACT: Perovskite photovoltaic cells have seen a remarkable rise in power conversion efficiencies over a period of only a few years. Much of this performance is underpinned by the favorable charge-carrier mobilities in metal halide perovskites (MHPs), which are remarkably high for materials with such facile and versatile processing routes. This Perspective outlines the mechanisms that set a fundamental upper limit to charge-carrier mobility values in MHPs and reveals how they may be tuned through changes in stoichiometry. In addition, extrinsic effects such as grain size, energetic disorder, and self-doping are discussed for specific MHPs in the context of remedies designed to avoid them.



- Charge career mobility varies with ionic composition
- Two factors are found to influence charge-career mobility
    1. Intrinsic effects – charge interactions with the underlying lattice
    2. Extrinsic effects – material imperfections (lattice disorder, impurities etc.)

Motivation

Elastic properties and charge mobility

ARTICLE

Received 6 Sep 2016 | Accepted 21 Dec 2016 | Published 8 Feb 2017 DOI: 10.1038/ncomms14398 OPEN

Electron–acoustic phonon coupling in single crystal $CH_3NH_3PbI_3$ perovskites revealed by coherent acoustic phonons

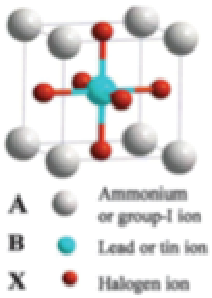
Pierre-Adrien Mante[1], Constantinos C. Stoumpos[2], Mercouri G. Kanatzidis[2] & Arkady Yartsev[1]

$$\mu = \frac{(8\pi)^{1/2}\hbar^4 eC}{3(m^*)^{5/2}(k_b T)^{3/2} d^2}$$ - Carrier-charge mobility

C - Elastic constant

d - Conductance/valence band deformation potential

GOAL: study mechanical properties of HOIPs with variation of A- and X-sites

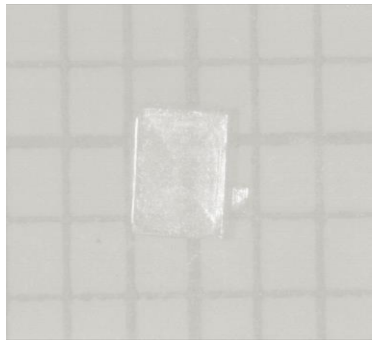


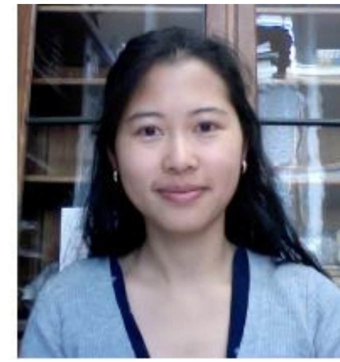
$MAPbCl_3$ methylammonium (MA) lead chloride
$MAPbCl_xBr_{1-x}$
$MAPbBr_3$
$FAPbBr_3$ formamidinium (FA) lead bromide

Outline

- Fabrication of samples
- Clarification of mixture crystal composition
- Brillouin spectroscopy measurements
- Density functional theory calculations
- Discussion of the results
- Outlook

