EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Acoustic Velocities of $CaSiO_3$ perovskite	**Experiment number**: es-801
Beamline: ID06-LVP	**Date of experiment**: from: 21/11/2018 to: 27/11/2018	**Date of report**: 12/09/2022
Shifts: 18	**Local contact(s)**: Dr W Crichton	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The travel times of seismic waves through Earth's interior provide one of the few direct constraints on the physical properties of mantle rocks. If carefully compared with experimental and computational measurements of the elastic properties of minerals this data may be interpreted in terms of mantle mineralogy, chemistry and temperature; information that is not otherwise directly attainable. Over several decades our knowledge of Earth's seismic structure has developed from simple 1-D velocity models, constructed from stacked seismograms (Dziewonski and Anderson 1981), into full 3-D tomographic models of Earth's velocity structure (Ritsema et al. 2011). In order to accurately interpret this vast array of high quality data it is absolutely vital there are high quality measurements of the elastic properties of the main Earth forming minerals.

Calcium silicate perovskite is one of the most abundant minerals in the Earth's deep mantle, consisting ~ 10 % of ambient mantle and up to ~ 30 % of subducting slabs assemblages (Stixrude and Lithgow-Bertelloni 2012). However, existing estimates (at the time of beamtime) of its thermo-elastic properties (V_p, V_s and G) and even its crystal structure were in complete disarray. Predictions of V_p and V_s vary from 0 to +10% faster and -10 to +14% faster than PREM respectively and different studies predict orthorhombic or tetragonal ground states that become cubic at < 500 K or > 4000 K respectively (e.g. Adams and Oganov 2006; Li et al. 2006; Stixrude et al. 2007; Kawai and Tsuchiya 2015). There were no existing experimental measurements of V_p, V_s and G of calcium perovskite at mantle conditions. Therefore, its presence is often ignored in models of the deep Earth (e.g. Murakami et al. 2012), despite it being the second or third most abundant mineral in lower mantle assemblages and despite some simulations predicting a large shear softening of the tetragonal structure that could explain much of the seismic heterogeneity throughout the lower mantle. We set out to measure the acoustic velocities of calcium perovskite at mantle conditions on ID06-LVP. The major hurdle in measuring the elastic properties of end-member $CaSiO_3$ perosvkite using traditional high pressure experiments is that this phase is unquenchable, and it becomes amorphous at room pressure and temperature. This makes it extremely challenging to work with and prevents pre-synthesising fully dense, double polished samples usually required for ultrasonic interferometry. For this reason, we adopted a tailored approach to measuring the acoustic properties of calcium perovskite. We intended to measure the acoustic properties of three recoverable Ti-bearing compositions ($Ca(Si_{0.8}Ti_{0.2})O_3$, $Ca(Si_{0.7}Ti_{0.3})O_3$ and $Ca(Si_{0.6}Ti_{0.4})O_3$) allowing extrapolation to the endmember properites. Additionally, we would attempt to directly measure the endmember $CaSiO_3$'s properties.

We utilised the same ultrasonic interferometry setup that we developed during previous beamtime allocations, and is now fully integrated into the ID06-LVP control system and available to the user community to make acoustic velocity measurements. During previous experimental sessions we had successully measured the acoustic and crystallographic properites of endmember and titanium-bearing capv at conditions extending to ~ 14 GPa and 1500 K. The aim of this beamtime was to extend these measurements to higher pressures and allow direct constraint of the pressure derivatives of elastic moduli (rather than relying on literature constraints – which are virtually absent for *G* in particular). To this end we adopted 7/3 assemblies, combined with a range of regular TF05 WC anvils as well as testing tapered WC anvils, which can generate higher pressure conditions (Ishii et al., 2019). Table 1 documents the experiments attempted throughout beamline allocation ES-801.

Table 1: summary of experimental runs performed in es-801

experiment	starting material	Max *PT* conditions	notes
es801_1	$CaSiO_3$ in 7/3	21 GPa	• Blow out before heating
es801_2	$CaSiO_3$ in 7/3	20 GPa, 1400 K	• Sample not visible at high PT conditions (not in anvil gap) • Calculated buffer rod length adjustment that is required • No length means travel time cannot be converted to velocity • Collected ultrasonic data on T down • Blow out on decompression
es801_3	$Ca(Si_{0.6}Ti_{0.4})O_3$ in 10/4	12 GPa	• Blowout on compression
es801_4	$CaSiO_3$ in 7/3	21 GPa, 1400 K	• Synthesised capv on first heating at 19 GPa • Image and travel time data collected on heating and cooling • Increase pressure to 21 GPa • More ultrasonic data • Blowout on decompression
es801_5	$Ca(Si_{0.6}Ti_{0.4})O_3$ in 7/3	22 GPa, 1400 K	• Ultrasonics dead due to power leakage through Earth during heating • Study structural evolution only up to 1400 K • Blowout on cooling
es801_6	$CaSiO_3$ in 7/3	17 GPa, 900 K	• During first heating unexpected temperature surge • This killed ultrasonic signal Decompress as no ultrasonics
es801_7	$Ca(Si_{0.6}Ti_{0.4})O_3$ in 7/3 [tapered anvils]	31 GPa	• Cannot heat on arrival to target load • There is a short in the press – have to decompress • Blowout on decompression
Realised an electrical short in the press is causing the problems with ultrasonics so completely dissemble the press and clean everything			
es801_8	$CaSiO_3$ in 7/3	21 GPa	• Blowout on compression (no more beam for a year, and then COVID)

As documented in Table 1, 3 out of 8 runs suffered blowouts on compression. Whilst this rate is somewhat higher than expected it probably resulted from using old (previously run) cubes right at the end of the beamtime cycle before shutdown for EBS upgrade. In one experiment the sample compressed out of the sanvil gap, preventing velocity measurements. 3 more experiments (numbers 5-7) all compressed successfully, but heating behaved abnormally and the ultrasonic signal was destroyed in this process. After run 7, this was recognised as being a symptom of a high resistance electrical short within the primary press tooling (likely a fragment of carbide from an earlier blowout), which caused the furnace power to heat the ultrasonics earth cable and cause it to fail. The final experiment was successful, during which capv velocity data was collected at 19-21 GPa. This data in itself is insufficient to achieve the experimental goals of this session. It is intended that this proposal will be resubmitted after EBS upgrade (and subsequent COVID disruption – once the PI has suffcient time after increase in teaching load).

References

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