

## 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://www.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 from 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

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> 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.



	<b>Experiment title:</b> High temperature analysis of Ca/Ce-co-doped LaPO <sub>4</sub>	<b>Experiment number:</b> A20-1 837
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 08.03.2022 to: 11.03.2022	<b>Date of report:</b> 22.12.2022
<b>Shifts:</b> 9	<b>Local contact(s):</b> Christoph Hennig, Volodymyr Svitlyk	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Theresa Lender and Lars Peters / Institute of Crystallography, RWTH Aachen University		

## Report:

In this work, the high temperature behaviour of the solid solution  $\text{La}_{1-x}(\text{Ca,Ce})_x\text{PO}_4$  was analysed *via in-situ* X-ray diffraction. To this end, monazite powders with different levels of Ca/Ce-co-substitution produced *via* a co-precipitation procedure were investigated in the temperature range 300-1250 K. Prior to the measurements at ESRF, elemental mappings of the material were performed using electron probe micro-analysis. These measurements showed two distinct phases in powders subjected to temperatures as high as 1500 K while samples that were not subjected to temperatures higher than 1050 K showed no clear segregation. The phases visible in the high-temperature samples were identified as  $\text{La}_{1-x}\text{Ce}_x\text{PO}_4$  with a monazite structure and a calcium phosphate phase with an unknown structure. In Figure 1, the elemental mapping of a grain boundary is shown with a monazite grain in the lower right corner and the surrounding calcium phosphate phase. To shed light on the desegregation process as well as its starting temperature experiments were performed at BM20 at the ESRF.

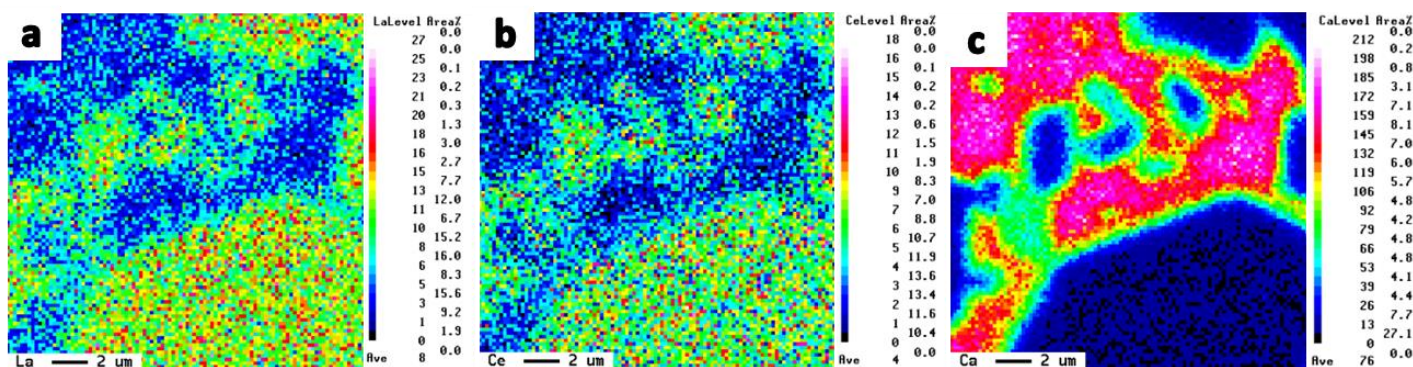


Figure 1: Elemental mappings of (a) Lanthanum, (b) Cerium and (c) Calcium showing the corner of a monazite crystallite surrounded by a calcium phosphate phase.

Initially, three standard samples were measured to calibrate the newly acquired Anton Paar heating chamber used in this experiment. The standard samples were  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, ZrW<sub>2</sub>O<sub>8</sub> und SiO<sub>2</sub>. O repeated measurements were taken on all samples, following the procedures:

- $\alpha$ -Al<sub>2</sub>O<sub>3</sub>: 1000 K to room temperature
- ZrW<sub>2</sub>O<sub>8</sub>: room temperature to 750 K to room temperature
- SiO<sub>2</sub>: room temperature to 1000 K to room temperature

The calibration of the chamber was successful and was shared with the beamline staff for future applications and users.

From the monazite powder data, the identification of the calcium phosphate phase was not possible. From Rietveld refinement of the monazite-type phases, the changes in unit cell volume were determined for different compositions as shown in Figure 2. While LaPO<sub>4</sub> and La<sub>0.8</sub>(Ca,Ce)<sub>0.2</sub>PO<sub>4</sub> display the expected (almost) linear dependency, marked deviations were observed for samples with higher degrees of substitution. The sample containing 50 % Lanthanum exhibits a sudden decrease in unit cell volume at 800 K while the highly doped samples deviate from a linear behaviour starting at 800 K. This indicates that the desegregation coupled with a reduction of cerium sets in at 800 K.

*In-situ* XANES studies on the corresponding phases are planned to test this hypothesis.

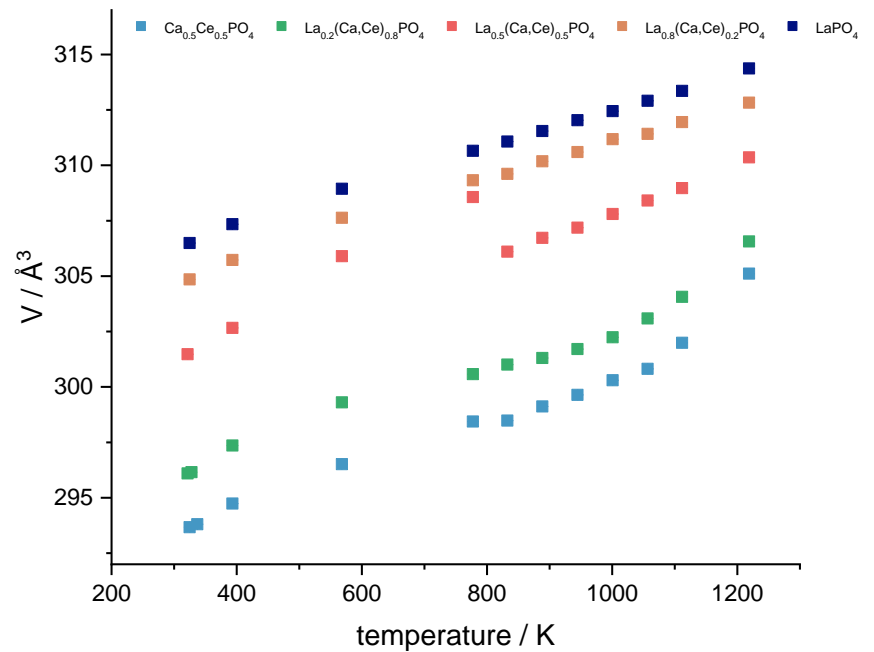


Figure 2: Temperature dependent evolution of the unit cell volume over the range of the solid solution  $La_{1-x}(Ca,Ce)_xPO_4$ .