Crystal fabrication

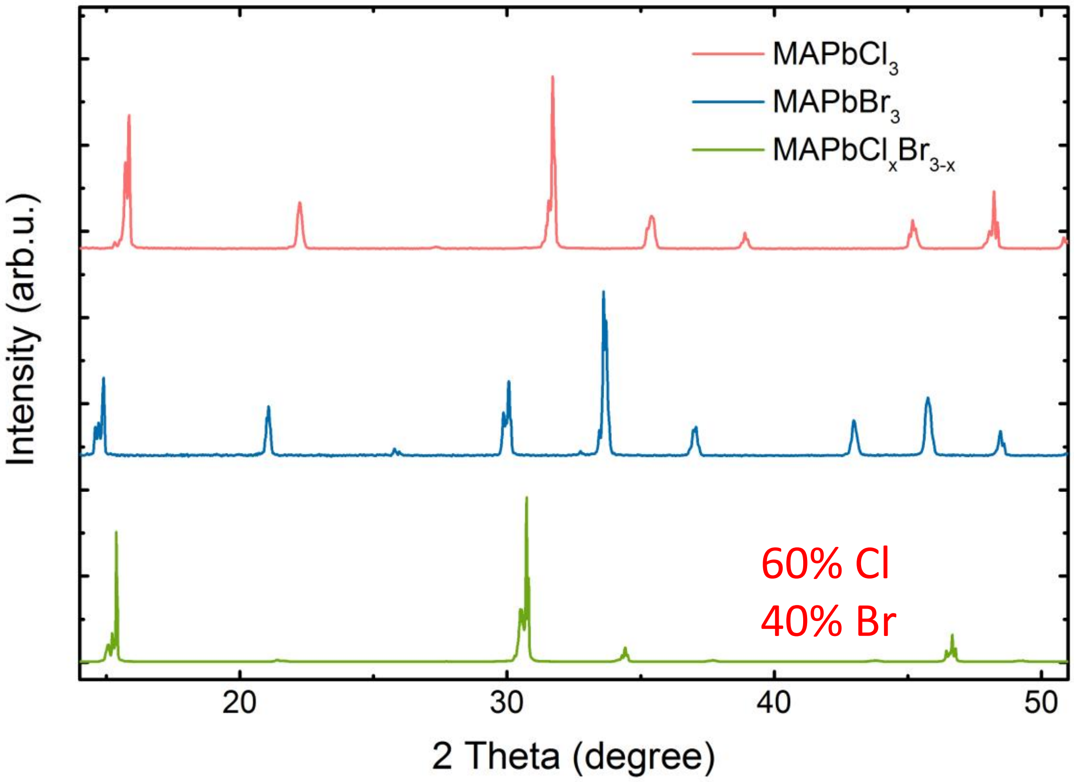


Dr Zhuoying Chen
ESPCI Paris

- Crystals are prepared by dissolving MACl/MABr and $PbCl_2$ into solution
- The mixture is kept in an oil bath for 12 hr at 55° C
- Formed crystals are dried under vacuum at 50° C for 6 hours
- Typical crystal size obtained – $1m^3$
- The color varies from transparent (Cl) to yellow (ClBr) to bright orange (Br)

Dr Pabitra Nayak
Oxford University

XRD measurements



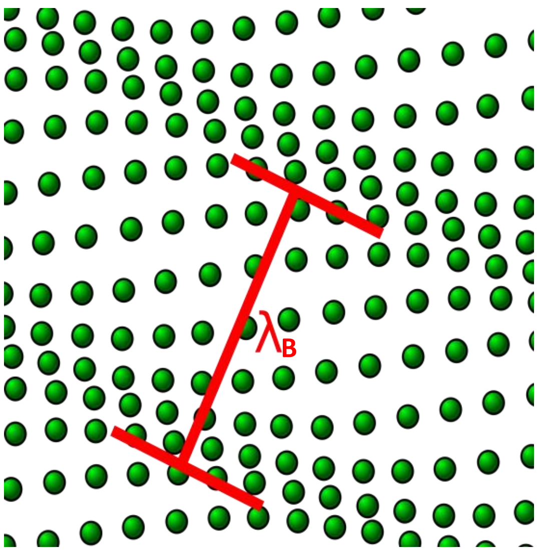
	2 theta (100)	2 theta (200)	theta (100)	theta (200)	d (100)	d (200)
Cl crystal	15.84	31.71	7.92	15.86	5.59	2.82
mixed Cl-Br crystal	15.37	30.73	7.69	15.36	5.76	2.91
prediction 60%Cl-40%Br	15.46	31.05	7.73	15.52	5.73	2.88
Br crystal	14.90	30.05	7.45	15.02	5.94	2.97

Brillouin light scattering

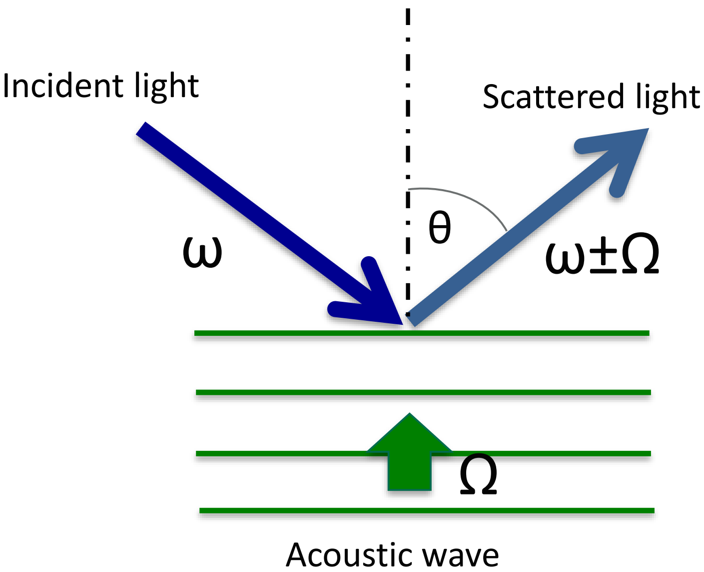
Light
Frequency f ~ 100 THz
Speed in vacuum c = 3•10^8 m/s
Wavelength λ ~ 500 nm

