Experimental report

05/08/2019

Proposal: **7-02-180**

Council: 10/2018

Title: Soft phonon mode in BaZrO3

Research area: Physics

This proposal is a new proposal

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Samples: BaZrO3

Instrument	Requested days	Allocated days	From	To
IN8	6	0		
IN22	0	3	20/06/2019	24/06/2019

Abstract:

The aim of this proposal is to contribute to the understanding of the structure and lattice dynamics of the cubic perovskite BaZrO3 by measuring for the first time its "soft" phonon mode, the associated branch, and its evolution with temperature.

Preliminary report on proposal 7-02-180

The objective of the project is to study the octahedra "tilt" phonon mode in $BaZrO_3$, which is predicted to be unstable by DFT but remains stable in experiments at all investigated temperatures[1,2,3]. We want in particular to determine its dispersion, and check his expected softening at low temperatures. The main experimental challenge lies in the limited size of the available crystals. For that reason, 3 days were allocated on IN22 for a test measurement.

Experimental details

The experiment was performed using a $BaZrO_3$ single crystal of ~200 mg, extracted directly from a boule grown by the floating zone technique. Sample preparation was minimal in order to keep as much sample volume as possible, and the crystal was oriented with respect to natural faces that could be identified as [001] due to their respective orientations at right angles. The crystal was glued on an Al pin and placed in an Orange Cyrostat. Diffraction revealed the presence of a very small crystallite with a different orientation, but in such a small amount that it did not preclude the inelastic scattering measurement. Different regions of reciprocal space were explored, mostly at room temperature and at 2 K, around the (0.5 0.5 0.5) point in different Brillouin zones. Signals are quite low in general; typical scans were performed for 4000000 monitor counts (~2.5 hours per scan).

Main results

In the following, we show the main results obtained and illustrate them with representative datasets. In this preliminary version, all results shown are the result of a first rough data analysis, but do not yet include proper peak fitting.

<u>Result n°1:</u> A low frequency mode can be found at room temperature at 8.5 meV (69 cm^{-1}). It obeys the selection rules expected for the anticipated tilt mode.

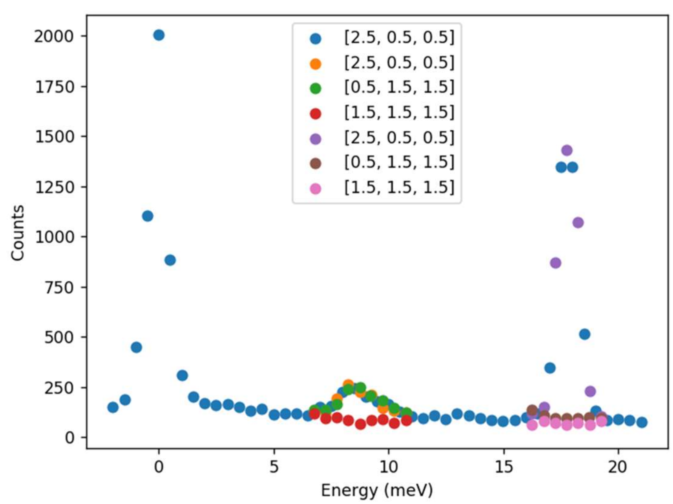

Figure 1: Inelastic scans at room temperature at different R-points. The mode at 8.5 meV is assigned to the soft mode of interest. The more intense mode at 18 meV has been conclusively identified as a "spurion" due to a Bragg reflection from the monochromator.

Result n°2: This mode disperses very strongly, and could not be followed further than 0.1 in reciprocal lattice unit, around the R point. Three directions were explored: R→Γ, R→M and R→X. We also measured some scans at constant E, but that did not allow us to follow the mode any further.

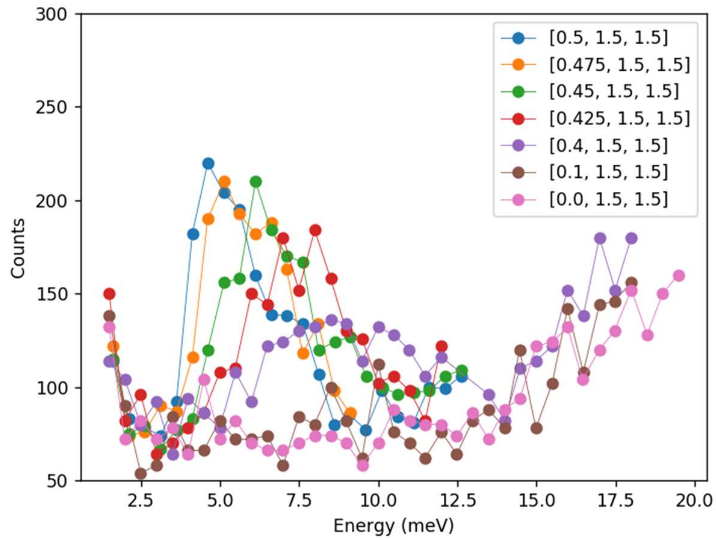

Figure 2: Typical dispersion at 2K from R to M. The soft mode goes quickly up in energy and becomes very broad. This could be due to the mode splitting along that direction and/or to the dispersion itself.

