Experimental report

15/02/2021

Proposal: 7-01-523 **Council:** 4/2020

Title: Study of lattice dynamics in the lead-free hybrid perovskite CH3NH3BaCl3

Research area: Physics

This proposal is a new proposal

Main proposer: Manila SONGVILAY

Experimental team: Manila SONGVILAY

Local contacts: Karin SCHMALZL

Samples: CH3NH3PbCl3
CH3NH3BaCl3

Instrument	Requested days	Allocated days	From	To
IN22	7	4	28/01/2021	01/02/2021

Abstract:

We propose to investigate the lattice dynamics in a new lead-free organic-inorganic halide perovskite, CH3NH3BaCl3. Previous study on the lead variant has shown a strong damping of the transverse acoustic phonon modes towards the X and M Brillouin zone boundaries at 300K, due to the coupling to the disordered molecular cation. Such damping is responsible for the ultra-low thermal conductivity observed in these systems. We would like to investigate the lattice dynamics in a lead-free variant, CH3NH3BaCl3, in order to establish wether these new materials present similar behaviour. These systems have attracted attention recently, in the context of developing lead-free photovoltaic materials with enhanced efficiencies. We request 7 days on IN22 to map out the transverse acoustic phonons in the (HK0) scattering plane.

Experimental report for experiment 7-01-523

While this experiment should have been performed on the lead-free hybrid perovskite $CH_3NH_3BaCl_3$, we have been experiencing issues with the sample shipment from the UK before the experiment, due to the COVID and Brexit situation.
Instead, a similar sample containing lead on the Ba site ($CH_3NH_3PbCl_3$) and already available at the ILL was measured.

$MAPbCl_3$ is an organic-inorganic hybrid perovskite, consisting of an inorganic perovskite host framework composed of corner-bonded $PbCl_3$ octahedra, with an organic molecular cation (MA is methylammonium CH_3NH_3) occupying the interstitial space. This compound displays three structural transitions from cubic to tetragonal to orthorhombic phase as temperature is decreased. These transitions are driven by the rotation and distortion of the $PbCl_3$ octahedra and associated rotation of the MA cation. In this compound, we used neutron inelastic scattering to map out the transverse optical phonon modes in several key directions in the Brillouin zone, namely towards the X (1/2 0 0) and M (1/2 1/2 0) zone boundaries. We also followed their temperature dependence throughout the different structural transitions (from cubic to tetragonal to orthorhombic symmetries). The results show that the optical modes are flat as a function of Q, and are probably associated to molecular dynamics. The temperature dependence shows that the different modes however become overdamped at different temperatures.

To go further, we would like to carry out the study of the acoustic phonon modes in the lead-free perovskite system $MABaCl_3$, following the results obtained on the Pb variant. These previous results were obtained on the IN22 spectrometer and are already published [1,2]. In order to investigate the effect of a bigger atomic radius provided by the Ba ion on the lattice dynamics, we would like to resubmit our original proposal for experiment 07-01-523 using the right sample. By the time the experiment was complete, the sample finally arrived at the ILL and is now available. We therefore kindly ask for the same beamtime to perform the original experiment.

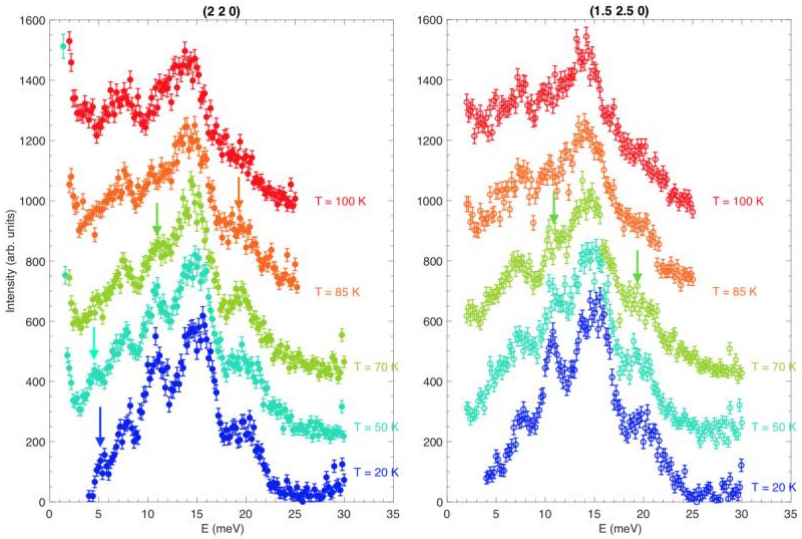

Fig. Transverse optical phonon modes at different temperatures, toward the Brillouin zone center and the (3/2 5/2 0) zone boundary. The arrows indicate the modes damping at different tempratures.

[1] M. Songvilay et al., Physical Review Materials 2, 123601 (2018)
[2] M. Songvilay et al., Physical Review Materials 3, 093602 (2019)