Sound
Frequency f ~ MHz-GHz
Speed in water v = 1470 m/s
Wavelength λ ~500nm (f~GHz)

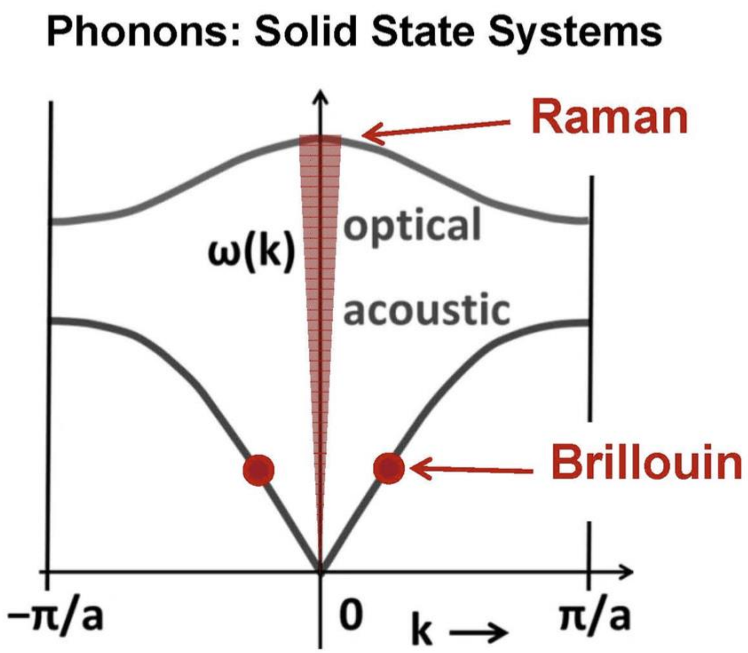
Thermal pressure waves

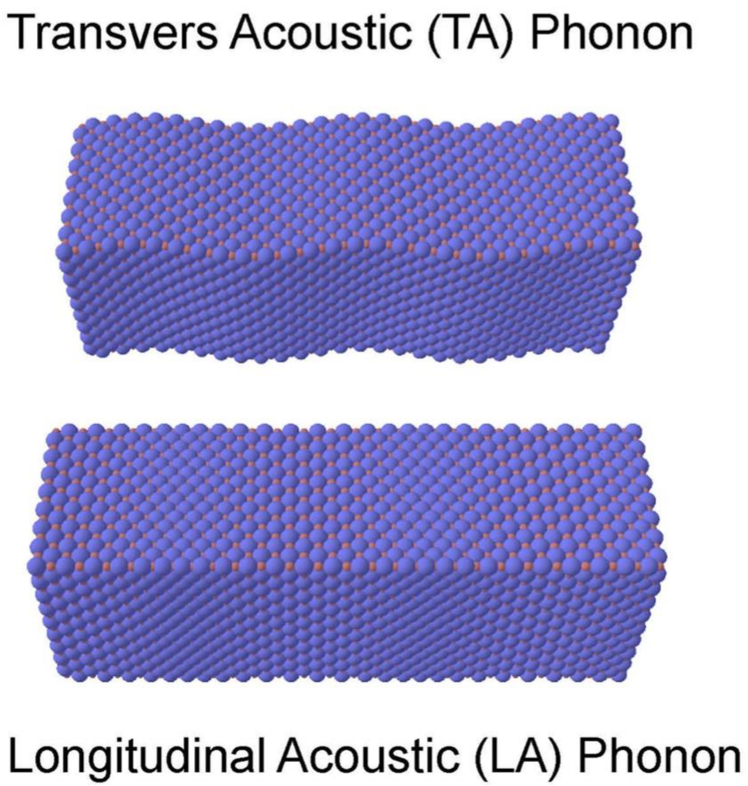


Brillouin light scattering (BLS)