Result n°3: This mode softens with temperature, from ~8.5 meV at room temperature to ~5 meV at 2 K. The mode becomes also much more asymmetric; it is not yet clear why.

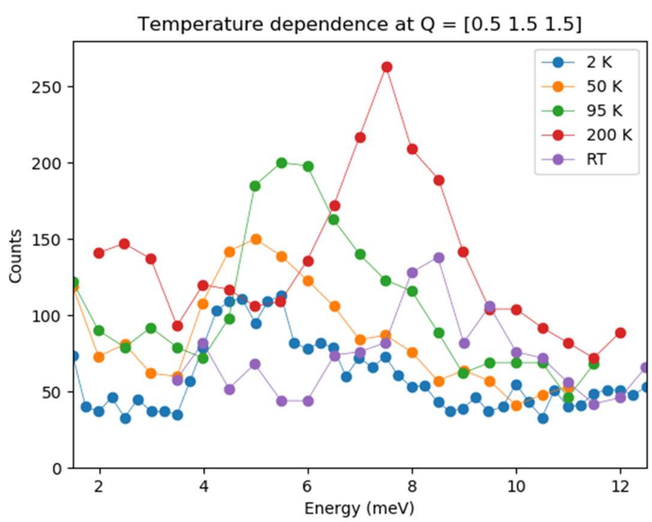

Figure 3: Scans at the R point at different temperatures

Result n°4: Part of the acoustic branches could be measured in the vicinity of the Γ point. At the R-point however, or anywhere else at the zone boundary, the acoustic mode(s) could not be found. This is consistent with the calculations of the inelastic structure factors: they show that they are much less intense that the soft mode, by one order of magnitude at least, so that they can hardly be seen with the counting times used in this experiment.

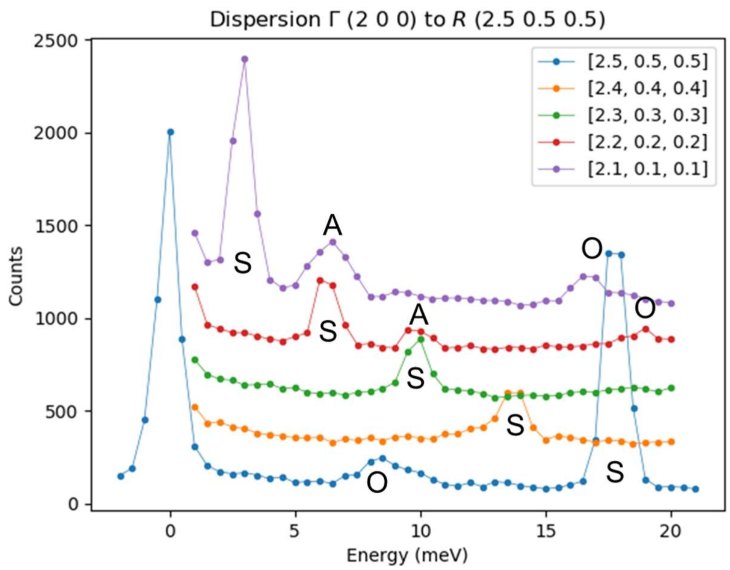

Figure 4: Dispersion from Γ to R at room temperature, with assignments as follows: A = acoustic mode, O = optic mode, S = Spurion.

Conclusions and open questions

This test experiment is altogether very successful. We notably now have experimental evidence for the soft tilt mode, with its energy and its softening with temperature. This already allows us to support our recent interpretation of the Raman spectrum of $BaZrO_3$[3]. It also enables us to calculate reasonable inelastic structure factors, which was impossible with imaginary frequencies.

On the other hand, it still leaves a couple of open questions. The full dispersion could not be completely determined in any direction, and it is not clear how this branch connects to the other special points in the Brillouin zone. In particular, it is not clear whether it crosses the acoustic branch as predicted along the Γ→R direction. Complementary measurements will be needed for that purpose.

References

[1] Akbarzadeh et al., Phys. Rev. B 72, 205104 (2005)
[2] Bennett et al., Phys. Rev. B 73, 180102 (2006)
[3] Toulouse et al., Phys. Rev. B, submitted (2019). Also : arXiv:1907.02008