Brillouin light scattering





Acoustic waves - collective motion of particles/molecules

Brillouin light scattering in crystals

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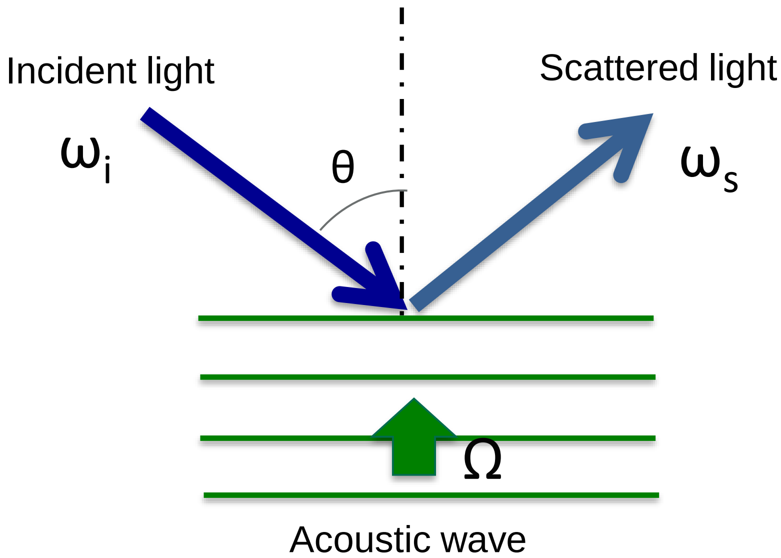


Energy conservation

$$\omega_s = \omega_i \pm \Omega$$

Phase matching

$$k_B \cong 2 k_i \cos\theta$$

Brillouin frequency shift

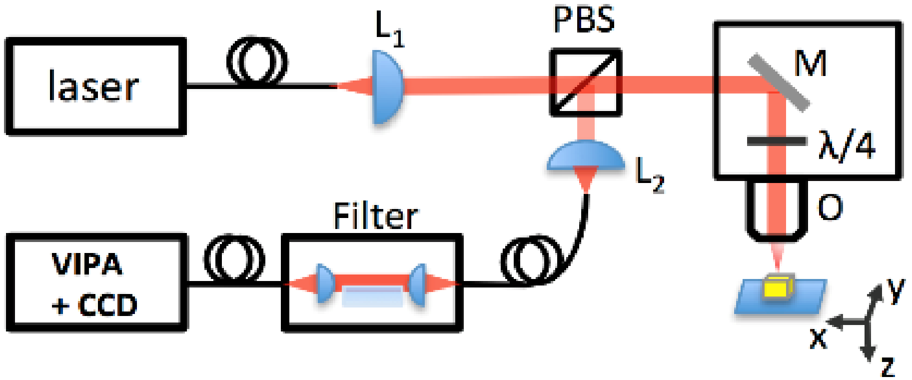
$$\Omega = v \cdot k_B = \frac{4\pi n}{\lambda} v \cos\theta$$

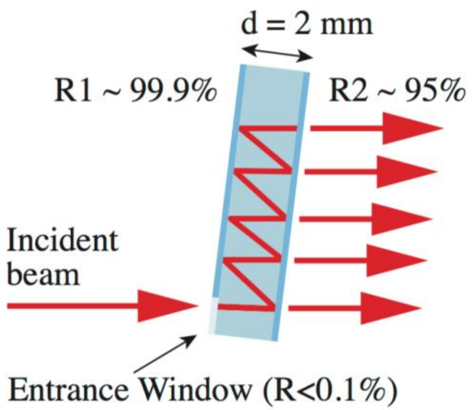
In crystals with cubic symmetry Christoffel's equation holds

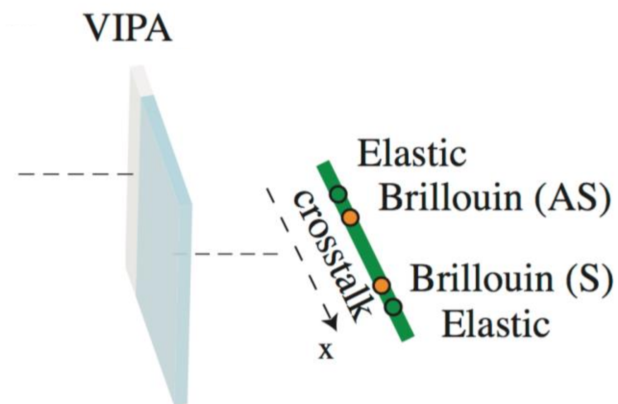
3 independent elastic constants C_{11}, C_{12}, C_{44} and 3 acoustic waves QL, QT, T

$$\det\left[C_{ijkl} n_j n_l - \rho v^2 \delta_{ik} \right] = 0$$

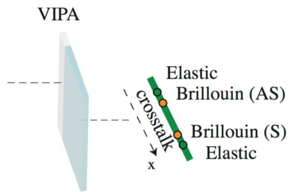
Experimental setup for Brillouin spectrosc

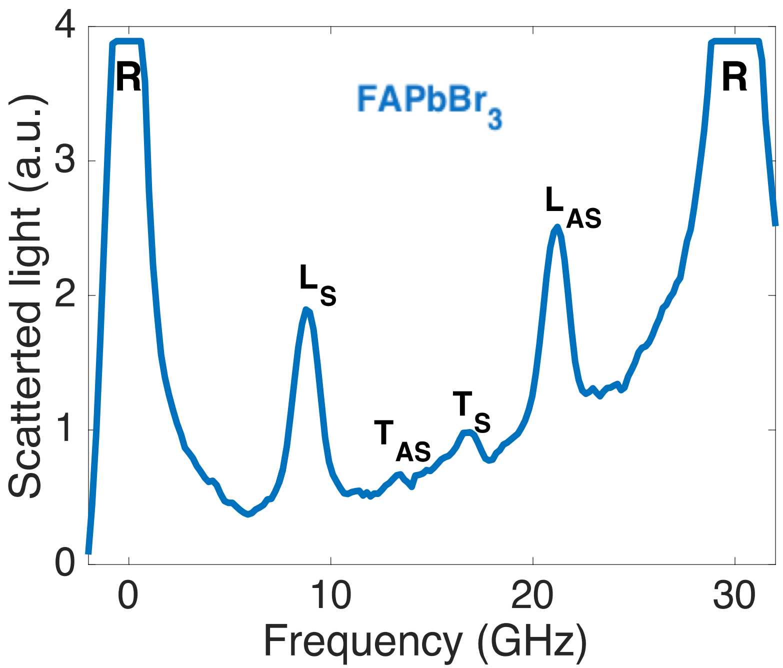


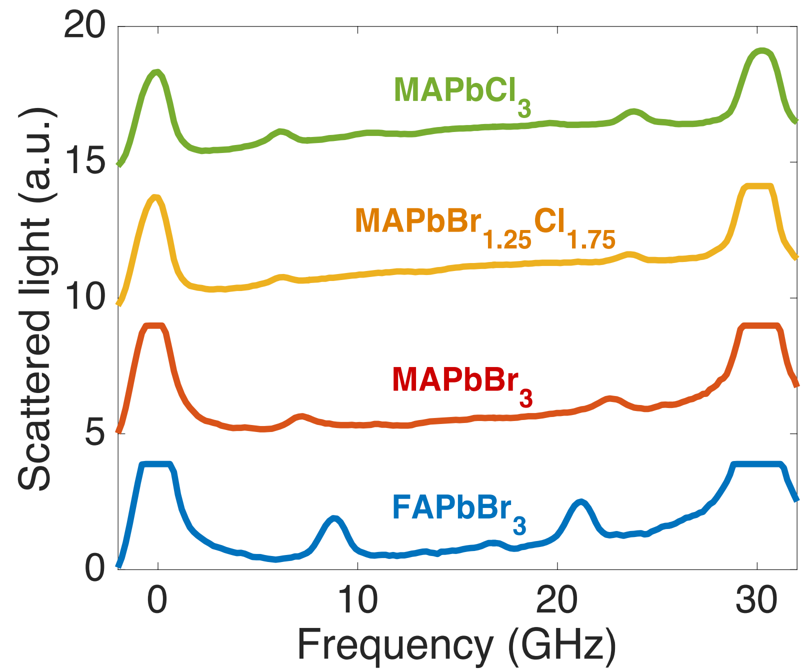




Brillouin measurement results







Brillouin measurement results

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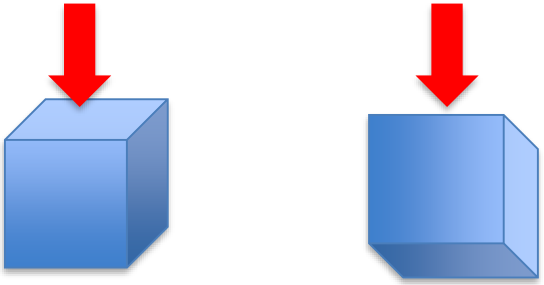

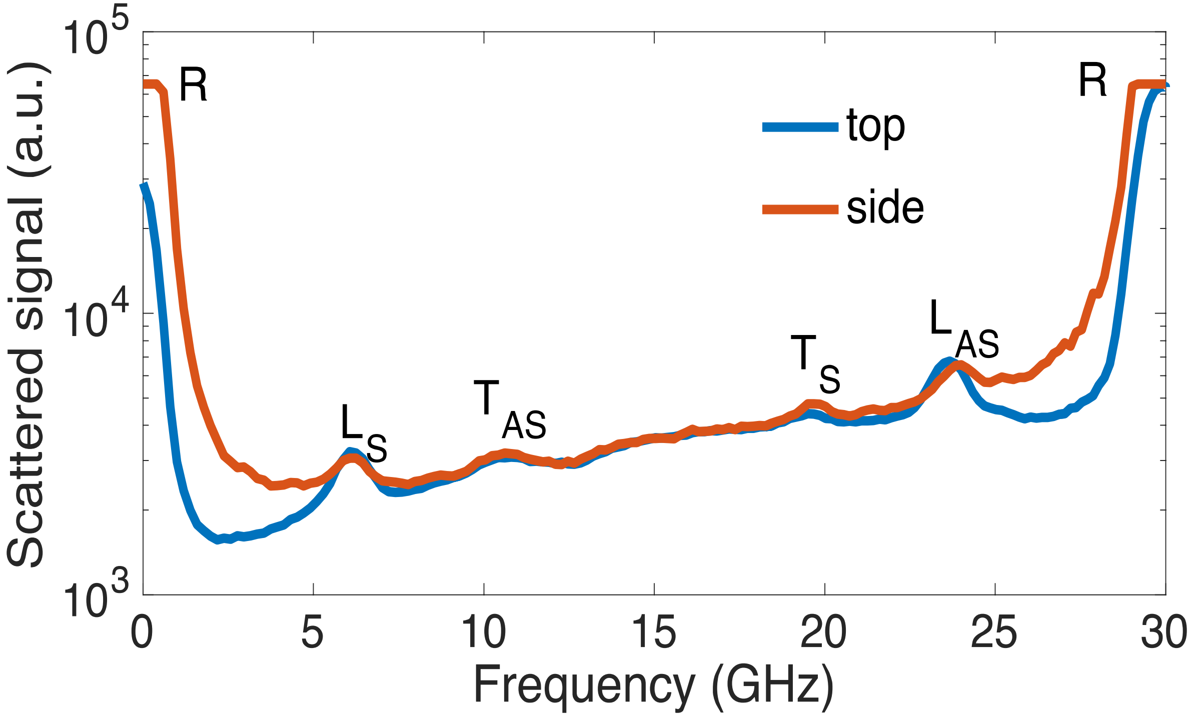

Brillouin spectra measured from the top and for a 90°-rotated (side) $MAPbCl_3$ crystal. The difference between the Brillouin shift for each type of the acoustic mode is within ~100-200 MHz.

Density functional theory calculatio

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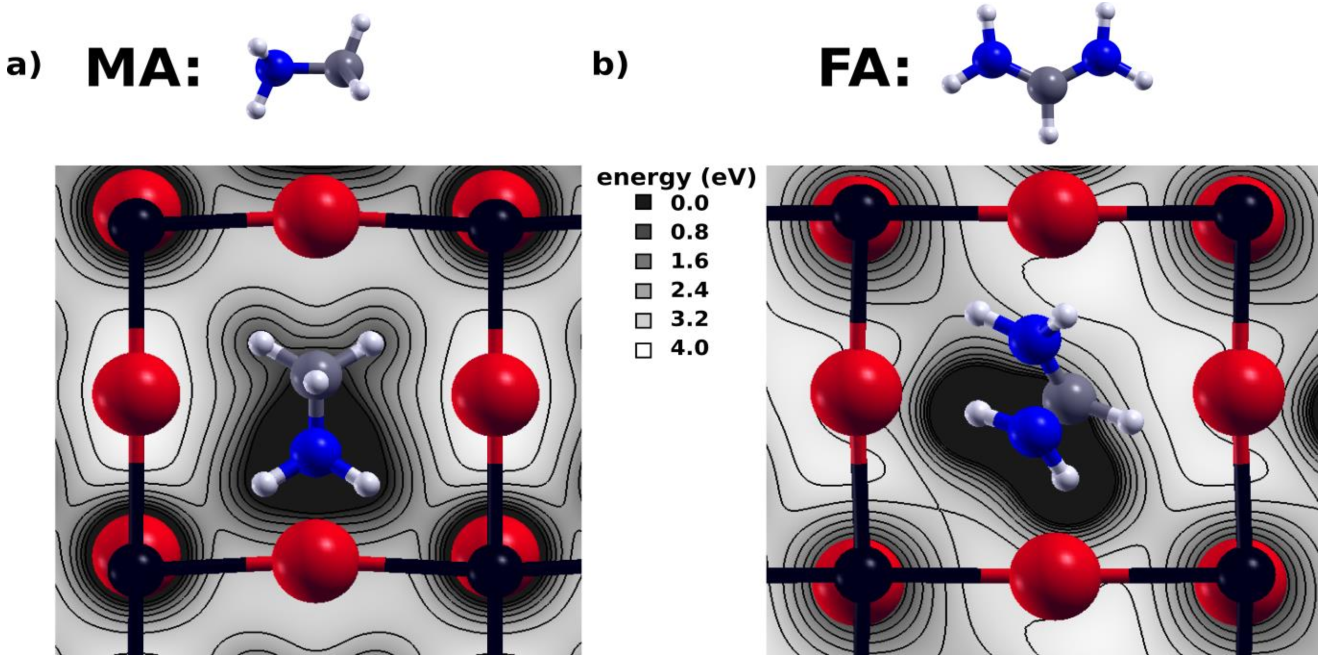


- Periodic DFT calculations using VASP plane wave code (open source computer program for atomic scale material modeling developed by a research group in Vienna)
- Elastic constants are calculated by perturbation theory as implemented in VASP
- Christoffel’s equation is used to obtain acoustic velocities

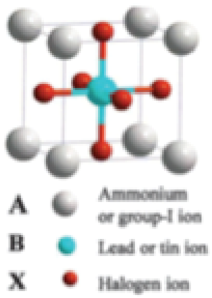
Experiment and theory in compariso

Crystal	Mode	**Ω**, GHz	Experiment **v**, m/s	Theory **v**, m/s		
				[1 0 0]	**[0 1 0]**	**[0 0 1]**
$MAPbCl_3$	QL	23.9±0.1	4000±25	4201	3702	4020
	QT	10.6±0.1	1770±25	1538	1396	1379
	T	–	–	1205	1260	1255
$MAPbBr_{1.25}Cl_{1.75}$	QL	23.6±0.1	3880±25	3832	3366	3308
	QT	–	–	1391	1280	1230
	T	–	–	1090	1162	1159
$MAPbBr_3$	QL	22.7±0.1	3620±25	3540	3204	3306
	QT	–	–	1266	1201	1169
	T	–	–	1091	1096	1094
$FAPbBr_3$	QL	21.2±0.1	3380±25	3482	3535	3529
	QT	13.2±0.1	2110±25	–	–	–

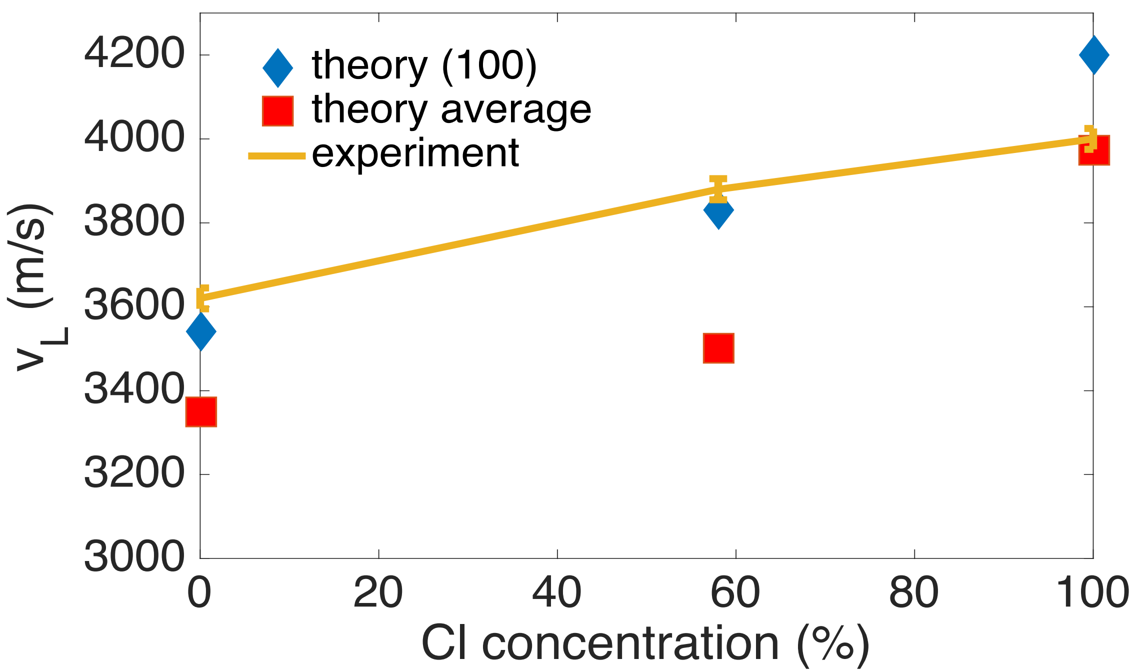
Agreement between theory and experiment within 10%
Agreement with previous studies* within 20%

*Letoublon et. al. Phys. Chem. Lett. 2016, 7, 3776-3784
*J. Feng APL Mater. 2014, 2, 081801

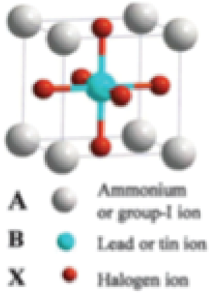
Substitution of X-site



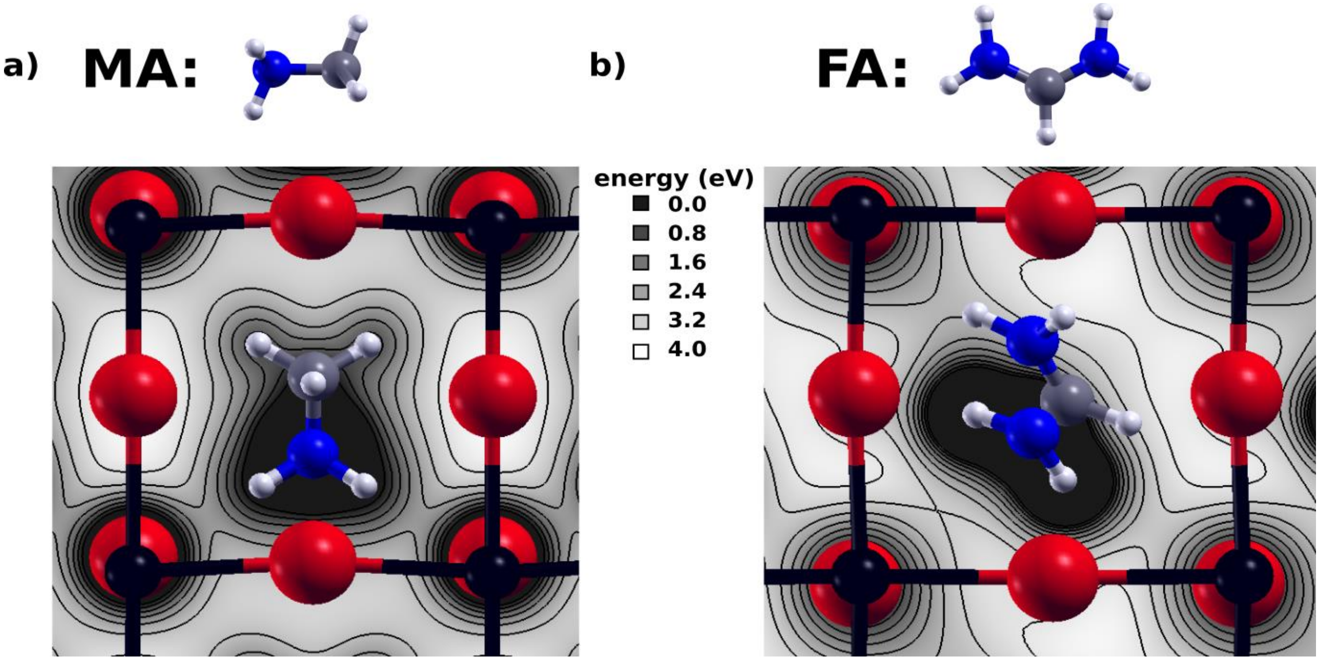
$MAPbBr_3$ -> $MAPbCl_xBr_{1-x}$ -> $MAPbCl_3$



Substitution of A-site



$FAPbBr_3$ -> $MAPbBr_3$



Elastic anisotropy

Crystal	Mode	**Ω**, GHz	Experiment **v**, m/s	Theory **v**, m/s		
				[1 0 0]	**[0 1 0]**	**[0 0 1]**
$MAPbCl_3$	QL	23.9±0.1	4000±25	4201	3702	4020
	QT	10.6±0.1	1770±25	1538	1396	1379
	T	–	–	1205	1260	1255
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$FAPbBr_3$	QL	21.2±0.1	3380±25	3482	3535	3529
	QT	13.2±0.1	2110±25	–	–	–

Elastic anisotropy*: v_T/v_L=44% for $MAPbCl_3$ and v_T/v_L=62% for $FAPbBr_3$

*J. Feng APL Mater. 2014, 2, 081801

Outlook

- Exploring electronic properties and carrier mobility
- Exploring line shape of Brillouin peaks (can be linked to dynamic lattices and non-harmonic phonon states)
- Temperature-dependent study (phase transitions)
- For these all a higher resolution and higher sensitivity Brillouin system is required. This is currently being build at UTS.

Thank you!